Select methods in chemical analysis (chiefly inorganic) / by Sir William Crookes.

Contributors

Crookes, William, 1832-1919.

Publication/Creation

London ; New York : Longmans, Green, 1905.

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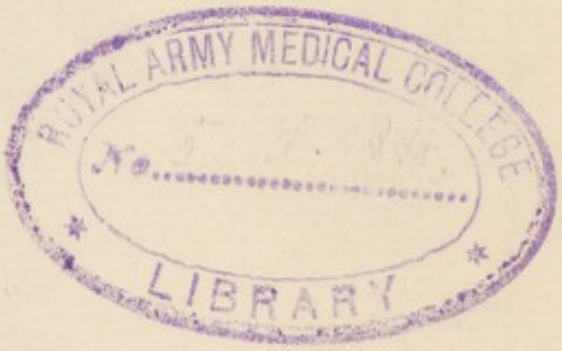
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SELECT METHODS

IN

CHEMICAL ANALYSIS

(CHIEFLY INORGANIC)

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BY

SIR WILLIAM CROOKES

HON. D.SC. (OXFORD AND DUBLIN), F.R.S., P.P.C.S., P.P.INST.E.E.

EDITOR OF 'THE CHEMICAL NEWS'

FOURTH EDITION, REWRITTEN AND ENLARGED

SUPPLIED FOR THE PUBLIC SERVICE

ILLUSTRATED WITH 68 WOODCUTS

LONGMANS, GREEN, AND CO.

39 PATERNOSTER ROW, LONDON

NEW YORK AND BOMBAY

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PREFACE

TO

THE FOURTH EDITION

In the eleven years which have elapsed since the publication of the last edition of this book a great and constantly increasing number of fresh analytical processes of various descriptions, many of which the Author has had occasion to test, have been described in current literature, and hence it seemed desirable to revise the text and embody in it the results of the Author's personal investigations. In doing so it has been found necessary to rewrite entirely many parts of the book, enlarging considerably in some places and curtailing in others.

The new methods which are now included for the first time are those which have been found to yield satisfactory results under the conditions described. In keeping rigidly to the rule of omitting methods of which he has no personal experience the Author believes that he has added to the value of the book as a work of reference, to which appeal may safely be made in cases of difficulty and indecision; and while the omission of any special method does not necessarily mean that it is to be regarded either as unimportant or untrustworthy, its inclusion on the other hand may be taken as a testimony to its accuracy and trustworthiness.

London: *July* 1905.

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PREFACE

TO

THE THIRD EDITION

A Third Edition of 'Select Methods in Chemical Analysis' having been called for, advantage has been taken to go over the whole work and remove some of the processes to make room for others which have been proposed and found to be successful during the eight years which have elapsed since the Second Edition was published. It must, however, not be assumed that the processes so discarded are of little value. Indeed, some are at the present time in constant use, having taken their position as regular laboratory processes, and have only been removed from these pages because their value is now too well known to make it advisable to retain them in a book which the Author wishes to be looked upon as mainly a collection of novel or little-known processes. As soon as a new process takes its place among ordinary laboratory processes, there is no reason for its retention here. Other processes have been omitted because further experience with them has shown the Author that they are not so trustworthy as other newer processes which have taken their place. Others, again, have been omitted to prevent the book becoming of an unwieldy size. Thus, most volumetric operations have been omitted, as there are now several standard works which are devoted to this branch of analysis. Then, mere detections which are not separations, and processes of only technical importance, have to a great extent been left out; the latter are well provided for in the technical literature. It has also

been thought advisable to omit many purely assaying and furnace operations, as not exactly coming within the scope of the book, and being more fully treated in special works on assaying, such as 'Mitchell's Manual of Practical Assaying.'

The space gained by these omissions has been partly filled up by new processes which the Author has considered worth introducing; but chiefly it has been utilised in giving to the chemical world a series of electrical separations and other processes from the standard work of Dr. Classen. The Author here desires to offer his thanks to Dr. Classen for his great kindness in not only permitting him to make use of a considerable portion of his book, 'Quantitative Chemical Analyses by Electrolysis,' but also for the woodcuts which are used to illustrate the operations.

The Author wishes to point out that this book is not to be looked upon as an encyclopædia of chemical analysis, in which is laid down every good method for the qualitative and quantitative examination of every known substance under every possible combination of circumstances. The Author has merely given such methods as have been proved in his own laboratory. Others—possibly no less efficient—have been passed over because he cannot vouch personally for their value. A main object has been to bring into notice a number of little-known expedients and precautions which prevent mistakes, ensure accuracy, or economise time.

The arrangement of the book has been adopted, not without careful consideration, as the one which necessitated the smallest number of back references.

London: *June* 1894.

PREFACE

TO

THE FIRST EDITION

It will be perceived from the title of this work that the Author has not intended to provide the student with a complete text-book of analysis, but rather with a laboratory companion, containing information not usually found in ordinary works on analysis. The Author has tested most of the new processes which have appeared during the last twelve years in the 'Chemical News'; and as some of these have proved to be of great value, it was thought that a service would be rendered to analytical chemistry if these trustworthy methods of analysis were systematically arranged in a convenient form for laboratory use. In some instances the descriptions are given in the language of the original writer, but in all cases where the Author has improved the processes the necessary modifications have been introduced.

It is strange that modern works on analysis should ignore about twenty of the elements. Even Fresenius gives only a separate form for their detection. Were investigators more in the habit of looking for the 'rare' elements, they would no doubt turn up unexpectedly in many minerals. In the present work equal prominence is given both to the rare and to the ordinary elements.

The order in which the analytical separation of the metals is carried out will be readily understood. Take, for instance, the case of copper. After giving the best method for the detection and quantitative estimation of this metal, comes a description of the processes for separating it from those metals which have

been previously passed under review, as mercury, silver, and zinc; but no attention is paid to the separation of copper from such metals as lead, tin, &c., which have not previously been treated of. Under the respective headings 'Lead' and 'Tin' the separation of these metals from copper is described.

A complete list of separations has not been attempted. Where no process of separation or estimation is given, it may be inferred that the Author has had no experience in any but the well-known methods employed in most laboratories; and to have introduced these ordinary processes into the work, simply for the sake of filling up gaps, would have largely increased its bulk without adding materially to its value. To save space, the description of a process is frequently discontinued at the point where the substances under separation are brought to such a state that the concluding steps are obvious.

No special system of weights and measures has been employed; many of the descriptions having been condensed from the original memoirs, it was thought better to retain the system therein adopted, so as to have simple numbers to deal with, instead of having to convert them to one common scale and to introduce decimals. Thus, when an author says, take 8 grains of a substance, 0·51816 gramme has not been substituted; and where 10 grammes are mentioned, he has not put 154·3840 grains. When not otherwise expressed, all degrees are according to the Centigrade scale. Formulæ have been avoided as far as practicable.

The names of discoverers of really novel or valuable processes are mentioned; but the introduction in a laboratory guide-book of the name of everyone who has contributed some trifling modification of a process would materially interfere with the concise description of the various methods, and, as a rule, such names have been omitted.

Some processes of great historic interest, as Professor Stas's method for the preparation of pure silver by distillation and otherwise, have been given in considerable detail; for this the Author thinks no apology is necessary, for it is always well for the student to have before him the highest models, in order that he may strive to attain a like perfection.

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SELECT METHODS

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CHEMICAL ANALYSIS

CHAPTER I

POTASSIUM, SODIUM, LITHIUM, CÆSIUM, RUBIDIUM (AMMONIUM)

POTASSIUM

Test for Potassium

M. L. DE KONINCK finds that if a 10 per cent. solution of sodium nitrite is mixed with cobalt chloride and acetic acid, the liquid forms a reagent for the detection of potassium much more sensitive than platinum chloride. An immediate yellow precipitate is obtained in a solution containing 1 part potassium chloride in 100 parts of water. It is still perceptible if diluted to 1 : 1000, but in the proportion of 1 : 2000 a precipitate is no longer obtained. Ammonia gives a similar but much less sensitive reaction; sodium, magnesium, calcium, barium, strontium, iron, aluminium, and zinc salts are not precipitated by this reagent.

Estimation of Potassium

(*A*) Potassium is usually estimated in the form of platinum salt. The results are exact and unvarying, and they are attended with the great advantage that, owing to the high atomic weight of platinum, any errors of manipulation, unless beyond the limits of probability, affect but slightly the percentage result of potassium. To obtain trustworthy results several precautions have to be attended to; these have been fully described by Messrs. F. T. Teschemacher and J. Denham Smith, and the following process, which the author has verified on many occasions, is condensed from their description.[1]

It is assumed that the salt under examination is a sample of commercial potassium chloride, or that the alkalies exist in such a condition

[1] *Chemical News*, xvii. 244.

that, by the addition of hydrochloric acid in excess, they will be converted into chlorides. Take 500 grains of the salt, previously carefully ground and mixed, and dissolve it in water, filtering if requisite, and washing the insoluble portion till solution and washings measure 5000 grains. Mix this solution by pouring from one glass to another, and take 500 measured grains of the liquid (measured accurately, always at one level of the eye and one level of liquid and line of measurement), dilute these 500 grains till they measure 5000 liquid grains, and mix ; 1000 measured grains of this solution contain 10 grains of the original salt.

Now, to 1000 measured grains of this solution, add excess, say 50 grains, of hydrochloric acid, if the alkalies are not present as chlorides, and pour into a shallow porcelain dish, making, with the rinsings of the measure, &c., some 1500 grains of solution. Heat the dish and contents nearly to ebullition, and add to the hot liquid so much solution of platinum chloride as is equal to 20 grains of the metal. Evaporate this mixture on the water-bath nearly to dryness : that is, to the point when the thick syrupy liquid, on the momentary removal of the dish from the bath, passes into an orange-coloured pasty mass. At this point remove the dish from the bath, and at the same instant and before the dish and its contents have had time to cool, drench it with 500 to 600 grains of rectified methylated spirit, containing about 15 per cent. of water and 85 of alcohol ; mix rapidly by imparting a rotatory motion to the contents of the dish ; then cover it and allow it to digest for five minutes. Have a filter ready, not too small, of 400 to 500 grains capacity, in a funnel with a cover : wash the filter first with hot water, and then with spirit, and after a short digestion pour the alcoholic solution of the platinum salts on to the filter, draining the crystalline solid scales of the potassium salt as dry as possible, and again drench, agitate, and digest the insoluble salt with spirit ; repeat this a third time, when the spirit will come away nearly colourless. Now collect the light orange crystalline scales of the potassium platino-chloride on the filter, by means of a wash-bottle, and, if need be, wash with spirit till it passes perfectly colourless. It is very advisable to wash the potassium platino-chloride by decantation, and finally by a stream of spirit from a wash-bottle, to avoid the use of stirrers so as to prevent the scales being broken down, and to keep both dish and funnel lightly covered till the washing is completed.

There is now nothing more to be done than to dry and weigh the potassium platino-chloride, and to ignite and weigh the filter and add this to the weight of the salt. Owing, however, to the crystalline nature of the salt thus obtained, but a slight stain adheres to the filter, so that the loss by ignition is very minute and does not affect the result. As this crystalline precipitate is not hygrometric, its weight is easily and accurately determined.

In this process the following points must be chiefly attended to :—

I. Strength of solutions.

II. Use of platinum chloride in large excess, about 20 grains of metallic platinum to 10 grains of the salt examined.

III. Heating of solutions, and evaporation so conducted as to obtain the potassium salt in a crystalline scale-like condition.

IV. Evaporation on water-bath to a pasty condition—no further.

V. Drenching with spirit whilst the salt and dish are hot, and instantly on removal from water-bath.

VI. Washing by decantation, and avoiding breaking down of the crystalline precipitate.

In practice, the process is a rapid one, from beginning to end requiring about two hours—less time, indeed, than is frequently expended in merely washing the dense pulverulent precipitate which is obtained by the usual mode of manipulation.

The results are very accurate. The authors take 244·20 as the equivalent of the potassium platino-chloride.

(*B*) Precht conducts the determination of potassium as follows :— The sulphuric acid is removed by barium chloride in a solution containing 0·5 of hydrochloric acid to 1 of the salt. The clear liquid should contain neither barium chloride nor sulphuric acid. Traces of the latter may be removed in the measuring vessel by finely pulverised barium chloride. Small quantities of sulphuric acid are admissible if the solution with platinum chloride is not evaporated quite to dryness. In acid solutions the objection to the removal of sulphuric acid by means of barium chloride, viz. that alkalies are carried down along with the barium sulphate, has little weight.

In neutral solutions so much potassium sulphate is thrown down that an error of 1 per cent. may be occasioned. In evaporating down with platinum chloride care should be taken that large crystals of sodium platino-chloride are not formed which would interfere with washing. The latter process is best performed with hot alcohol, there being no danger of the reduction of the platinum. A mixture of alcohol and ether is not to be recommended, nor an addition of glycerin. For the determination of small quantities of potassium chloride along with an excess of sodium chloride, Precht evaporates 10 to 100 grammes with a solution of sodium platino-chloride of known strength. The potassic salts are thus thrown down, the excess of the sodium compound is washed away with the absolute alcohol, and the platinum reduced on the filter and weighed.

(*C*) The committee appointed by the Chemical Section of the British Association reports that (1) potassium in the form of pure chloride can be determined with great accuracy by precipitation as platino-chloride. If a large excess of platinum solution be employed, and alcohol only used for washing the precipitate, the results have a tendency to exceed the truth. By avoiding the use of a large excess of platinum solution

more accurate results are obtained. If a small volume of platinum solution be employed in the first instance for washing the precipitate (as recommended by Tatlock), and the washing then completed with alcohol in the usual way, the results are accurate. Potassium platino-chloride appears to be practically insoluble in a concentrated solution of platinum chloride.

(2) In the presence of a considerable proportion of sodium chloride, washing the precipitate with alcohol alone tends to give results in excess of the truth. If the precipitate be first treated with platinum solution, the results are somewhat low, apparently owing to the solubility of the precipitate in solutions of sodium platino-chloride; the error increases with the amount of sodium, but is never very large, and a correction may be applied if desired.

(3) If Tatlock's method be employed, there is no occasion to separate sulphates, nitrates, or magnesium; but if the amount of chloride present is insufficient for the existence of all the potassium as potassium chloride, the deficiency must be supplied by the addition of sodium chloride or hydrochloric acid. The results obtained are in many cases accurate, but have a tendency to be somewhat below the truth.

(4) There is practically no advantage in drying potassium platino-chloride at 130° C. rather than at 100° C.; the loss at the higher temperature was found to exceed 0·07 per cent. of the weight of the precipitate, but is probably governed by the conditions of precipitation.

(5) The committee is of opinion that a preliminary washing of the precipitate of potassium with a solution of platinum chloride is a valuable modification of the usual process. As the method so modified is capable of direct application to commercial potassium salts, and does not necessitate the removal of sulphates, nitrates, or magnesium, the committee considers that it deserves to be generally applied to the determination of potassium in commercial products containing it.

(*D*) Mr. R. Tatlock's modification of the platinum process above referred to is as follows:—Dissolve 35 grammes of the sample in water, filter if necessary, and make up the bulk to 500 c.c. Deliver 10 c.c. of the solution into a small porcelain basin, add 20 c.c. of water, stir, and then add 30 c.c. of a solution of platinum chloride containing 7 grammes of metallic platinum in every 100 c.c. Evaporate on a water-bath, but not to perfect dryness. Add a few drops of water, and evaporate again; remove the basin and stir the precipitate well with 2 c.c. of the platinum solution; then wash the precipitate on the filter with 1 c.c. more. Now wash the basin, filter and contents with the smallest possible quantity of alcohol at 95 per cent. Dry the filter containing the precipitate on the water-bath; remove the precipitate as completely as possible into a small platinum capsule; dry at 100° C. and weigh. Ignite the filter with trace of adhering

precipitate; weigh the residue which is left; calculate its weight of $2(KCl)PtCl_2$, and add the weight to that of the precipitate already obtained.

(*E*) The process employed at Leopold's-hall and Stassfurt is described by Drs. Zuckschwerdt and West as follows:—10 grammes of a well-mixed sample are dissolved in a 500 c.c. flask filled up to the mark, shaken, an aliquot part filtered, and 20 c.c. (=0·4 gramme) measured off. This is mixed in a porcelain capsule with 7 c.c. of a solution of platinum chloride, containing 10 grammes of platinum in 100 c.c.

As commercial samples rarely contain more than 20 per cent. of sodium chloride, whilst the above quantity of platinum would suffice for 0·4 gramme of sodium chloride at 100 per cent., there is always a considerable excess of platinum chloride present.

The contents of the capsule are then evaporated on the water-bath with frequent stirring, to the consistency of syrup, so that when cold the mass appears dry. The free hydrochloric acid is thus chiefly expelled. When cold the mass is covered with 10 c.c. of alcohol at 95 per cent., well rubbed up with a glass rod, and the washings poured upon a tared filter. Alcohol is again spirted on in smaller quantity; the mass is again rubbed up, the washings poured off, and the operation repeated once more. As a rule, at the second decantation the colour of the washings, and consequently the proportion of the platinum double salt, will be very slight, and in the third operation it disappears altogether; otherwise the operation must be repeated once more. The precipitate, which now consists of perfectly pure potassium platino-chloride, is brought upon the filter by means of the alcohol washing-bottle; and after drying for half an hour at 110° to 115°, it is weighed under the same conditions as it had been when empty.

The total quantity of alcohol consumed is generally 50 c.c. The errors fall within the narrowest limits of permissible experimental errors, and could scarcely be removed or avoided by greater complication.

(*F*) MM. Corenwinder and G. Coutamine add to the portion taken for analysis a slight excess of hydrochloric acid, and then, without taking any notice of the possible presence of sulphuric acid, silica, or phosphoric acid, they evaporate on the water-bath, after having added a sufficiency of platinum chloride. The potassium platino-chloride thus obtained is digested with alcohol at 95° mixed with ether, and washed in the ordinary way with the same liquid. When this operation is complete, boiling water is poured upon the filter by means of a pipette, till the platino-chloride is entirely dissolved, and the filtered liquid is collected. Water containing sodium formate is then heated, and while it is boiling the preceding solution of potassium platino-chloride is carefully poured into it by degrees. In a few moments the platinum is thrown down as a black powder, which merely needs to be washed, dried, heated to redness, and weighed in order to find the quantity of potassium present in the sample.

The following processes are based upon different reactions :—

Estimation of Potassium Sulphate

At Stassfurt the following method is in use :—10 grammes of the salt in question are placed in a 500 c.c. flask with 350 to 400 c.c. of water and 25 c.c. of hydrochloric acid at 25 per cent., and a solution of barium chloride (almost saturated and containing 50 c.c. aqueous hydrochloric acid per litre) is gradually added, boiling up each time till the sulphuric acid is entirely thrown down, a point easily reached with practice. A very small excess of sulphuric acid has no effect upon the result, while an excess of barium chloride increases the result: or the sulphuric acid in the salt may be determined volumetrically in a separate portion with barium chloride and potassium chromate, and the quantity of barium chloride thus found is added to the potassium salt in an acid solution. In evaporating, care must be taken that the free hydrochloric acid is entirely expelled (which is not easy in presence of much magnesia), otherwise an error may arise of 0·5 per cent. The correction for the potassium chloride retained by the barium sulphate is as follows : in 10 grammes of potassium sulphate there are 4·59 of sulphuric anhydride=13·79 grammes barium sulphate, which occupy the space of 3 c.c. Each c.c. of the precipitate contains as much potassium as 6 c.c. of the solution.

Estimation of Potassium by Means of Perchloric Acid

(*A*) Armand Bertrand finds that if the substance in question contains an ammoniacal salt the ammonia must be expelled by boiling with a little caustic lime. The solution should be perfectly clear. The filtered solution of the sample is evaporated on the water-bath in a small porcelain capsule with 5 c.c. of perchloric acid at 45° B., until the volume of the liquid is reduced to about 10 c.c. The capsule is taken off the water-bath, alcohol at 95 per cent. is added : it is cooled, and the potassium perchlorate is collected on a small filter. The precipitate is washed with alcohol at 95 per cent., containing 10 per cent. by volume of perchloric acid, until the liquid running through no longer shows the reaction of sulphuric acid. The washing is then completed with alcohol at 95 per cent. without the admixture of perchloric acid. It is then dried in the water-oven. At the end of from twenty to thirty minutes the precipitate is detached from the filter and spread out on a tared watch-glass. It is heated and weighed twice to be certain that the desiccation is complete, and the weight of the potassium perchlorate thus obtained is noted. On the other hand, as there always remains a little perchlorate adhering to the filter, instead of using a tared filter, the author considers it more expeditious to operate as follows :—During the desiccation of the perchlorate in the watch-

glass the filter is burnt in a platinum capsule fitted with a lid. The potassium chloride, resulting from the calcination, is washed into a glass, and the chlorine is determined with a centinormal silver solution. A multiplication indicates the perchlorate to be added to that which has been weighed. This process gives accurate results in presence of lime, magnesia, soda, baryta, iron, alumina, and sulphuric or phosphoric acids, free or combined.

The author prepares his perchloric acid as follows:—He dissolves purified barium chlorate in lukewarm water, and precipitates with dilute sulphuric acid. He allows it to settle, draws off the clear liquid with a syphon, and washes the precipitate of barium sulphate. The solution of chloric acid is evaporated in a porcelain capsule over a naked fire until the concentrated liquid becomes yellow and emits a peculiar sound if heated further. It is then divided into capsules of 19 centimetres in diameter, each capable of containing about 700 c.c., and the evaporation is continued until the liquid is completely colourless and emits dense white fumes. In order to diminish the inevitable loss of perchloric acid a little water may be added from time to time during the concentration. Four parts of barium chlorate yield, in general, 1 part of perchloric acid at 45° B. The colourless liquid is distilled in a retort heated on a sand-bath. A long-necked tubulated receiver is adapted to the retort without the use of a cork.

(*B*) In applying perchloric acid to the determination of potassium very satisfactory results have been obtained by D. Albert Krieder.[1] Briefly the method is as follows:—The substance, free from sulphuric acid, is evaporated for the expulsion of free hydrochloric acid, the residue stirred with 20 cubic centimetres of hot water, and then treated with perchloric acid in quantity not less than one and a half times that required by the bases present, when it is evaporated with frequent stirring to a thick syrup-like consistency, again dissolved in hot water, and evaporated with continued stirring, till all hydrochloric acid has been expelled and the fumes of perchloric acid appear. Further loss of perchloric acid is to be compensated for by addition of more. The cold mass is then well stirred with about 20 cubic centimetres of wash alcohol—97 per cent. alcohol containing 0·2 per cent. by weight of pure perchloric acid—with precautions against reducing the potassium perchlorate crystals to too fine a powder. After settling, the alcohol is decanted on the asbestos filter and the residue similarly treated with about the same amount of wash alcohol, settling and again decanting. The residual salt is then deprived of alcohol by gently heating, dissolved in 10 cubic centimetres of hot water and a little perchloric acid, when it is evaporated once more with stirring until fumes of perchloric acid rise. It is then washed with 1 cubic centimetre of wash alcohol, transferred to the asbestos, preferably by means of an indiarubber-tipped glass rod to avoid excessive use of alcohol, and covered finally with

[1] *American Journal of Science*, vol. xlix., June 1895.

pure alcohol, the whole wash process requiring about 50 to 70 cubic centimetres of alcohol. It is then dried at about 130° C. and weighed.

The substitution of a Gooch crucible for the truncated pipette employed by Caspari will be found advantageous; and asbestos capable of forming a close, compact felt should be selected, inasmuch as the perchlorate is in part unavoidably reduced, during the necessary stirring, to so fine a condition that it tends to run through the filter when under pressure. A special felt of an excellent quality of asbestos was prepared for the determinations given below, and seemed to hold the finer particles of the perchlorate very satisfactorily.

A number of determinations made of potassium unmixed with other bases of non-volatile acids gave very good results, but considerable difficulty was experienced in obtaining equally satisfactory determinations of potassium associated with sulphuric and phosphoric acids. As Caspari has pointed out, the sulphuric acid must be removed by precipitation as barium sulphate before the treatment with perchloric acid is attempted, and unless the precipitation is made in a strongly acid solution, some potassium is carried down with the barium. Phosphoric acid need not be previously removed; but to secure a nearly complete separation of this acid from the potassium, a considerable excess of perchloric acid should be left upon the potassium perchlorate before it is treated with the alcohol. When these conditions are carefully complied with, fairly good results may be justly expected.

Preparation of Perchloric Acid

D. Albert Krieder advises the use of sodium chlorate in preference to the potassium salt, thus avoiding the necessity for the complete removal of the base. The method is as follows:—

A convenient quantity of sodium chlorate, from 100 to 300 grammes, is melted in a round-bottomed flask and gradually raised to a temperature at which oxygen is freely, but not too rapidly, evolved, and kept at this temperature till the fused mass thickens throughout, indicating the complete conversion of the chlorate to the chloride and perchlorate, and requiring between one and a half and two hours. The product thus obtained is washed in a capacious evaporating dish, where it is treated with sufficient hydrochloric acid to effect the complete reduction of the residual chlorate, which, if the ignition has been carefully conducted with well-distributed heat, will be present in but small amount. It is then evaporated to dryness on a water-bath, and with but little attention until a point near to dryness has been reached, when stirring will be found of great advantage in facilitating the volatilisation of the remaining liquid and in breaking up the mass of salt. Otherwise the perchlorate seems to solidify with a certain amount of water, and removal from the dish without moistening and re-heating is impossible.

After triturating the residue in a porcelain mortar, an excess of the strongest hydrochloric acid is added to the dry salt, preferably in a tall beaker, where there is less surface for the escape of hydrochloric acid, and from which the acid can be decanted without disturbing the precipitated chloride. If the salt has been reduced to a very fine powder, by stirring energetically for a minute, the hydrochloric acid will set free the perchloric acid and precipitate the sodium as chloride, which in a few minutes settles, leaving a clear solution of the perchloric acid with the excess of hydrochloric acid. The clear supernatant liquid is then decanted upon a Gooch filter, through which it may be rapidly drawn by the aid of suction, and the residue re-treated with the strongest hydrochloric acid, settled and again decanted, the salt being finally brought upon the filter, where it is washed with a little strong hydrochloric acid. A large platinum cone will be found more convenient than the crucible, because of its greater capacity and filtering surface.

The filtrate containing the perchloric acid, with the excess of hydrochloric acid and the small per cent. of sodium chloride which is soluble in the latter, is then evaporated over a steam bath till all hydrochloric acid is expelled and the heavy white fumes of perchloric acid appear, when it is ready for use in potassium determinations. Evidently the acid will not be chemically pure, because the sodium chloride is not absolutely insoluble in hydrochloric acid. If, however, a portion of pure acid be required, it may be obtained by distilling this product under diminished pressure, and without great loss, providing the heat is regulated according to the fumes in the distilling flask.

Some modification of the above treatment will be found necessary in case the sodium chlorate contains any potassium as an impurity, or if the latter has been introduced from the vessel in which the fusion was made. Under these circumstances the hydrochloric acid would not suffice for the removal of potassium, since a trace might also go over with the sodium, and thus, on evaporation, a residue insoluble in 97 per cent. alcohol be obtained. To avoid this difficulty, the mixture of sodium perchlorate and chloride, after being treated with hydrochloric acid for the reduction of the residual chlorate, being reduced to a fine powder, is well digested with 97 per cent. alcohol, which dissolves the sodium perchlorate, but leaves the chloride, as well as any potassium salt, insoluble. By giving the alcohol time to become saturated, which is facilitated by stirring, it is found, on filtering and evaporating, that an average of 0·2 gramme of sodium perchlorate is obtained for every cubic centimetre of alcohol, and that the product thus obtained is comparatively free from chlorides, until the perchlorate is nearly all removed, when more of the chloride seems to dissolve. This treatment with alcohol is continued until, on evaporation of a small portion of the latest filtrate, only a small residue is found. The alcoholic solution of the perchlorate is then distilled from a large flask until the perchlorate

begins to crystallise, when the heat is removed and the contents quickly emptied into an evaporating dish, the same liquid being used to wash out the remaining portions of the salt. The salt is then evaporated to dryness on the steam-bath, and subsequently treated with strong hydrochloric acid for the separation of the perchloric acid.

(*C*) Another process for the estimation and detection of potassium has been devised by M. A. Carnot.

He makes use of a reaction of potassium salts in a solution mixed with alcohol, in presence of sodium thiosulphate and a bismuth salt.

Dissolve in a few drops of hydrochloric acid 1 part of bismuth subnitrate—say half a gramme—and on the other hand about 2 parts (1 gramme to 1¼) of crystallised sodium thiosulphate in a few c.c. of water. The second solution is then poured into the first, and concentrated alcohol is added in large excess. This mixture is the reagent.

If brought into contact with a few drops of the solution of a potassium salt, it at once gives a yellow precipitate. With an undissolved potassium salt it produces a decidedly yellow colouration, easily recognised.

All potassium salts with mineral acids are equally susceptible of this reaction, sulphates and phosphates as well as nitrates, carbonates, chlorides, &c. It is also very sensitive with the organic salts, tartrates, citrates, &c.

The reaction is not interfered with by the presence of other bases, with which nothing analogous is produced. The character is, therefore, perfectly distinct.

Baryta and strontia alone may occasion some difficulty, by reason of the white precipitates of double thiosulphates which they form with the same reagent, but it is very rare to meet them along with potash, and they are very easily detected and removed.

If we have a solution containing merely a few milligrammes of potash, it is reduced by evaporation to a very small volume, or even to dryness, when the characteristic reaction readily appears. Or slips of filter-paper may be repeatedly saturated with the dilute solution, and after drying be steeped in the alcoholic reagent, when the yellow colour will appear, especially on the margins of the paper.

The author's quantitative experiments refer chiefly to nitrates, chlorides, and mixtures of the two salts. With some special precautions the method may probably be applied directly to sulphates, though these are easily converted into chlorides by barium chloride, removing the excess of barium with sodium or ammonium carbonate.

The thiosulphate of commerce is sufficiently pure for use; the crystals are dissolved in a small quantity of water at the moment of the experiment.

The bismuth chloride is prepared by treating the pulverised metal with a few drops of nitric acid, evaporating to dryness, and then heating with a very small quantity of hydrochloric acid. The lead possibly

present in the bismuth is got rid of by adding to the cold solution concentrated alcohol, which causes lead chloride to be deposited. Or bismuth subnitrate may be dissolved in a few drops of hydrochloric acid.

The liquid in which the potassium is to be determined should not exceed 10 or 15 c.c. in bulk, so that the entire volume of the aqueous solution may not exceed 20 or 25 c.c. For 1 part of supposed potash we take 2 parts of bismuth, or $2\frac{1}{2}$ of subnitrate with 7 parts of crystalline thiosulphate.

The solution of the potassium salt is placed in a small flask, the bismuth solution is added, then the thiosulphate; the whole is mixed rapidly, and from 200 to 250 c.c. of concentrated alcohol are added. The whole is agitated for a few moments and left to settle. The yellow precipitate collects at the bottom of the flask, and may be filtered after a quarter of an hour, and carefully washed with alcohol.

The precipitate cannot be weighed; it is dissolved upon the filter in excess of water; the bismuth is thrown down as sulphide by ammonium sulphide, washed by decantation, collected on a tared filter, dried at 100°, and weighed. The weight obtained may be corrected by separating from the filter a part of the dried precipitate and heating it again to 150° or 200° in a small platinum crucible, weighing before and after, and correcting the total weight of the sulphide accordingly. The weight of the potash is ascertained by multiplying the weight of the bismuth sulphide by 0·549. The method has been found accurate in presence of soda, lithia, ammonia, lime, magnesia, alumina, and iron.

Precipitation of Potassium as Fluosilicate

In some cases it is preferable to precipitate the potassium in the form of fluosilicate. This is usually effected by the addition of hydrofluosilicic acid. A great improvement on this plan has been proposed by Drs. Knop and Wolf, who employ fluosilicate of aniline as the precipitant for potassium.

To prepare this reagent, dilute the aniline with twice its volume of alcohol at 80° to 90°; then add an equal volume of saturated fluosilicated alcohol. The liquid first becomes heated, and then almost immediately solidifies. Spread the mass in a capsule, dry in the air, and reduce to powder.

The powder is composed of the desired fluosilicate, and of all the silicic acid produced during the reaction. The acid being in its insoluble modification, one washing in water suffices to separate the soluble aniline fluosilicate from the inert silica which remains on the filter.

If coloured aniline is used, the powder must be previously washed in ether, which dissolves only the colouring matter.

Aniline fluosilicate crystallises in nacreous scales. Soluble in

water, insoluble in alcohol and ether, this salt is very useful in separating potassium from sodium, and even from ammonium, provided the liquid does not contain much excess. When this is the case the ammonia or its saline combination must first be expelled by heat.

In using this reagent, the salts are first acidulated by hydrochloric acid. Absolute alcohol is then added. On addition of an aqueous solution of aniline fluosilicate the potassium is precipitated in the state of fluosilicate, even in the presence of phosphoric acid.

SODIUM

Analysis of Salt-Cake

(*A*) The method preferred for the examination of salt-cake, black-ash, soda-ash, and other commercial products of the alkali manufacture, is that given by Dr. C. R. A. Wright, F.R.S. Ordinary salt-cake is valued according to the percentage of available sodium sulphate contained ; *i.e.* the percentage of sodium sulphate existing mainly as such and partly as sodium bisulphate. The mode of estimation of the available sulphate usually pursued is the following :—

1. The sodium chloride is determined volumetrically by a standard silver solution.

2. The quantity of a standard alkaline solution required to render a known weight of salt-cake exactly neutral to test papers is determined, and the result sometimes calculated as anhydrous sulphuric acid, sometimes as monohydrated sulphuric acid, called ' free acid.'

3. The difference between the sum of the two previous determinations and 100 is assumed to be ' available sodium sulphate.'

By this mode of proceeding errors of one to three or more per cent. are introduced ; ordinary salt-cake containing, in addition to sodium sulphate, bisulphate, and chloride, perceptible quantities of lead sulphate, iron persulphate, iron sesquioxide, calcium sulphate, magnesium sulphate, moisture, and particles of sand, brick, &c., derived from the furnace during the manufacturing processes. Where a greater degree of accuracy is desirable, a known weight of salt-cake may be treated with water, ammonia and ammonium oxalate added to the unfiltered solution, and the precipitated iron sesquioxide and calcium oxalate, with the insoluble matters, weighed after ignition : by moistening the ignited precipitate with pure sulphuric acid, and igniting again, the calcium oxalate is converted into calcium sulphate, and then the weight of the mixed substances indicates all the ' impurities ' present in the salt-cake, with the exception of the magnesium sulphate, which rarely amounts to more than traces, and the moisture, which is occasionally a very perceptible quantity, especially in samples that have been made some length of time.

The amount of iron persulphate present depends on the degree of heat to which the salt-cake has been subjected during manufacture. In highly roasted samples, cold water yields a solution containing no iron whatever, all the iron present in the salt-cake consequently existing as sesquioxide; specimens of under-roasted salt-cake, on the other hand, when treated with cold water, leave only fragments of brick, calcium sulphate, &c., undissolved, all the iron existing as persulphate. In ordinary salt-cake, however, there is so little ferric sulphate that no perceptible error is committed in assuming that all iron present exists as sesquioxide, and all the 'free acid' as sodium bisulphate. Accordingly, the following methods have been found to give tolerably expeditiously the exact composition of such salt-cake:—

(*a*) A known weight, 5 or 10 grammes, is dried at 110° or 120° C., till constant in weight, too great elevation in temperature being avoided to prevent any possible loss of hydrochloric acid by reaction of the sodium bisulphate on the sodium chloride present.

(*b*) The sodium chloride is determined volumetrically by a standard silver solution.

(*c*) A solution of sodium hydrate free from carbonate, or of caustic ammonia, of known strength, is added to a known weight of salt-cake until test papers indicate exact neutrality of the liquid; the alkaline solution used accordingly corresponds to the iron persulphate and sodium bisulphate together, and may therefore be safely calculated as the latter.

(*d*) A known weight of salt-cake is boiled with an excess of a standard sodium carbonate solution, and filtered; the unneutralised alkali is then determined by a standard acid solution. The amount of alkaline solution neutralised by the salt-cake indicates the calcium sulphate, sodium bisulphate, and iron persulphate together; and hence the difference between (*c*) and (*d*) indicates the calcium sulphate. Or the calcium sulphate may be determined gravimetrically by precipitation with ammonium oxalate, after separation of the iron sesquioxide by ammonia from the solution of a known weight of salt-cake in hydrochloric acid.

(*e*) The precipitate thrown down in (*c*) may be collected and boiled with hydrochloric acid; the insoluble sand, &c., may be weighed, the ferric salt reduced by zinc or other reducing agent, and titrated volumetrically by permanganate or otherwise.

(*f*) When the lead sulphate is to be determined, it may be done by treating a considerable quantity, say 20 grammes, with water, and boiling the insoluble residue with strong hydrochloric acid till the lead sulphate is entirely dissolved; from this solution lead sulphide may be thrown down by sulphuretted hydrogen, and the lead determined in the ordinary way.

(*g*) If magnesium sulphate is to be determined, it may be done by dissolving a known weight, say 20 grammes, in hydrochloric acid,

adding ammonia and ammonium oxalate, precipitating the magnesium from the filtrate by a phosphate, and ultimately weighing the magnesium pyrophosphate.

(*h*) If the preceding determinations have been carefully conducted, the difference between 100 and the sum of them may be safely taken as sodium sulphate; if this is to be directly determined, however, it may be done either by determining the total sulphuric acid present by dissolving a known weight of salt-cake in hydrochloric acid, precipitating by barium chloride, and weighing the barium sulphate; subtracting the sulphuric acid contained as calcium sulphate, sodium bisulphate, magnesium sulphate, and lead sulphate, the remainder being calculated as sodium bisulphate; or by adding ammonia and ammonium oxalate to the aqueous solution of a known weight, and estimating the residue left on evaporation of the filtrate and ignition with sulphuric acid; on subtraction from this of the amounts due to magnesium sulphate, sodium chloride, and sodium bisulphate, the sodium sulphate is ascertained directly.

The total 'available sodium sulphate' is found by adding $\frac{71}{120}$ of the sodium bisulphate to the amount of sodium sulphate found.

Black-Ash.—(*A*) Commercially, the only valuable ingredient is the sodium carbonate, the amount of which is generally determined by lixiviation of a known weight of black-ash, and titration, by normal test acid, of the liquor obtained. In manufacturing establishments it is frequently the practice to lixiviate the ash with water at some definite temperature, considered to be about the average temperature of the lixiviating vats; the liquor so obtained is examined (*a*) for alkali, determined by test acid; (*b*) for sodium sulphate, generally estimated roughly, but with sufficient nearness for manufacturing purposes, by the addition of a standard barium chloride solution to a portion of the acidulated lixiviate, till no further precipitate is thrown down; (*c*) for sulphide, estimated by passing chlorine through the alkaline lixiviate till all the sulphide is destroyed; boiling with hydrochloric acid, and volumetric determination of the sulphate as before, the increased amount representing the sulphide. Prizes are frequently given to those workmen who produce black-ash containing but little sulphate, showing a nearly complete decomposition of the salt-cake employed; and occasionally prizes are given when the sulphate after oxidation is low in amount, it being supposed that this indicates that over-roasting of the black-ash has not occurred. A slight misapprehension, however, usually attends this mode of analysis; although an over-roasted black-ash will yield a perceptible quantity of sulphide when treated with nearly absolute alcohol, yet the fact of an aqueous solution containing sulphide by no means proves that the ash was over-roasted, inasmuch as, on addition of water to black-ash, there is always a mutual reaction between the calcium sulphide and sodium carbonate contained therein. The amount of sodium sulphide formed depends

on the temperature and dilution of the liquid, and the time employed; and accordingly it is often found that the sulphide existing in the black-ash lye from the vats is very different in amount from that calculated from the laboratory analyses of the black-ash worked. The laboratory test for 'sulphate after oxidation,' therefore, is really useless, as it neither denotes the quality of work done by the furnace-man nor that of the black-ash lye.

In ordinary black-ash a sodium compound is contained [1] insoluble in hot water, even on long digestion, but decomposable by long-continued boiling. In cases, therefore, where the total 'available alkali' is to be exactly determined, either this long boiling must be performed or the total sodium present must be determined gravimetrically, and that contained as chloride and sulphate subtracted—in either case a tedious operation. The same applies in the case of the analysis of the lixiviated black-ash, or vat-waste. Ordinarily, the vat-waste is examined by lixiviating, or washing on a filter, a known weight of waste fresh from the vats or previously completely dried. In either case a considerable amount of calcium sulphide comes into solution, and hence if the solution so obtained be immediately titrated with test acid, more sodium is indicated as present than really has been dissolved out. By passing carbonic acid through the solution till sulphuretted hydrogen is completely expelled, boiling to decompose calcium bicarbonate, and filtration from the precipitated calcium carbonate, this error is avoided. The same effect is produced by adding ammonium carbonate to the solution, and boiling in a flask till no further evolution of ammoniacal gases takes place; but in either case the sodium contained in the insoluble compound, or as sulphate (found by oxidation of calcium sulphide and subsequent reaction on the sodium carbonate, especially if the waste has been previously dried), remains unestimated. When accuracy is required, therefore, a gravimetric determination of sodium is unavoidable.

Soda-Ash.—The commercial valuation of soda-ash is usually restricted to the determination of the percentage of 'available alkali' contained therein, by this term being meant the total anhydrous sodium oxide contained in a state capable of saturating a strong acid, such as sulphuric; and hence including hydrate, carbonate, aluminate, silicate, sulphide, sulphite, and thiosulphate. The analysis is usually performed by adding the standard acid to the hot aqueous solution of a known weight of ash, until a slight acid reaction is obtained; by this means all the lime, and the alumina contained as aluminate, are estimated as though they were soda. Practically this error is of little importance; it may readily be avoided by addition of a very slight excess of acid along with some tincture of litmus, then adding a slight excess of standard sodium carbonate solution, boiling and filtering from the precipitated lake and calcium carbonate; the excess of sodium

[1] *Chem. Soc. Journ.* xx. 407.

added is now again determined by the standard acid, and thus the exact amount of acid used to saturate the sodium oxide present in the 'available' state is known.

(*A*) When the exact composition of a sample of soda-ash is required, the following method may be adopted:—

(*a*) A known weight is heated to 150°–200° C., and the loss of weight considered to be moisture.

(*b*) The residue of (*a*) treated with hydrochloric acid leaves sand and insoluble matter, and in the filtrate the sulphuric acid may be estimated volumetrically, or, better, gravimetrically by barium chloride.

(*c*) The carbonic acid present is estimated in Mohr's apparatus, or in Fresenius and Will's, with the addition of some potassium chromate.

(*d*) A known weight is treated with water, and the solution evaporated to dryness with hydrochloric acid; thus the silica is determined: in the filtrate from this, ammonia throws down alumina, from which the aluminium, as aluminate, is found.

(*e*) The insoluble residue of (*d*) with hydrochloric acid and ammonia gives the iron and alumina (not as aluminate); the filtrate from this with ammonium oxalate gives the calcium (usually only traces).

(*f*) A known weight is dissolved in nitric acid, and the chlorine estimated by a standard silver solution.

(*g*) A known weight dissolved in water is oxidised by chlorine, and the sulphate thus formed determined; another known weight is dissolved in water and the solution divided into two equal parts; in one the iodine required to yield a blue colour when starch and acetic acid are added, is determined, to the other zinc sulphate is added, and in the filtrate the iodine required after removal of the precipitated zinc sulphide is again determined. From these data the sulphide, sulphite, and thiosulphate are calculated.

(*h*) The total 'available alkali' is determined, the error due to the aluminium of the aluminate being eliminated as previously mentioned; subtracting from this, calculated as sodium, the sodium corresponding to the silica, alumina, sulphide, sulphite, thiosulphate, and carbonic acid found, the difference is calculated as hydrate: this may be checked by adding barium chloride to a known weight, and determining the amount of acid required to neutralise the filtrate; rather more hydrate is usually indicated by this mode than what is really present, owing to the presence of a portion of aluminate, thiosulphate, &c., incompletely thrown down by the barium salt.

Carefully executed analyses according to this method have yielded results adding up to between 99·8 and 100·1.

When ferrocyanide is present, it may be estimated by dissolving a known weight of ash in hydrochloric acid, and adding iron perchloride; after standing some time, the precipitated Prussian blue must be well washed, treated with pure potash, and the ferrocyanide determined in the solution by permanganate.

Estimation of Soluble Sulphides in Commercial Soda and Soda-Ash.—These may be readily estimated by the following method, based on the insolubility of silver sulphide, and the solubility of all the other argentiferous salts, in presence of ammonia. The process was originally devised by H. Lestelle.

Prepare a normal solution of ammoniacal silver nitrate by dissolving 27·69 grammes of fine silver in pure nitric acid, adding 250 c.c. of ammonia, and diluting with water to bring the volume to 1 litre. Each c.c. of this solution corresponds to 0·01 gramme of sodium monosulphide.

Dissolve the substance to be analysed in water, add ammonia, boil, and then add, drop by drop, by means of a burette divided into tenths of a c.c., the ammoniacal silver solution, and a black precipitate of silver sulphide is formed. When nearly all the sulphur is precipitated, filter, and into the filtered liquid pour a fresh quantity of silver solution, until, after repeated filtrations, a drop of this liquid produces only a slight opacity. The estimation is then at an end, and it is only necessary to read the divisions indicated by the burette, and to convert this number into the corresponding amount of sodium sulphide.

To estimate very small quantities of sulphide, the argentiferous liquid must be more diluted, so that each c.c. corresponds to 0·005 gramme of sulphide. The presence of chloride, sulphate, and sodium carbonate, caustic soda, &c., makes no difference in the accuracy of this method, by reason of the solubility in ammonia of the precipitates given by these bodies with silver nitrate.

Analysis of Mixtures of Alkaline Mono- and Bi-carbonates. A. Mebus.—Two equal portions of the mixture are weighed out, and in one of them the total alkali is determined by means of a standard acid. Into the solution of the other portion is poured a standard solution of caustic soda perfectly free from carbonic acid, and corresponding in quantity with the alkali just found to be present, *i.e.* as many equivalents of alkali are added as are already contained. Of the alkali thus added, one portion combines with half the carbonic acid of the bicarbonate, and the remainder, which is precisely equal in quantity or equivalent (according as the base added is identical with or different from the base of the salts under examination) to the alkali of the monocarbonate, remains in a free state in the liquid. This solution is then precipitated with an excess of barium chloride, the carbonates are thus eliminated as barium carbonate, and after filtration there remains in the filtrate merely the excess of barium chloride, sodium chloride, and a quantity of free caustic soda equivalent to the alkali of the monocarbonate. All that remains is to take a known fraction of this liquid, and determine the alkali in the usual manner. We have thus the alkali of the monocarbonate, and by subtracting it from the total alkali we find the alkali of the bicarbonate.

Separation of Potassium from Sodium

To separate potassium from sodium when in presence of sulphuric acid, Finkener proposes the following :—Add hydrochloric acid to the aqueous solution to be analysed ; then solution of platinum chloride until the liquid is deep yellow. Add water sufficient, when boiling, to dissolve the double salt precipitated ; evaporate to syrupy consistency, but do not dry ; extract, and wash on a filter with a mixture of alcohol (specific gravity 0·8) 2 volumes, ether 1 volume. Wash well with solution of ammonium chloride ; this decomposes the sodium sulphate and allows it to be washed away. The filtrate, alcoholic extract, and washings contain the sodium. Heat the filter and its contents in a stream of hydrogen—a temperature of 240° suffices ; extract the potassium chloride with water, and weigh, or titrate with silver solution.

A great excess of sulphuric acid is to be avoided. The ammonium chloride solution dissolves about 0·13 to 0·26 per cent. of the potassium platino-chloride, but the quantity so lost varies with the strength of the solution, its temperature, and the quantity of free hydrochloric acid in it. On the other hand the double salt carries down with it about 0·16 to 0·35 per cent. of sodium salt.

The fact that, in the form of the perchlorate, potassium is insoluble, while sodium is readily soluble in 97 per cent. alcohol, affords a means for the separation of the two elements as well as for the identification of the former. By converting the sodium in the filtrate from the precipitate potassium salt either to the chloride or sulphate, in which forms it is insoluble in alcohol, Messrs. D. A. Krieder and J. E. Breckenridge [1] have given a means for the detection of sodium.

In converting sodium from the perchlorate to the chloride, attempts were first made to substitute some soluble chloride for the free acid, the addition of which to the alcoholic solution of sodium perchlorate it was feared might result in the formation of the dangerously explosive compound, perchloric ether. After many experiments, gaseous hydrochloric acid proved most effectual. The dehydrating effect of the acid upon the alcohol greatly increases the insolubility of sodium and secures a remarkable delicacy.

By the use of 10 cubic centimetres of 97 per cent. alcohol with gaseous hydrochloric acid, 0·0003 gramme of sodium oxide can be found with certainty ; and when the alcohol is allowed to become saturated with the gas, even 0·00006 gramme of sodium oxide will be unmistakably revealed. The quantity of alcohol, 10 cubic centimetres, is sufficient for all purposes, since this amount will dissolve about 2 grammes of sodium perchlorate ; but even in 40 cubic centimetres 0·0002 gramme of sodium oxide may be seen distinctly ; from which fact it is evident that this method can be applied to the quantitative

[1] *American Journal of Science*, vol. ii. Fourth Series, October 1896.

determination of sodium. Absolute alcohol does not materially increase the delicacy of the test.

Before applying this method, however, it is necessary to remove certain interfering substances. While potassium may be safely tested for in the presence of other bases and acids, except ammonium, cæsium and rubidium, and sulphuric acid (*loc. cit.*), the large number of elements whose chlorides are insoluble in alcohol necessitates their removal before testing for sodium. But among the common alkalies, ammonium is the only one whose presence is objectionable. Lithium does not affect either the test for potassium or sodium, as was determined by an experiment in which about 0·1 gramme of lithium chloride was converted into the perchlorate by evaporating with an excess of perchloric acid, and treated with 10 cubic centimetres of 97 per cent. alcohol. A perfectly clear solution was obtained, which upon saturation with gaseous hydrochloric acid, and cooling, remained clear. The removal of sulphuric acid is necessitated by the insolubility of sodium sulphate in alcohol.

In the experiments made with potassium and sodium associated with other acids and bases, the following treatment was adopted. The several groups of bases were successively removed in the ordinary way: hydrogen sulphide in ammoniacal solution removed the lead, mercury, copper, and zinc. Barium and calcium were removed by ammonium carbonate, the final filtrate being evaporated and ignited to the complete volatilisation of ammonia. The residue was dissolved and treated with barium hydrate for the removal of magnesium, and, after filtering, the barium was again removed by ammonium carbonate, and the filtrate evaporated and ignited as before. This residue was then treated with 10 cubic centimetres of boiling water, and, after stirring, was filtered in order to remove the organic matter usually found at this stage of the treatment. To the filtrate was added 0·1 to 0·5 cubic centimetre of pure perchloric acid, about 1·7 specific gravity, according to the amount of residue, and evaporated over the steam-bath until the white fumes of perchloric acid appeared. When the quantity of sodium is large it is safer to evaporate several times in order to secure a complete conversion to the perchlorate, and in such case precautions must be taken to have sufficient of the acid present. Upon treating with 97 per cent. alcohol, the presence of potassium is revealed by an insoluble residue. This is removed by a dry filter, and the filtrate saturated with gaseous hydrochloric acid, whereupon sodium, if originally present in amount greater than 0·0005 gramme of the oxide, will be precipitated in granular condition.

Indirect Estimation of Potassium and Sodium

The direct method of estimating potassium and sodium—viz. by the precipitation of the former as potassium platino-chloride, and reckoning sodium from the loss—though sufficiently accurate in patient

and skilful hands, is yet open to many sources of error, and at the best is exceedingly tedious and troublesome.

The indirect method does not appear to possess the confidence of chemists—at least, it is rarely mentioned in published investigations. Mr. P. Collier, B.A., Assistant in the Sheffield Laboratory, Yale College, U.S.A., has published [1] a number of experiments to ascertain the limits of error in this process.

The volumetric estimation of chlorine as perfected by Mohr offers by far the best basis for an indirect determination of the alkalies. It is, in fact, requisite, in employing the usual direct method, to procure the alkalies in the condition of pure chlorides before precipitation.

When the alkaline chlorides are obtained free from all foreign matters, it is but the work of a few moments to ascertain their contents of chlorine.

The silver solution used for this purpose is best prepared by weighing off in a porcelain crucible about 4·8 grammes of clear crystallised silver nitrate, fusing it at the lowest possible heat, and then ascertaining its weight accurately. After fusion it should weigh a little more than 4·7933 grammes, the quantity that, contained in a litre of water, gives a solution of which 1 c.c.=0·001 gramme of chlorine. The fused salt is dissolved in a little warm water, the solution brought into a litre flask and filled to the mark, observing the usual precautions as to temperature, &c. When thus adjusted, add to the contents of the flask, from a burette, enough water to bring the excess of silver nitrate above 4·7933 grammes to the requisite dilution. In this way it is easy, with a burette and litre flask, to make a perfectly accurate standard solution, while this would be hardly possible should the operator weigh off less than 4·7933 grammes of silver nitrate.

This solution, which may be preserved in a well-stoppered bottle indefinitely, without change, is next tested by means of a solution of pure sodium chloride or ammonium chloride; a quantity, say about 2 grammes, of one of these salts being dissolved in a litre of water and 10 c.c. of the liquid taken for the comparison. The solution being ready, the estimation of chlorine is conducted as described by Mohr, Fresenius, Sutton, and others, potassium chromate being employed to indicate the completion of the reaction. The use of Erdmann's float in a burette (which may hold 70 c.c.) graduated to fifths ensures the needful accuracy of reading. Two-tenths c.c. of silver solution may be deducted as the excess needed to produce a visible quantity of silver chromate.

From a long list of analyses given by the author, it is shown that the indirect method is in all cases equal in accuracy to the ordinary separation, while in the matter of convenience and economy of time there is no comparison between them. In no case does the difference between the quantities taken and found of either alkaline chloride

[1] *Am. Journ. Sci.* xxxvii. 344.

exceed 2 milligrammes, and in most instances it is less than 1 milligramme. The correspondence between the amounts of chlorine as taken and found is, of course, still nearer. The error that appears in the estimation of the chlorides would be considerably reduced if, as usually happens, the metals were calculated as oxides.

The following are the formulæ employed for calculating the quantities of NaCl and KCl, or of Na_2O and K_2O, contained in or corresponding to any mixture of alkaline chlorides whose total weight and amount of chlorine are known :—

$$W = \text{weight of mixed chlorides}$$
$$C = \text{weight of chlorine}$$
$$NaCl = C \times 7{\cdot}6311 - W \times 3{\cdot}6288$$
$$KCl = W \times 4{\cdot}6288 - C \times 7{\cdot}6311$$
$$Na_2O = C \times 4{\cdot}0466 - W \times 1{\cdot}9243$$
$$K_2O = W \times 2{\cdot}9243 - C \times 4{\cdot}8210$$

Rapid Estimation of Potassium and Sodium

(*A*) M. Jean grinds up the saline mixture, in which it is desired to determine the potash and soda, with an excess of ammonium sulphate, moistened with a few drops of water, heated to redness in a platinum crucible till the ammoniacal salts have completely disappeared, and heated once more with ammonium sulphate in the same manner, so as to ensure the expulsion of all acids capable of displacement by sulphuric acid. The substance is then dissolved in boiling water, a slight excess of baryta-water is added, and the sulphates and insoluble matters are removed by filtration. The filtrate is then treated with a little carbonated water, and kept at a boil till all excess of carbonic acid has been expelled and all the barium carbonate rendered insoluble. The solution is then filtered, when the potash and soda remain in the filtrate in the state of carbonates, and are exactly neutralised with a standard solution of hydrochloric acid at the boiling-point. In this neutral liquid the weight of the chlorides present is determined by bringing the solution—by evaporation or by the addition of water, as the case may be—to a volume of 50 or 100 c.c., the specific gravity of which is then determined; or the solution may be evaporated to dryness, and the residue may be weighed. Knowing, therefore, from the quantity of hydrochloric acid used in filtration, the weight of chlorine corresponding to the two alkalies, and the weight of the two chlorides, it is easy to calculate the proportions of potash and soda. If the chlorine found be multiplied by 2·1029, the weight of the chlorides subtracted from the product, and the remainder multiplied by 3·6288, we obtain the weight of sodium chloride, while the difference will be the potassium chloride. If it is required to determine alkalies in presence of a superphosphate, it is prudent to neutralise with baryta-

water before adding ammonium sulphate to prevent the formation of pyrophosphates.

(*B*) M. F. Maxwell Lyte proposes the following indirect method for determining potash and soda. Having obtained the mixed sulphates free from any other salts, and in solution, evaporate the mixture to dryness, heat to redness, and weigh. Now redissolve the salts, and estimate the *percentage* of sulphuric anhydride they contain by any convenient volumetric or gravimetric method, and from the percentage thus found subtract the *percentage* of sulphuric anhydride the salt would contain were it pure potassium sulphate. The figures 45·977 are a sufficiently close approximation to this last-named percentage, and by simply multiplying the remainder by 9·66, the result will be the percentage of sodium sulphate the mixed salts contained.

This result is not absolutely correct, for the multiplier is a little too high, but the error is not $\frac{1}{10000}$, which is near enough for all practical purposes.

The result obtained deducted from 100, the remainder will be the percentage of potassium sulphate, and from these results the quantities of each of the alkalies sought may be calculated.

Estimation of Potash and Soda in Minerals

W. Knop and J. Hazard dissolve in hydrofluoric acid, evaporate, and drench the residue with concentrated sulphuric acid, thus removing the bulk of the silicon fluoride. The sulphuric acid is then evaporated off, the dry residue moistened with five or six drops of concentrated sulphuric acid, heated, drenched with 150 c.c. water, and barium hydrate added till red litmus-paper is turned distinctly blue. The mixture of barium sulphate, silica, alumina, magnesia, and ferric oxide is then filtered off and well washed. The filtrate is evaporated to dryness, adding, when it is concentrated down to about 200 c.c., a few grammes of dry ammonium sesquicarbonate. When perfectly dry the residue of barium and calcium carbonates is extracted successively fifteen times, each time with 20 c.c. water, the liquid being each time filtered through a small filter of 3 to 4 cm. diameter into a platinum capsule, and evaporated to dryness. The residue is drenched again with 20 c.c. water, the water is decanted through a similar fresh filter, and the solution, after it has deposited a little barium carbonate with some alumina and iron, is collected along with the washings in a fresh platinum capsule. The alkaline carbonate, to which a few more granules of ammonium carbonate have been added, is again dissolved in 20 c.c. water, observing that no residue remains. The liquid is then neutralised with hydrochloric acid, evaporated, the chlorides dried strongly, and the potassium and sodium separated by means of platinum chloride.

Separation of the Alkalies from Silicates not Soluble in Acids

One of the best processes for separating the alkalies from silicates is the one devised by Professor J. Lawrence Smith, M.D. It is sufficiently accurate to be available for their quantitative estimation. This process has scarcely received the attention it deserves, and as it appears to be almost unknown in England, it is considered advisable to give the description mainly in Dr. Smith's own words rather than as a condensed abstract.

1. 'In this description of separating and determining the alkalies, it is my intention to give the minutest details, although it may be thought useless by some; but numerous analyses have given me the experience here detailed; and I am convinced that analytical chemists, if they follow them out, will never resort to any other known method after a few trials; and if there be a better method, it is yet to be discovered. The presence of boracic, hydrofluoric, and phosphoric acids in the minerals in no way interferes with the process. Even in silicates *soluble in acids*, I prefer this method, in common with other analysts, for its ease and accuracy.

2. 'During the latter part of 1852 I made the researches, the details of which were published early in 1853.[1] Since that time I have employed the process many hundreds of times with the greatest satisfaction, most accurate results, and ready manipulation; some minor points were not completed satisfactorily until several years after the first notice of the method; these have been subsequently perfected, and in my mind there is nothing further now to be desired. I might state that many analytical chemists have for years constantly used this process to the exclusion of all others.

3. 'The purpose of this article is to give all the perfections, and a minute detail of the manipulations, with whatever precautions are necessary, all of which are simple and easily executed. In the two articles on the subject of alkali determination in minerals, published in 1853, the whole subject was reviewed, which it is needless to recur to now. I then reviewed the process by caustic baryta and its salts, by hydrofluoric acid, also detailing some experiments on the separation of the different alkalies from each other, microscopic examinations of the same, &c. It was shown that after the caustic alkalies, the most powerful agent to attack silicates at a high temperature is caustic lime, a fact not new to chemists, for as early as 1847 I used this process for attacking silicates, and others had done the same prior to that period. But for the purpose of arriving conveniently at *a quantitative determination of the alkalies in silicates*, certain methods of manipulation,

[1] 'Shortly after my first publication, M. St. Claire Deville made known his method of analysing the silicates by *fusion* with lime; but the nature of his process and the objects to be arrived at were quite different from those attained by the process under consideration.

quantity of material, admixture, &c., had to be discovered, and in them resides the success of my process—converting the most difficult parts of the analysis of a silicate into the easiest.

4. 'The methods of analysis of the silicates by caustic baryta and its carbonate are well known; but for various reasons fully detailed by Rose, in his "Analytical Chemistry," are now no longer used. The method still employed extensively is the one proposed by Berzelius, with hydrofluoric acid, and when applied with numerous precautions, it seems to decompose all silicates; still, according to Rose, there are siliceous compounds that cannot be completely decomposed by hydrofluoric acid.[1] Dismissing all criticism, I at once proceed to the method which is the subject of this article.

5. '**Decomposition of Silicates by Ignition with Calcium Carbonate and Sal-Ammoniac.**—This mixture of calcium carbonate and sal-ammoniac is used simply for the purpose of bringing in a most thorough manner caustic lime to act upon the silicates at a red heat.[2] The first step in the process is to have pure *carbonate of lime.*

6. 'This is made in my laboratory as follows:—Take as good marble as can be conveniently found (not dolomitic), or calc spar, and dissolve in hydrochloric acid. It is not necessary that the acid be perfectly pure. Add an excess of the marble and warm the solution: to it add lime-water or some milk of lime, made from pure or nearly pure lime, until the solution is alkaline to test-paper; the lime is added to precipitate any magnesia, phosphate of lime, &c., that may have been in the marble. Filter this solution, and after heating it to at least 160° F., precipitate with ammonium carbonate.[3] The calcium carbonate thus precipitated is to be thrown on a filter and well washed with pure rain-water or with distilled water.

7. 'Thus prepared, the calcium carbonate is a dense powder and perfectly pure: or, if it contain any impurity, it will be a trace of barium or strontium carbonate which in no way interferes with the use of the calcium carbonate.

8. '**Sal-Ammoniac.**—To give to this reagent the most convenient form, take fragments of clean sublimed sal-ammoniac, dissolve them

[1] 'The process used by Deville in fusing with lime is in most cases better than that by hydrofluoric acid, and one that I should use in preference to all others, except the one now being described.

[2] 'Calcium chloride at a red heat will dissolve more or less caustic lime.

[3] 'This precaution must not be overlooked, as it is desirable to obtain the precipitated calcium carbonate as dense as possible. If the ammonium carbonate be added to the cold solution, the precipitate, at first gelatinous, will ultimately become much more dense and settle readily; the same is true if the mixture be heated after the addition of the ammonium carbonate; but in neither case will it be as dense as when the carbonate is added to the hot solution of calcium chloride. The reaction in this process of analysis is in no way affected by the form of the calcium carbonate; but by using the denser form, the mixture occupies less space in the crucible in which it is heated.

in water over a gentle fire, filter, evaporate the filtered solution over a steam-bath, or on a sand-bath, or any other convenient gentle heat, and as the small crystals deposit themselves, stir the solution to keep the crystals small; when one-half or two-thirds of the sal-ammoniac is deposited, pour off the liquid without waiting for it to cool, throw on a cotton filter, and dry the crystals at the temperature of the atmosphere. In this way, sal-ammoniac is furnished that is easily pulverised.

9. '**Vessels for Producing the Decomposition.**—The ordinary platinum crucible can be employed for this purpose, and is now most commonly used, and for many years was used by myself. It was, however, found that, while this method exceeds in precision and ease all other known methods for alkali determinations in silicates, there was yet a very minute quantity of alkalies lost by volatilisation, and while the method gave satisfaction to those who used it, I yet continued my researches to overcome even this small loss. This has been successfully accomplished, and for some time I have been in the constant habit of using an improved form. Instead of the ordinary platinum crucible, I use an elongated one, which may be made of various dimensions. The one employed, with from $\frac{1}{2}$ to 1 gramme of silicate, is of the following form and dimensions.

10. 'An elongated slightly conical crucible with rounded bottom, and having a cover with or without a central wire to hold the cover; its length is 95 millimetres; diameter of opening 22 millimetres; diameter of small end, just at the turn of the bottom, 16 millimetres; and weight about 35 or 40 grammes. It can be made lighter, but experience has shown that it is better if stiff and solid. Messrs. Johnson and Matthey, Hatton Garden, London, have made a number for me, and they have my drawings and directions. It is thus made for the purpose of having that portion of the crucible containing the mixture heated strongly, while the upper portion is below a red heat.

11. '**Manner of Heating the Crucible.**—If the ordinary crucible be used, it is heated in the manner usually employed for the fusion of silicates. If the new form of crucible be employed, then the upper part may be grasped by a convenient metallic clamp in a slightly inclined position, and a moderate blast from the table blowpipe made to play upon it for about 25 or 30 minutes. But now gas is to be found in every well-mounted laboratory, Bunsen burners of all dimensions are used, and when properly applied, can be made to give gradations of heat, from the mildest to that sufficient to melt cast-iron. A simple, cheap, and convenient furnace, with a properly arranged draught, can be made to accomplish all silicate fusions without the aid of any manual labour, and therefore I employ such an apparatus, of which a description will be given at the end of this article.

12. '**Method of Analysis.**—We have now the pure calcium carbonate, granular sal-ammoniac, and the proper crucible. The silicate

is to be well pulverised in an agate mortar;[1] for the analysis I take ½ or 1 gramme, the former is most commonly used, as being sufficient, and best manipulated in the crucible; a gramme, however, may be conveniently employed. The weighed mineral is placed in a large agate mortar, or better in a glazed porcelain mortar of ½ to 1 pint capacity. Weigh out an equal quantity of the granular sal-ammoniac (a centigramme more or less is of no consequence), put it in the mortar with the mineral, rub the two together intimately; after which add 8 parts of calcium carbonate in three or four portions, and mix intimately after each addition; empty the contents of the mortar completely upon a piece of glazed paper, that ought always to be under the mortar, and introduce into the crucible. The crucible is tapped gently upon the table and the contents settled down.

13. 'It is then clasped by a metallic clamp in an inclined position, or it is placed in the support referred to in the latter part of this article, leaving outside about ½ or ¾ inch; a small Bunsen burner is now placed beneath the crucible, and the heat brought to bear just about the top of the mixture, and gradually carried toward the lower part, until the sal-ammoniac is completely decomposed, which takes about 4 or 5 minutes; heat is then applied in the manner suggested, either with the blast or with the burner referred to, acting by its own draught, and the whole kept up to a bright red heat, for from 40 to 60 minutes. It is well to avoid too intense a heat, as it may vitrify the mass too much.

14. 'The crucible is now allowed to cool, and, when cold, the contents will be found to be more or less agglomerated in the form of a semi-fused mass; a glass rod or blunt steel point will most commonly detach the mass, which is to be dropped into a platinum or porcelain capsule of about 150 c.c. capacity, and 60 or 80 c.c. of distilled water is added. In the course of a longer or shorter space of time, the mass will slake and crumble after the manner of lime; still better, this may be hastened by bringing the contents of the capsule to the boiling-point, either over a lamp or a water-bath. At the same time, water is put into the crucible to slake out any small particles that may adhere to it, and subsequently this is added to that from the capsule, *washing off the cover of the crucible also.*

15. 'After the mass is completely slaked, the analysis may be proceeded with, although, as a general rule, I prefer to allow the digestion to continue for six or eight hours; this, however, is not necessary. If the contents of the crucible are not easily detached, do not use

[1] 'While in all mineral analyses, thorough pulverisation of the mineral is usually essential, still it is a singular fact that very good analyses can be made with this method, even when the powder is tolerably coarse, and in some experiments with lepidolite, powder was used with much of it in particles from $\frac{1}{40}$ to $\frac{1}{30}$ of an inch in size, giving good results. Notwithstanding this, thorough trituration of the mineral is recommended.

unnecessary force, as the crucible may be injured by it, but fill the crucible to about two-thirds of its capacity with water, bring almost to the boiling-point and lay it in the capsule, with the upper portion resting on the edge ; the lime will slake in the crucible, and then may be washed thoroughly into the dish, and, as before, the cover is to be washed off.

16. 'We have now by this treatment with water the excess of lime slaked into a hydrate, and some of the lime, combined with the silica and other ingredients of the silicate, in an impalpable form ; in solution there is the excess of the calcium chloride formed in the operation, and all the alkalies originally contained in the mineral as chlorides, and all that now remains to be done is to filter, separate the lime as carbonate, and we have nothing left but the chlorides of the alkalies. To do this, I proceed as follows :—

17. 'Throw the contents of the capsule on a filter (the size preferred for the quantity above specified is one 3 to $3\frac{1}{2}$ inches in diameter), wash well, to do which requires about 200 c.c. of water ; the washing is executed rapidly. The contents of the filter (except in those cases where the amount of the mineral is very small, and there is no more for the estimation of the other constituents) are of no use, unless it be desired to heat again, first adding a little sal-ammoniac to see if any alkali still remains in it, a precaution I find unnecessary. The filtrate contains in solution all the alkalies of the mineral, together with some calcium chloride and caustic lime ; to this solution, after it has been placed in a platinum or porcelain capsule, is added a solution of pure ammonium carbonate (about $1\frac{1}{2}$ gramme is required).

18. 'This precipitates all the lime as carbonate ; it is not, however, filtered immediately, but is evaporated over a water-bath to about 40 c.c., and to this we add again a little ammonium carbonate and a few drops of caustic ammonia to precipitate a little lime that is redissolved by the action of the sal-ammoniac on the carbonate of lime. Filter on a small filter (2 inches), which is readily and thoroughly washed with but little water, and allow the filtrate to run into a small glass beaker. In this filtrate are all the alkalies as chlorides and a little sal-ammoniac ; add a drop of a solution of ammonium carbonate to make sure that no lime is present. Evaporate over a water-bath in a tared platinum dish, in which the alkalies are to be weighed ; the capsule used holds about 30 to 60 c.c., and during the evaporation is never filled to more than two-thirds its capacity.

19. 'After the filtrate has been evaporated over the water-bath to dryness, the bottom of the dish is dried, and on a proper support heated *very gently* by a Bunsen flame to drive off the little sal-ammoniac. It is well to cover the capsule with a piece of thin platinum to prevent any possible loss by the spitting of the salt after the sal-ammoniac has been driven off. Gradually increasing the heat, the

temperature of the dish is brought to a point a little below redness, the cover being off (the cover can be cleansed from any sal-ammoniac that may have condensed by heating it over a lamp). The capsule is again covered, and when sufficiently cool, before becoming quite cold, is placed on the balance and weighed. This weight gives as chlorides the amount of alkalies contained in the mineral.

20. 'If lithium chloride be present, it is necessary to weigh quickly, for the salt being very deliquescent attracts moisture rapidly.

'It not unfrequently occurs that the chlorides at the end of the analysis are more or less coloured with a small amount of carbon, arising from certain constituents in ammonium carbonate; the quantity is usually very minute, and in no way affects the accuracy of the analysis. In selecting pure ammonium carbonate for analytical purposes, it is well to select specimens that are not coloured by the action of the light.

21. 'It only now remains to separate the alkali by the known methods.

'**The Removal of the Sal-Ammoniac unavoidably Accumulated in the Process of Analysis.**—This is probably one of the greatest annoyances to the analyst in his examination of minerals: (1st) from the manner in which the salt creeps up the sides of the vessel in which the evaporation to dryness is carried on; and (2nd) from the great difficulty of preventing loss of the chlorides of the fixed alkalies mixed with sal-ammoniac. Owing to these difficulties, which my experience has often led me to contend with, the method about to be mentioned was contrived. It recommends itself both on account of its simplicity and certainty of operation.

'Having some time back noticed the decomposing effect produced by heating sal-ammoniac with nitric acid, the result of the investigation was that the sal-ammoniac could be completely decomposed at a low temperature into gaseous products, and it was immediately adopted in my analytical process, giving the greatest satisfaction, both as to accuracy of results as well as economy of labour.

'The manner of proceeding is as follows:—To the filtrate and washings concentrated in the way mentioned above, and still remaining in the flask, pure nitric acid is added, about 3 grammes of it to every gramme of sal-ammoniac supposed to exist in the liquid; a little experience will suffice to guide one in adding the nitric acid, as even a large excess has no effect on the accuracy of the analysis.

'The flask is now warmed very gently, and before it reaches the boiling-point of water a gaseous decomposition will take place with great rapidity. This is caused by the decomposition of the sal-ammoniac. It is no great advantage to push the decomposition with too great rapidity; a moderately warm place on the sand-bath is best adapted for this purpose. With proper precautions the heat can be continued, and the contents of the flask evaporated to dryness in that

vessel; but it is more judicious to pour the contents of the flask after the liquid has been reduced to ½ an ounce into a porcelain capsule (always preferring one of Berlin porcelain) of about 3½ to 4 inches diameter, inverting a clean funnel of small diameter over it, and evaporating to dryness on the sand-bath or over a lamp. I prefer the latter, as at the end of the operation the heat can be increased to 400° or 500°.

'By this operation, which requires no superintendence, 100 grammes of sal-ammoniac might be separated as easily and safely as 1 gramme from 5 milligrammes of alkalies, and no loss of the latter be experienced. What remains in the capsule occupies a very small bulk; this is now dissolved in the capsule with a little water (the funnel must be washed with a little water), small quantities of a solution of ammonium carbonate added, and the solution gently evaporated nearly to dryness. This is done to separate what little lime may have escaped the first action of the ammonium carbonate, or may have passed through the filter in solution in carbonic acid. If any of the earths soluble in ammonium carbonate existed in the mineral, they now become separated along with the lime.

'A little more water is now added to the contents of the capsule, and the whole thrown on a small filter; the filtrate as well as washings are received in a small porcelain capsule. The liquid contains only the alkalies (as chlorides and nitrates) mixed with a minute quantity of sal-ammoniac. This is evaporated to dryness over a water-bath, and then heated cautiously over the lamp, to drive off what sal-ammoniac may have formed, which is exceedingly minute if the process as pointed out be closely adhered to. It is not absolutely necessary to heat the capsule over the lamp to get rid of the sal-ammoniac, for the little ammonium sulphate which may be formed in the next step is easily removed in the final heating in a platinum vessel.

'On the contents of the capsule, as taken either from the water-bath or after being treated over the lamp, pure dilute sulphuric acid is poured (1 part acid, 2 water), and the contents boiled for a little time, when all the nitric acid and chlorine in combination with the alkalies will be expelled; the acid solution of the alkalies is now poured into a platinum capsule or crucible, evaporated to dryness, and ignited. In order to ensure complete reduction of the bisulphates to the neutral sulphates, the usual method must be adopted of throwing some pulverised ammonium carbonate in the platinum capsule or crucible, and covering it up so as to have an ammoniacal atmosphere around the salt, which will ensure the volatilisation of the last traces of free sulphuric acid. The alkalies are now in the state of pure sulphates, and may be weighed as such.

'Thus far, the mineral has been supposed to contain no magnesia. If this alkaline earth be present, take the residue as found in the capsule, dissolve it in a little water, then add sufficient pure lime-water[1] to

[1] 'If lime-water is made, it is well to make it of lime of the best quality, and

render the solution alkaline, boil and filter; the magnesia will, in this simple way, be separated from the alkalies. The solution which has passed through the filter is treated with ammonium carbonate in the manner already alluded to on the previous page, and the process continued and completed as described.

'**Conversion of the Sulphates of the Alkalies into Chlorides.** The method ordinarily adopted to accomplish this change is to precipitate the sulphuric acid by means of barium chloride, care being taken to avoid the slightest excess of the latter. The annoyance attendant upon this exact precipitation is familiar to all who may have had occasion to make the trial.

'Instead of barium chloride lead acetate is used; a solution of this salt is poured in excess upon the solution of sulphates; warming the latter slightly, the lead sulphate readily separates; the whole can be immediately thrown on a filter and washed; a drop or two of the lead acetate should be added to the filtrate to ensure there being an excess of the lead salt.

'The filtrate is then warmed and sulphuretted hydrogen added; care must be taken to see that there is an excess of sulphuretted hydrogen, a test most readily performed by means of a piece of lead-paper. The liquid is thrown on a filter to separate the lead sulphide; the filtrate containing the alkalies as acetates is evaporated, and, when nearly dry, an excess of hydrochloric acid is added, and the whole evaporated to dryness, over a water-bath, and finally heated to above 250°. A hot solution of the lead chloride can be used instead of the acetate, rendering the addition of hydrochloric acid unnecessary.

'It needs but little experience to convince one of the superiority of this method over that by the barium chloride for converting the sulphates into the chlorides, its principal recommendation being the indifference with which an excess of the lead salt can be added to precipitate the sulphuric acid, and the subsequent facility with which that excess of lead can be got rid of. It may be well to state that experiments were made to prove the perfect precipitation of the sulphuric acid from the sulphates of the alkalies by lead salts, and it is only after numerous comparative results that it is now recommended.

'**Substitution of Ammonium Chloride for Calcium Fluoride to mix with Calcium Carbonate for Decomposing the Silicates.** It is mentioned above (page 24) on this subject how calcium carbonate could be rendered as powerful in its decomposing agency on the silicates as caustic potash, the effect being due to the use of a flux, fluoride or calcium chloride being used for that purpose. I have since tested more carefully the merits of the calcium chloride, and for various reasons prefer it to the exclusion of the fluoride. In the first place, it

the first two or three portions of distilled water shaken up should be thrown away, as containing the small amount of alkalies sometimes present in lime.

introduces chlorine instead of fluorine into the analysis ; and secondly, the fused mass is more easily detached from the crucible, and dissolved by hydrochloric acid.

'The manner of introducing the calcium chloride into the mixture of mineral and calcium carbonate was a point of some little importance, as from the deliquescent nature of that compound it was inconvenient to weigh and mix it with the calcium carbonate and mineral ; these difficulties are obviated by employing *ammonium chloride* to form indirectly the calcium chloride.

'The process, which appears to leave hardly anything to be desired, is to take 1 *part of the finely pulverised mineral*, 5 *to* 6 *of calcium carbonate, and* $\frac{1}{2}$ *to* $\frac{3}{4}$ *of ammonium chloride* ;[1] mix them intimately in a glazed mortar, place the mixture in a platinum crucible, and heat to bright redness in a furnace[2] from 30 to 40 minutes.

'There is no silicate which, after having undergone this process, is not easily dissolved by hydrochloric acid. For the action of the lime to have been complete, it is not necessary that the mass should have settled down in perfect fusion. The contents of the crucible are dissolved, and the analysis continued as pointed out in the preceding pages.

'This method ensures the obtaining of every particle of the alkalies in the mineral examined, requiring no more precaution than any good analyst is expected to take in the simplest of his processes : and not the least of the advantages is the ready method of separating all the other ingredients, and the small accumulation of water arising from the little washing necessary.

'**A Speedy Method of Separating the Alkalies directly from the Lime-Fusion, for both Qualitative and Quantitative Determination.**—As soon as the fusion with calcium carbonate and sal-ammoniac gave evidence of the mineral being so thoroughly attacked, the question naturally arose as to the condition the alkalies were in after the fusion, and the possibility of dissolving them out by the agency of water alone, at least for the purpose of qualitative determination. Experiments directed to this object soon made it evident that the alkalies might be obtained from any silicate, without resorting to the use of acid as a solvent for the fusion.

'The mass as it comes from the crucible is placed in a capsule with water, and then heated in a sand-bath or over a lamp for two or three

[1] 'The ammonium chloride is best obtained in a pulverulent condition by dissolving some of the salt in hot water, and evaporating rapidly ; the greater portion of the ammonium chloride will deposit itself in a pulverulent condition, the water is poured off, and the salt, thrown on bibulous paper, allowed to dry, the final desiccation being effected on a water-bath, or in any other way with a corresponding temperature.

[2] 'An ordinary portable furnace with a conical sheet-iron cap of from 2 to 3 feet high answers the purpose perfectly well, all the requisite heat being afforded by it,

hours, renewing the water from time to time as it evaporates. The mass disintegrates very shortly after being placed in the water. The contents of the capsule are next thrown on a filter, and the water passes through, containing the chloride of the alkali, a little calcium chloride and caustic lime; all else that the mineral may have contained remains on the filter, except baryta and strontia, if they be present in the mineral; but as these oxides are of rare occurrence in silicates, no allusion will be made to them here.

'To the filtrate add ammonium carbonate, and boil for some time, when all the calcium will be precipitated as carbonate; add a few drops of a solution of ammonium carbonate to the hot solution to be sure that all the calcium is precipitated; should this be the case, filter; the filtrate will contain the chlorides of the alkalies and ammonium chloride; it is evaporated to dryness over a water-bath in a small platinum capsule; the capsule is carefully heated to expel the sal-ammoniac, and finally heated to about 400°; it is then weighed with its contents, and the chlorides, if mixed, separated in any convenient manner. The amount of sal-ammoniac to be expelled is quite small, not equalling the weight of mineral originally employed.

'Nothing in analysis can be simpler or more speedy than this process. Its constant accuracy still lacked something to render it perfect, as, usually an amount of alkali remained behind amounting to from 0·2 to 1 per cent. of the mineral used, certainly a small quantity, but still too much to be omitted in an accurate analysis. This also must be arrived at, and it can be accomplished in the following manner:—

'After the fused mass has been treated with water, filtered, and washed as above, the filter and its contents are dried; the latter are detached from the filter and rubbed up in a glazed mortar with an amount of sal-ammoniac equal to one-half the weight of the mineral and reheated in a platinum crucible exactly as in the first instance, treated with water, thrown on a filter and washed, the filtrate added to that from the first fusion, the whole treated with ammonium carbonate and completed as above described.

'This second fusion complicates the method but little, as the residue on the filter readily dries in a water-bath into a powder that is easily detached from the filter, and the small portion adhering to the latter may be disregarded, as the alkalies remaining rarely exceed more than $\frac{1}{500}$ of the whole mass, and, in most instances, not more than $\frac{1}{1000}$. In many analyses made, one fusion sufficed for the entire extraction of the alkalies; but as a few tenths would occasionally remain behind, we preferred the additional fusion to get that small quantity, and to entitle it to rank as a method by which all but the merest trace of the alkalies could be extracted from the insoluble silicates.

'The proportion of sal-ammoniac added to the calcium carbonate as here recommended was arrived at after numerous experiments. By

increasing the sal-ammoniac, and thereby augmenting the amount of calcium chloride formed, the mass fuses more thoroughly, but the water does not disintegrate it as completely as when the ammoniacal salt is less—an object not to be disregarded.

'The advantage of thus estimating the alkalies in insoluble silicates is obvious; the long routine of separating silica, alumina, lime, &c., is done away with; the accumulation of ammonium chloride is very trifling; and lastly, the alkalies are obtained directly in the form of chlorides. The method will vie in accuracy with any other, including the one already mentioned in the first part of this description, and at the same time it is unequalled in simplicity, speed of execution, and constancy of results.

'In examining for alkalies qualitatively, one fusion will of course be all that is necessary, and the action of the heat need not be continued for more than 30 minutes before filtering. This method will not answer when boracic acid is present in the silicate.' For methods of proceeding in such a case, see the chapter on Boron.

In a subsequent note on the subject of alkalies in silicates Professor Lawrence Smith gives some interesting particulars respecting the presence of rare alkalies in the mineral leucite:—

'The specimens of leucite examined came from four localities—Vesuvius, Andernach, Borghetta, and Frascati. They were about as good specimens as are obtained from those localities, although all of them were not equally pure. The alkalies found in each, calculated as potash, were—

Vesuvius	21·85
Andernach	20·06
Borghetta	20·68
Frascati	20·38

'Although they are said to be "calculated as potash," there is a notable quantity of rubidium and cæsium present in all the specimens above mentioned. In fact, by the method adopted in testing for these alkalies, abundant indications are obtained of the presence of rubidium and cæsium (the last not so readily), even when operating on but ½ a gramme of the mineral. The quantity of these alkalies in leucite is found to be about 0·9 per cent. of the entire mineral. Of course it is not at all remarkable that the amount of potash in the different specimens of leucite should be the same: but it is a matter of interest to know that, from whatsoever locality it comes, this minute quantity of rubidium and cæsium occurs with it.

22. **'A Special Arrangement for Heating the Crucibles by Gas.**—The support and burner, where gas is to be had (as it is in almost all analytical laboratories), are simple in their character, and have been arrived at after a great variety of experiments with gas furnaces. The figure here given illustrates the stand, burner, crucible, &c., and is

about one-sixth the natural size. H is the stand with its rod, G. D is a brass clamp, with two holes at right angles to each other; having two binding screws, it slides on the rod, G; the second hole is for a round arm attached to B, the binding screw, E, fixing it in any position. B is a plate of cast-iron, 5 to 6 millimetres thick, 10 to 11 centimetres long, and 4½ centimetres broad, having a hole in its centre large enough to admit the crucible to within about 15 millimetres of the cover without binding. A is the crucible already referred to, which is made to incline a few degrees downwards, by turning the plate of iron that supports it. C is a chimney of sheet iron, 8 to 9 centimetres long, 10 centimetres high, the width at the bottom being about 4 centimetres at one end and about 3 centimetres at the other end. It is made with the side straight for about 4 centimetres, then inclines towards the top, so as to leave the width of the opening at the top about 1 centimetre. A piece is cut out of the front of the chimney of the width of the diameter of the hole in the iron support, and about 4 centimetres in length, being semicircular at the top, fitting over the platinum crucible. Just above this part of the chimney is rivetted a piece of sheet iron in the form of a flattened hook, N, which holds the chimney in place by being slipped over the top of the crucible support; it serves as a protection to the crucible against the cooling effects of the currents of air. F is the burner, which has been described in an article on flame heat in the *American Journal of Science*, November 1870, p. 341, the upper opening of which is a slit from 1½ to 2 millimetres in width, and from 3 to 4 centimetres long, and when used it is brought within about 2 centimetres of the lowest point of the crucible, the end of the flame just playing around the lower end of the crucible. The gas enters the lower part of the burner by two small holes of $\frac{1}{16}$ of an inch, furnishing at 1 inch pressure about 5½ cubic feet of gas per hour. The precaution must be observed, already referred to, of heating the crucible at first gently.

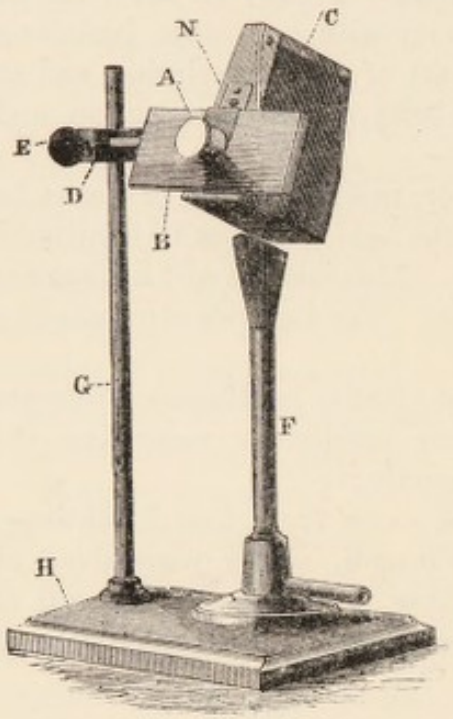


Fig. 1.[1]

23. 'It is surprising to see the effect produced by this simple burner as here used; 8 grammes of precipitated calcium carbonate can be

[1] These burners and stands, as well as the platinum crucibles, made according to Professor Lawrence Smith's pattern, can be obtained of Johnson, Matthey & Co., Hatton Garden.

decomposed to within 2 or 3 per cent. in one hour, and when mixed with silica or a silicate, in a very much shorter space of time, although in my analyses I employ one hour, as it requires no attention after the operation is once started. This form of furnace and crucible is found to be convenient for other operations.

24. 'Although the details given here are lengthy, the time occupied in the analysis is short and the precautions necessary are of a simple character, so much so that results obtained by students beginning chemical analysis have been found by me reliable, and less variable on the alkalies of the silicates than of any of the other constituents of this class of bodies. I have often made good alkali determinations in three hours from the commencement of the operations, hastening the evaporations by more direct application of heat, which, of course, requires close watching.

25. 'It is a common practice, when a silicate comes under my examination that is not easily made out by its physical properties, to make at once an alkali determination, which often indicates at once what it is if it be a known silicate. If not, the alkali determination serves as one step in its examination.'

Estimation of Alkalies in Fire-Clays and other Insoluble Silicates

Mr. G. Gore, F.R.S., has described a modification of the hydrofluoric process of treating silicates, which has been found useful when only the alkalies are required. An intimate mixture of the finely powdered fire-clay, barium nitrate, and barium fluoride is projected into a heated crucible; when all the mixture has been thrown in, the crucible is covered and gradually heated in a furnace until the contents are completely melted; the mixture is poured into a cast-iron vessel and immediately covered over. The resulting fused mass is finely powdered, digested with sulphuric acid, evaporated to dryness, and afterwards treated in the usual manner. The results of analyses made in this manner agree with those obtained by the hydrofluoric acid process.

Estimation of Lithium by Sodium Phosphate

Berzelius detected lithium in Carlsbad water by evaporating the solution of the alkalies with phosphoric acid and sodium carbonate. On treating the whole with water, an insoluble sodium and lithium phosphate remained. This double salt has been shown by C. Rammelsberg to be a variable mixture of the two phosphates. Mayer, however, contradicted these results and denied the existence of a double phosphate, and contended that the above residue was pure lithium phosphate. C. Rammelsberg has repeated his former experiments

and completely confirmed them, preparing synthetically double salts having sodium to lithium as 1 to 3, or 9 to 2, and therefore he concludes that lithium cannot be determined by Mayer's method, which is also recommended by Fresenius. The employment of this process for the estimation of lithium in micas has led to too high a percentage of lithium. Lithium and sodium chlorides may be separated by treatment with ether and alcohol.

Extraction of Cæsium and Rubidium from Mineral Waters

Compounds of these rarer alkali metals may be separated in the following manner from saline mother-liquors derived from the evaporation of some mineral waters. A boiling dilute solution of platinum chloride added to a boiling, rather dilute solution, containing potassium, rubidium, and cæsium, will precipitate the latter metals with but a very small proportion of the first. The platinum being removed from this precipitate by means of sulphuretted hydrogen, the alkaline metals are again brought into dilute solution as chlorides; the solution is heated to boiling, and once more a dilute solution of platinum chloride is added in two portions. After each addition the liquor is filtered, while boiling, through a water-bath filter, and the precipitate is washed in hot water; the solution is then allowed to cool and deposit. In this way three precipitates are obtained; the first contains nearly all the cæsium, the second almost all the rubidium, and the third, deposited on cooling, is, for the most part, the potassium compound. By repeating these precipitations the compounds may be almost completely separated. The cæsium and rubidium may be finally separated from each other by one of the methods subsequently described (page 38).

Extraction of Cæsium and Rubidium from Lepidolite

Dr. Oscar D. Allen, of Yale College, has shown that the lepidolite occurring at Hebron, in Maine, U.S., contains these metals in comparative abundance, and he has recommended the following process for their extraction from this mineral. The process used is based upon that employed by Professor J. Lawrence Smith, for the determination of alkalies in silicates (for this process, see page 23). Ten parts of the pulverised lepidolite are first mixed with 40 parts of coarsely powdered quicklime; a mixture of enough water to slake the quicklime, with hydrochloric acid sufficient to form from 6 to 7 parts of calcium chloride, is next made ready; the two mixtures are then united and stirred vigorously during the process of slaking, thus intimately blending the mineral with suitable proportions of dry hydrate of lime and calcium chloride. Practically as good results are obtained when the lepidolite is powdered sufficiently fine to pass through a sieve of twenty

holes to the linear inch, as when it is more finely pulverised; the fact being that the foliated structure of the mineral exposes a large surface to the decomposing effect of the lime mixture.

This mixture is heated to redness for six or eight hours in Hessian crucibles. Care must be taken to avoid a heat much above redness, as otherwise alkaline chlorides volatilise in dense clouds, and the mass fusing is absorbed to a considerable extent into the crucible and lost.

The agglomerated product obtained from the ignition of this mixture is detached from the crucible, boiled with water from a quarter to half an hour, and washed till all but a trace of the chlorides is removed. The solution thus procured, containing calcium chloride and the chlorides of the alkali metals, is evaporated till crystals begin to form; then sulphuric acid is added as long as calcium sulphate separates, taking care to avoid excess: and the whole mass is evaporated to dryness and strongly heated to expel free hydrochloric acid. The residue is treated with water, and the small quantity of calcium sulphate which goes into solution is precipitated with ammonium carbonate. The filtered solution is again evaporated to dryness and ignited.

In this manner is obtained a mixture of salts, consisting of the chlorides with a small admixture of sodium, potassium, lithium, rubidium, and cæsium sulphates. By treating this by the process of fractional precipitation with platinum chloride, a mixture of the cæsium and rubidium platino-chlorides is obtained, in which no potassium can be detected with the spectroscope. The platinum salts are to be gently heated in a current of hydrogen, until a complete reduction of the platinum takes place, when the alkaline chlorides may be extracted with water.

By working in the above manner Dr. Allen obtained from 10½ kilogrammes of lepidolite 2169 grammes of crude alkaline chlorides, which yielded 172 grammes of mixed cæsium and rubidium platino-chlorides, equivalent to a yield of about ½ per cent. of the two metals from the lepidolite.

In separating the cæsium and rubidium platinum salts from that of potassium, a not inconsiderable amount of these metals goes into solution with the potassium salt, thus materially diminishing the quantity obtained; much the larger proportion of this loss is rubidium, due to the greater solubility of its platinum salt. This can in great measure be recovered by a repetition of the treatment.

Separation of Potassium, Sodium, and Lithium

If potassium, sodium, and lithium are present in the same solution, convert the three into platino-chlorides, extract the sodium and lithium salts with a mixture of alcohol and ether containing a little hydrochloric acid, and wash with a mixture of absolute alcohol 6 volumes,

ether 1 volume; the residue is pure potassium platino-chloride. Direct experiments show that the above method is not vitiated in any degree by the presence of hydrochloric, nitric, phosphoric, arsenic, or boric acids, or salts of magnesium, zinc, manganese, iron (ferrous or ferric), aluminium, nickel, or copper.

Antimony Chloride as Reagent for the Cæsium Salts

(*A*) If the solution of cæsium salt, not too dilute, is mixed with a solution of antimony chloride in concentrated hydrochloric acid, a white crystalline precipitate is at once formed which, according to R. Godeffroy, does not disappear on the addition of hydrochloric acid. The solutions of the other alkali metals yield no precipitate if similarly treated. The precipitate may be filtered, washed with concentrated hydrochloric acid, and redissolved in the same acid much diluted. The solution yields on evaporation, well-developed, hard, permanent crystals belonging to the hexagonal system. They may be obtained pure by repeated solution in dilute hydrochloric acid, and recrystallisation. They contain 33·419 per cent. of chlorine, and of antimony 30·531 per cent., corresponding to the formula $SbCl_3CsCl$. This salt is decomposed on the application of heat, and on treatment with water. It is completely soluble in dilute acids.

(*B*) Charples and Stolba observed a similar reaction of the cæsium salts with stannic chloride. The rubidium salts, however, give with tin chloride a precipitate which is very sparingly soluble. The presence of ammonia in the liquid contaminates the double cæsium and tin chloride with 'pink salt.' The reaction with antimony chloride is not interfered with either by ammonia or rubidium. The liquid must be strongly acid to prevent the precipitation of antimony oxychloride.

Separation of Cæsium from Rubidium

(*A*) The plan recommended by Dr. Allen for separating these metals depends upon the fact that bitartrate of rubidium requires about eight times as much water for its solution as the cæsium bitartrate, and hence they are easily separated by crystallisation.

The mixed chlorides are converted into carbonates by first converting them into sulphates, separating the sulphuric acid by caustic baryta, and removing the excess of baryta by carbonic acid. To the alkaline solution thus obtained twice as much tartaric acid is added as is necessary to neutralise it. This solution is concentrated until it is nearly saturated at 100° C. The crystals, which deposit on cooling, show the rubidium lines more intensely than did the original mixture, whilst the cæsium lines are much fainter. This product is dissolved and recrystallised from hot saturated solutions three times. The cæsium reaction in these successive crops diminishes until, in the fourth, it disappears, leaving the rubidium spectrum in entire purity.

The solution from which the first crystals have been removed is concentrated to nearly one-half its original volume, when, on cooling, a very small quantity of salts of the two alkalies is deposited. On repeating this operation three times, a portion of the solution, evaporated to dryness and examined by the spectroscope, gives only the lines belonging to cæsium. The several intermediate products containing both alkalies are then united, and another portion of each salt is separated from them in the same manner. By repeating this process of fractional crystallisation four times, about 90 per cent. of a mixture of these alkalies may be separated in a perfectly pure state. It requires no great expenditure of time, since the solutions employed can be concentrated at high temperatures, and, on cooling, immediately deposit well-formed crystals.

(*B*) Bunsen's recent method for the separation of cæsium and rubidium is somewhat similar to the above, but it has the advantage that it can be effected when working on less material. It is as follows :— In a mixture of pure cæsium and rubidium chlorides the chlorine is determined, and from its amount that of rubidium is calculated. The chlorides are converted into carbonates, and to the latter salts a little more tartaric acid is added than is necessary to produce neutral cæsium tartrate and rubidium bitartrate. The mixture, dried and pulverised, is brought upon a funnel, whose neck is stopped by a small filter, and the whole is plaeed in an atmosphere saturated with moisture. The neutral cæsium salt deliquesces, and passes the filter, while the acid rubidium salt remains behind.

AMMONIUM

Estimation of Ammonia in Gas Liquor

Mr. T. E. Davis considers that the direct titration of liquor with normal sulphuric acid and calculation into ammonia would be a test sufficient to base a contract upon ; and for the guidance of a manufacturer, and for all practical purposes, it may be looked upon as correct. Moreover, each test does not take five minutes, whereas the distillation process takes the best part of an hour.

The titration method of testing is as follows :—Into a flask of about 300 c.c. capacity, 10 c.c. of the sample to be tested are run in, and into this 15 c.c. of normal sulphuric acid. The contents of the flask are then raised to boiling over a naked flame, a few drops of litmus added and titrated back with normal soda. The number of c.c. of soda used is deducted from the 15 c.c. of acid employed, the result multiplied by 17 and divided by the specific gravity of the liquor. The result thus obtained represents the percentage of ammonia contained in the liquor. An example will make this clear :—10 c.c. of a liquor at 5° T. (sp. gr.=1025), boiled with 15 c.c. normal acid, require 5 c.c.

normal soda to neutralise it, consequently the sample contains 1·658 per cent. NH_3 : thus—

$$\frac{(15-5) \times 17}{1025} = 1{\cdot}658$$

Now as to the valuation. Suppose we consider 10*s.* per unit of NH_3 per ton to be fair value, then the above sample would be worth $1{\cdot}66 \times 105 = 17s.$ 5*d.* per ton. Such a system would induce gas managers to make the liquor as strong as possible, and ammonia manufacturers would do well if they were to refuse a contract for liquor containing less than 1 per cent. of NH_3 ; for if below this—unless the liquor were given them—they would barely clear expenses of manufacture.

Ammonium Chloride in Analysis.—For the best method of removing the ammonium chloride which unavoidably accumulates in the process of analysis, see *ante*, page 28.

CHAPTER II

CALCIUM, STRONTIUM, BARIUM, GLUCINUM, MAGNESIUM

Indirect Estimation of Calcium, Strontium, and Barium

THE estimation of these three earthy metals is generally effected after they are separated from each other. These separations can be dispensed with if an indirect method be employed, thereby avoiding the loss attendant upon different separations, and materially hastening and simplifying the whole estimation. The following indirect method, which is very successful for the estimation of these three metals, may also be employed in the presence of magnesium.

In the first place, the calcium, strontium, and barium must be precipitated as carbonates, by means of ammonium carbonate and hydrate. It must be borne in mind that in a liquid containing much sal-ammoniac or ammonium nitrate neither calcium, strontium, nor barium can be completely precipitated by ammonium carbonate, so that, after filtering, it is possible, by means of sulphuric acid or ammonium oxalate, to recognise a more or less considerable quantity. The cause of this is, that ammoniacal salts of strong acids have a solvent action upon calcium carbonate, and this action is still stronger upon the strontium and barium carbonates. On the other hand, should ammonium acetate or carbonate be used, instead of sal-ammoniac or ammonium nitrate in solution, the precipitation of the three bases by ammonium carbonate will be so complete that it will be impossible to discover in the filtrate, by means of the before-mentioned reagents, any traces of calcium, strontium, or barium.

In order to have in solution no other ammoniacal salts than acetate and carbonate, it will suffice to add to the tolerably neutral solution as much sodium acetate as there is supposed to be sal-ammoniac or ammonium nitrate held in solution, and then to supersaturate with ammonia and ammonium carbonate and, after a short digestion, to cool the solution ; the carbonated alkaline earths which have in this manner been completely precipitated are now filtered off.

Digestion is not absolutely necessary here ; it only serves to render those deposits granular which would otherwise be voluminous. On

the other hand, in order to obtain complete precipitation, it will be necessary to reduce the whole to the ordinary temperature before filtering, because hot ammonium acetate has a solvent action upon carbonated alkaline earths, although in a far less degree than sal-ammoniac.

A certain degree of dilution of the ammoniacal salt is to be recommended; in any case, the solution must not be more concentrated than in the proportion of 1 part of salt to 20 of water.

Sodium carbonate may be substituted for the acetate, in order to decompose the sal-ammoniac; but if, at the same time, magnesium be held in solution, the presence of a large quantity of an ammonium salt of stronger acid than carbonic will be necessary, in order that it may not be deposited with the alkaline earths. For this purpose, the addition of sodium acetate is eminently suitable, because the ammonium acetate thus formed (as with oxygenated ammonium salts generally) prevents the precipitation of the magnesium much more than sal-ammoniac does, without, as before remarked, dissolving barium, strontium, or calcium.

In the presence of magnesium, a too great excess of ammonium carbonate must be avoided as a reagent, in order to hinder the formation of ammoniacal magnesium carbonate, which is difficult to dissolve. After these precautionary measures, the barium, strontium, and calcium having been separated, the precipitate is washed, filtered, dried, heated, and weighed; it is then dissolved in a measured quantity of normal hydrochloric acid and titrated. This is done (after removing the carbonic acid by heat from the diluted solution, which is coloured with litmus) by estimating with normal standard ammonia solution the amount of hydrochloric acid which had been required to transform the three carbonates into chlorides. The solution is now mixed with a known amount of potassium bichromate, caustic ammonia being added in excess, to precipitate all the barium, so that no trace of it may be detected in the acidulated filtrate, by potassium fluosilicate and alcohol.[1] The barium chromate is filtered off and washed until lead acetate ceases to give a yellow precipitate in the filtrate; in the solution the excess of chromic acid is determined according to the usual process, with a standard solution of iron protosulphate; and the amount of baryta is then obtained, according to the formula—

$$\text{Chromic acid} \times 1{\cdot}527 = \text{Baryta},$$
$$\text{or} \qquad \text{Chromic acid} \times 1{\cdot}964 = \text{Barium carbonate}.$$

If, on the one hand, the amount of barium carbonate thus obtained be deducted from the weight of the three carbonates, and, on the other,

[1] Pure barium chloride solution produces no turbidity when, after the precipitation of baryta by potassium chromate and ammonia, the filtrate is mixed with sulphuric acid. It is, of course, assumed that the reagents employed in precipitation are quite free from sulphuric acid.

the amount of hydrochloric acid answering to the baryta be calculated, the difference between this amount of hydrochloric acid and the amount found, will be the quantity of hydrochloric acid which corresponds to the united weight of the calcium and strontium carbonates, which has just been calculated.

The amount of calcium and strontium carbonates is obtained as follows :—Calculate the amount of calcium carbonate (which is equivalent to the known quantity of hydrochloric acid) contained in the excess of calcium and strontium carbonates, deduct this from the weight of the two carbonates, multiply the remainder by the constant factor $3_1^1{}_2$, and the product will then be the required quantity of strontium carbonate ; this, when again subtracted from the united weight of both salts, yields, as its remainder, the quantity of calcium carbonate. The constant factor, $3_1^1{}_2$, is obtained by the following calculation :—

	Calcium carbonate =	100
	Strontium carbonate =	148
	Calcium and strontium carbonates =	248
hence	2 eqs. of calcium carbonate =	200

and this subtracted from the equivalent of strontium carbonate leaves 48, and 148 divided by 48 = $3_1^1{}_2$.

This method of estimating these three earthy metals always yields satisfactory results. It is quickly carried out, and is very exact, because the precipitations are all perfect, and the two volumetric estimations involved in the method admit of great accuracy. Moreover the troublesome and somewhat uncertain separation of the strontium and calcium with a concentrated solution of ammonium sulphate, which is very inconvenient in estimating the calcium, is avoided.

In the absence of strontium, either precipitate the calcium and barium as carbonates, estimating the precipitate alkalimetrically ; or precipitate the barium as sulphate, and the calcium as carbonate, by digesting the solutions of both with a mixture of 3 parts of potassium sulphate and 1 part of potassium carbonate ; weigh the dried and ignited precipitate, and estimate the calcium carbonate alkalimetrically.

Estimation of Calcium

(*A*) Dr. A. Cossa has determined the accuracy of estimating calcium as quicklime or caustic lime, instead of weighing it as calcium carbonate. The experiments were made—(1) with pure calcium oxalate previously dried at 100° ; (2) with calcium carbonate precipitated from a solution of pure calcium chloride by means of pure sodium carbonate ; (3) with pure native calcium carbonate. The result of an average of three experiments with No. 1 is 0·07 per cent. too low ; with No. 2, 0·35 per cent. too low ; with No. 3, 0·27 per cent. too high.

(*B*) To avoid the inaccuracy and loss of time nearly always resulting from the ordinary method of determining calcium, viz. by strongly heating the precipitate of calcium oxalate, and converting the same into carbonate by repeatedly moistening with solution of ammonium carbonate, Mr. Scott recommends weighing the precipitate as *sulphate* instead. The addition of sulphuric acid, or even of ammonium sulphate alone, to caustic lime is hardly a safe operation from an analytical point of view, if the mass in the crucible is at all bulky, but by using the following solution no inconvenience is experienced. Three parts of pure ammonia of the ordinary strength should be neutralised with pure sulphuric acid (previously diluted with its bulk of water), and two parts of the ammonia solution added. In each ounce of the fluid thus obtained 10 grains of ammonium chloride must be dissolved: the whole may then be filtered into a small reagent bottle and appropriately labelled. It must, of course, entirely volatilise when heated on platinum foil. In this manner the calcium is weighed as *sulphate*, which may be strongly ignited without change, *one weighing* therefore being sufficient.

F. B. Guthrie and C. R. Barker[1] propose an improvement on the usual process for separating calcium. They mix previously dried and powdered ammonium nitrate with the calcium oxalate precipitate obtained in the usual manner. The oxalate is converted into calcium nitrate, which is very readily and completely converted into oxide by a few minutes' ignition over a Bunsen burner.

Prolonged ignition over the blowpipe is quite unnecessary, and effects no further alteration of the weight of the precipitate.

Calcium Phosphates

The commercial estimation of superphosphates is given in the chapter on Phosphoric Acid. The following process, recommended by Professor F. Wöhler for the analysis of apatite and similar phosphates, will be found to be one of the most trustworthy:—Dissolve the mineral in nitric acid in a capsule, and then add pure mercury in such quantity that when the acid is saturated with it there still remains a portion of mercury undissolved. Evaporate the mixture on the water-bath to complete dryness. If a slight odour of nitric acid is still apparent, add more water, and evaporate again to dryness, so as to get rid of it completely; then extract with water, place it on the smallest possible filter, and well wash the residue, which contains all the phosphoric acid.

Besides the excess of mercury the filtrate contains all the calcium. Precipitate the mercury proto-salt with hydrochloric acid. As a little mercuric binoxide may have been formed, precipitate the solution with

[1] *Chemical News*, Oct. 24, 1902.

ammonia. If the mineral contains iron or other bases precipitable with ammonia, these remain after calcining the last precipitate. The solution is rapidly filtered, with as little exposure to the air as possible, and the calcium in it precipitated with ammonium oxalate.

The filter, which, besides the excess of mercury, contains phosphoric acid, is well dried, and the whole is placed in a platinum crucible and mixed with potassium and sodium carbonates. The crucible is then heated to a temperature below redness, under a chimney with a good draught, until all the mercury is volatilised, after which it may be heated to redness and the contents fused. Then dissolve in water, add an excess of hydrochloric acid, and precipitate the phosphoric acid with ammonia and magnesium sulphate.

To estimate the chlorine, dissolve a known weight of the mineral in dilute nitric acid,[1] and precipitate the chlorine with silver nitrate.

Some kinds of apatite contain a small quantity of fluorine. When it is desired to ascertain the presence of this body, finely powder the mineral and then mix it in a platinum crucible with concentrated sulphuric acid; cover the crucible with a piece of glass coated with wax and having characters traced on it with the point of a needle. Then heat the crucible, taking care not to melt the wax. If fluorine is present, the characters will be found engraved on the glass when the wax is removed. The amount of fluorine present may be deduced from the loss of weight obtained in the complete analysis.

Separation of Calcium from Strontium

(*A*) The best process is that originally devised by Stromeyer, based upon the solubility of calcium nitrate in absolute alcohol and the insolubility therein of strontium nitrate, but adding an equal volume of ether to the alcohol. A mixture of alcohol and ether does not dissolve more than $\frac{1}{60000}$ part of strontium nitrate, whilst it dissolves calcium nitrate perfectly.

(*B*) A similar separation may be effected by ammonium sulphate, in which calcium sulphate is soluble, whilst strontium sulphate remains unaffected. The proportions to employ are: 50 parts of ammonium sulphate and 200 parts of water to 1 part of strontium sulphate. There is then formed a soluble double salt, which resembles potassio-gypsite (calcium and potassium sulphate). This process is, however, less delicate than that of Stromeyer.

Detection of Calcium in the Presence of Strontium

C. L. Bloxam has devised a very delicate method of detecting calcium in the presence of strontium. If a solution of calcium

[1] Certain brown apatites leave as a residue a small quantity of a crystalline powder, which is cryptolite (cerous phosphate).

sulphate be mixed with ammonia and a little solution of arsenic acid, it yields on stirring with a glass rod a highly crystalline precipitate of ammonium-calcium arseniate which is deposited very strongly on the lines where the glass rod has rubbed the tube. This precipitate is nearly as insoluble as calcium oxalate, whilst it is far more crystalline.

When strontium chloride is precipitated by excess of sulphuric acid the minute quantity of strontium left in the solution is not precipitated by ammonia in excess and arsenic acid.

A solution containing 1 part (0·0381 grain) of calcium and 50 parts of strontium, acidulated with hydrochloric acid, precipitated by sulphuric acid, filtered, mixed with excess of ammonia, cooled, and stirred with a little solution of arsenic acid, gave a copious crystalline precipitate. With 1 part (0·019 grain) of calcium and 100 parts of strontium the precipitate appeared after two or three minutes.

With the same weight of calcium and 500 parts of strontium, the filtrate from the strontium sulphate was evaporated to a small bulk, mixed with excess of ammonia, filtered from a further deposit of strontium sulphate and stirred with arsenic acid; in a few seconds the precipitate of ammonium-calcium arseniate was deposited on the lines of friction and identified by the microscope.

Samples of strontium nitrate and carbonate, purchased as pure, were found to contain much calcium when examined in this way.

Separation of Strontium from Barium

When in the form of sulphates, prolonged digestion with a cold solution of ammonium carbonate will convert the strontium into carbonate, whilst it has no action on the barium. Boiling the solution or employing sodium carbonate is not so effectual. Finely pulverise the mixed salts, wash thoroughly with water, and treat with nitric acid. The strontium will dissolve as nitrate and leave the residue of the barium sulphate. Barium and calcium may be separated in a similar manner.

Separation of Calcium from Barium and Strontium

(*A*) P. E. Browning has found that when in the form of nitrates, boiling amyl alcohol dissolves the calcium salt while it has no action on the barium or strontium salt. For details of the operations the reader is referred to the author's papers in the *American Journal of Science*, vol. xliii., 1892.

(*B*) R. Fresenius sums up the results of a prolonged investigation on the separation of strontium from barium as follows:—

1. Barium chromate is not soluble in water containing acetic acid

if so much ammonium chromate is present that the liquid contains only alkaline acetate and bichromate.

2. Barium chromate dried at 110° is not anhydrous (as formerly assumed), but contains about 0·5 per cent. of moisture.

3. Barium chromate is not decomposed on gentle ignition, and if adhering to a filter it may be weighed without loss by cautiously incinerating the filter and gently igniting the residue.

4. The determination of barium by precipitation with ammonium chromate gives results which are perfectly satisfactory.

5. The complete separation of barium, from strontium by a single precipitation of the former as a chromate is not successful under any circumstances. The most favourable results obtained in this manner depend on the accidental compensation of errors of a conflicting nature.

6. A complete separation of barium and strontium, and an absolutely satisfactory result in the determination of both bases, can be obtained only by a twice repeated precipitation of the barium in an acetate solution with an excess of ammonium chromate; the strontium can then be thrown down as strontium carbonate, which is then purified by conversion into sulphate.

Although the estimation of both barium and calcium when present together, or of strontium when alone, presents but little trouble, yet, if the whole three members of the group be taken, the task becomes one of greatly increased difficulty, it being no easy matter to ensure either the complete precipitation or the entire retention in solution, according to the process to be employed, of the strontium.

Mr. S. L. Rawson [1] has described a method which depends entirely upon the behaviour of the nitrates of these three metals towards concentrated nitric acid. The method is also readily applicable to qualitative analysis :—The nitrates of barium and of strontium are quite insoluble in this acid, whilst calcium nitrate dissolves very rapidly.

The carbonates are evaporated with nitric acid, in a porcelain dish, upon the water-bath until the mass is quite dry. Concentrated nitric acid is added in excess, and the mixture is kept well stirred. The crystals settle out after each stirring very rapidly, and the clear supernatant liquid is poured through a double filter-paper which has been moistened previously with concentrated nitric acid. The residue may be washed either with the concentrated acid by decantation, a method to which the mass from its crystalline nature readily lends itself, or in the customary way upon the paper.

The filtrate is evaporated either to dryness, taken up with hydrochloric acid, and the calcium precipitated as oxalate, or evaporated down with sulphuric acid, and the residue after ignition weighed as sulphate.

The remaining nitrates are dissolved in water, and the solution made

[1] *Chemical News*, May 21, 1897.

alkaline with ammonium hydrate, acidulated with acetic acid, and the barium precipitated as chromate. The filtrate is warmed with hydrochloric acid and alcohol until the chromate is reduced, the chromium precipitated as hydrate and filtered off. The filtrate is evaporated to dryness upon the water-bath with a little sulphuric acid. The residue is treated with dilute alcohol and washed, and the residual strontium sulphate weighed as such.

For the qualitative separation the above process may be much simplified. The carbonates, after treating with the minimum amount of nitric acid, are boiled down just to dryness; then treated with concentrated nitric acid, the paper having been first moistened with this acid, filtered, and the residue washed by decantation. The filtrate is diluted considerably with water made alkaline with ammonia, and the lime thrown down as oxalate. The residue is dissolved in water (the filter-paper will not disintegrate unless boiling water be used), made alkaline with ammonia, acidulated with acetic acid, and the barium precipitated as chromate. To the filtrate is added hydrochloric acid, and it is boiled with a little alcohol, and the chromium precipitated as hydrate, which is filtered off. To the filtrate sulphuric acid is added, and the solution heated; if necessary alcohol is added, the strontium coming down as sulphate. The separation of the chromium as hydrate is not in all cases necessary.

The specific gravity of the nitric acid should be about 1·46 (corresponding to 80 per cent. of the acid), or even higher, but for most purposes the ordinary acid of specific gravity 1·42 (containing 70 per cent. of HNO_3) will suffice.

GLUCINUM

Preparation of Pure Glucina

The simplest way to prepare a chemically pure glucinum salt is to make use of the process devised by Dr. W. Gibbs. The crude glucina obtained in the ordinary manner from beryl, but still contaminated with alumina, iron, &c., is fused with twice its weight of acid potassium fluoride, and the fused mass treated with boiling water, to which a small quantity of hydrofluoric acid has been added. On filtering, a notable quantity of the insoluble aluminium and potassium fluoride almost always remains upon the filter, even when the separation of glucina has been carefully executed by means of ammonium carbonate. The filtrate, on cooling, deposits colourless transparent crusts of the double glucinum and potassium fluoride, which are easily purified by recrystallisation.

Glucina may be prepared direct from beryl by this process, but as beryl contains only 13 or 14 per cent. of glucinum, it will be more economical to separate the other oxides, as far as possible, by the

ordinary methods, and then to purify the crude glucina by the above process.

From the aqueous solution of the double fluoride, pure glucina may be precipitated directly by ammonia.

C. Lathrop Parsons[1] prepares glucina from beryl as follows :—

The powdered beryl is fused in a Battersea crucible with a mixture of sodium and potassium carbonates, and the fused mass turned out to cool on a smooth iron plate. The melt is pulverised and washed with water, which removes the soluble sodium and potassium salts, notable amounts of silica, and some glucinum, but the loss is more than compensated for by the greater ease of the subsequent operations. The moist residue is just barely covered with water, and concentrated sulphuric acid added in excess, by which procedure it becomes at once a dense jelly-like mass, which is easily broken up, dried, and heated on a sand-bath to render the silica insoluble. The fine, nearly white and dry powder so produced is washed with hot water, potassium sulphate added to the solution, and the major part of the aluminium crystallised out as alum. The mother-liquor is oxidised with potassium chlorate and sodium carbonate carefully added in small portions at a time, with intermediate boiling until the filtered solution is colourless. Most of the remaining iron and aluminium are thus precipitated before the glucinum, as Hart has pointed out,[2] and the selective action is undoubtedly due to the power which glucinum sulphate has of dissolving considerable amounts of its own carbonate. To the filtered solution sodium carbonate is added with care to avoid any great excess, as the precipitated basic glucinum carbonate is notably soluble in sodium carbonate solution, and the precipitate washed to remove sodium salts. It is then dissolved in excess of sulphuric acid, and the sulphate crystallised out on evaporation. After a second crystallisation from pure water the sulphate is again dissolved, precipitated by ammonia, filtered and washed, without any attempt, however, to free the gelatinous hydroxide entirely from sulphates. The removal of the main part of the ammonium sulphate is advisable, however, as the reverse reaction takes place to a greater or less extent on continued boiling, after precipitating the basic carbonate from ammonium carbonate solution, and is, of course, proportional to the amount of sulphate present. The reaction may be easily complete if excess of sulphuric acid is present before neutralisation. The glucinum hydroxide is transferred to a large bottle, covered with an excess of dilute ammonia, and carbon dioxide passed through the liquid. When nearly saturated, more ammonia is added, the carbon dioxide shut off, and the bottle allowed to stand in a warm place, with occasional shaking. The liquid is filtered from some undissolved aluminium hydroxide, and is treated with excess of

[1] *Journal of the American Chemical Society*, vol. xxvi. No. 7.

[2] *Ibid.* vol. xvii. p. 604.

ammonium sulphide, as recommended by Scheerer,[1] and Kruss and Moraht.[2] A small amount of black precipitate is invariably thrown down at this stage. After standing for several days, the solution is filtered, with special care that the black precipitate is at all times in contact with liquid containing ammonium sulphide. It is then boiled with constant stirring until ammonia is evolved and precipitation is complete. Vigorous stirring of some form is absolutely necessary, as the granular precipitate settles quickly and causes violent bumping. The basic carbonate thrown down varies continually in composition as precipitation progresses, but the final product has the approximate formula $Gl[Gl(OH)_2]_3CO_3 \cdot 2H_2O$ when dried over sulphuric acid. It is slightly soluble in water, so precipitation is never quite complete. At 100° it loses about 4·50 per cent. of water, and contains about 44 per cent. of glucina. Like all the basic compounds of glucinum which have come under my observation, except those of the acetate group to be described later, its composition is by no means definite. The carbonate is twice redissolved in pure sulphuric acid, and reprecipitated from ammonium carbonate as described above, except that the treatment with ammonium sulphide, although each time repeated, fails to separate any further black sulphide.

G. Wyrouboff[3] purifies glucina by taking advantage of the unsolubility of the oxalate of glucinum and potassium.

At 15° 100 parts of water dissolve 1·4 parts of this salt, and the solubility increases only slowly with the temperature. This salt only contains 9·5 per cent. of glucina ; it therefore follows that the solubility of the precipitated glucina is about 1 part per 1000.

It sufficed to attack the mineral with potash, eliminate the silica in the usual method, evaporate the solution of chlorides to a small volume, and add a concentrated solution of binoxalate of potash. After some time a crystalline precipitate is deposited, which is collected on a filter, and washed with water. The salt, which is very slightly soluble in water, dissolves with ease in dilute acids.

P. Lebeau[4] purifies crude glucina in the following manner :—

Impure glucinum carbonate is redissolved in nitric acid, and the dilute solution is mixed with a little potassium ferrocyanide, which throws down all the iron.

Filter, then remove the excess of ferrocyanide by means of copper nitrate ; the copper being finally eliminated by means of a current of hydrogen sulphide : we have thus a solution of glucinum nitrate free from iron. It is then only necessary to separate the alumina which was carried down in the first solution in ammonium carbonate.

To remove these last traces of alumina, we have utilised the property of aluminium hydroxide of being easily polymerised even in the cold, and of thus becoming much less easily attackable by reagents. If

[1] *Journ. Prakt. Chem.* [1] xxvii. 76. [2] Liebig's *Ann. Chem.* vol. cclxxi. p. 47.
[3] *Chemical News*, Aug. 8, 1902. [4] *Ibid.* Jan. 9, 1896.

the precipitate of hydroxide obtained on treating ammonium nitrate or sulphate with ammonia is allowed to remain in the liquid in which it has been formed, it loses its gelatinous aspect, and becomes much less easily soluble in acids. It is then completely insoluble in ammonium carbonate.

Glucina free from iron is precipitated from its nitric solution by ammonia. It is left to settle for three or four days, the supernatant liquid is decanted away and is replaced by a concentrated solution of ammonium carbonate, which slowly dissolves the glucina, leaving a slight white deposit of alumina.

The filtrate is heated to ebullition, and the precipitate thus formed is carefully washed, and dissolved in pure nitric acid. On evaporating and igniting the solution, glucina is obtained in a dense absolutely pure form.

MAGNESIUM

Determination of Magnesium as Pyrophosphate

(*A*) Mr. R. W. Emerson McIvor strongly recommends the process of Dr. Gibbs, who substitutes microcosmic salt for ordinary sodium phosphate. He heats the mixed solution of magnesium sulphate and ammonium chloride to the boiling point, and precipitates the magnesium from the boiling liquid by adding the ammonium phosphate solution. After having been allowed to cool, ammonium hydrate is added, and the whole allowed to stand for twenty-four hours. The precipitate of magnesium ammonio-phosphate is then collected upon a filter, dried at 100° C., ignited, and weighed as magnesium pyrophosphate in the usual manner. As magnesium is a substance which analysts have frequent occasion to estimate, Dr. Gibbs's suggestions are well worthy of their consideration.

(*B*) Experiments have been conducted by Mr. Lawrence Briant to determine whether the well-known accelerative action of agitation could not be applied to the precipitation of magnesia, so as to shorten the duration of the experiment.

The mode of procedure was as follows:—Comparative determinations were made in which the quantity of magnesia in given solutions was estimated by three ways. First, precipitation in the ordinary manner, allowing the liquid to stand in the cold for twenty-four hours; second, after twelve hours; and third, after violently shaking in a stoppered glass jar for ten minutes, at once throwing the liquid on to a filter. The volume of liquid was in each experiment the same, viz. 155 c.c., whilst the precipitate was washed with 100 c.c. of dilute ammonia (1 to 3), divided into three different washings, after each of which the filter was allowed to drain completely. The precipitate in the case of the experiments in which the liquid was violently shaken was very granular, and was without difficulty transferred to the filter.

The results are as follows :—

	Treatment	MgO found	MgO present
		grm.	grm.
1	stood twenty-four hours	0·050	0·050
2	„ twelve „	0·049	0·050
3	shaken ten minutes	0·051	0·050
4	„ „ „	0·050	0·050
5	„ „ „	0·050	0·050
6	stood twenty-four hours	0·022	0·022
7	„ twelve „	0·022	0·022
8	shaken ten minutes	0·021	0·022
9	„ „ „	0·020	0·022
10	stood twenty-four hours	0·002	0·002
11	„ twelve „	0·003	0·002
12	shaken ten minutes	0·002	0·002
13	„ „ „	0·0017	0·0015

These experiments seem to prove that whilst the method recommended vastly shortens the length of time occupied in making a determination of magnesia, it in no wise impairs its accuracy.

Separation of Magnesium from Calcium

(*A*) The method of separating calcium and magnesium by means of ammonium oxalate does not succeed when only a very small quantity of calcium is present. In such a case the calcium is either not precipitated at all, or but very incompletely. Free ammonia also tends to hinder the precipitation, and, when it has evaporated, crystals are obtained, which consist of calcium oxalate with magnesium oxalate, and the liquid still contains calcium.

(*B*) A better result, Scheerer says, is obtained by converting the alkaline earths into neutral sulphates, and adding alcohol to the aqueous solution until a persistent cloudiness is produced. After some hours all the calcium sulphate is deposited. When too much alcohol has been used, some of the magnesium sulphate is deposited as well ; it is sufficient then to redissolve the sulphates in water and precipitate a second time with alcohol, or the calcium may now be thrown down by the ammonium oxalate. The magnesium, not being in excess, no longer hinders the precipitation.

(*C*) With regard to the analysis of dolomite, Dr. A. Cossa states, that when care is not taken to redissolve the precipitate of calcium oxalate first obtained, and precipitate this a second time, it is always so contaminated with magnesium oxalate or magnesium ammonio-oxalate, that the quantity of calcium found as carbonate may be 0·62 per cent. in excess of what it ought to be, while the loss of magnesium carbonate may even be as high as 0·78 per cent.

When, in the ordinary course of qualitative analysis, ammonium carbonate is used to separate calcium from magnesium, unless the former

metal is present in notable proportion to the latter, a very insoluble double magnesium and ammonium carbonate always accompanies the calcium carbonate, if this is allowed sufficient time to form. If much magnesium and no calcium be present, the magnesium precipitate still falls after a while. Both metals are precipitated by this reagent, the only difference being that the calcium precipitate forms somewhat earlier than the magnesium precipitate. Calcium, therefore, can only be separated from magnesium by this reagent by fractional precipitation, which necessarily involves loss of substance; and, in qualitative examination, the method is sure to mislead when the proportion of calcium present is small, unless it is controlled by other methods. The same remarks apply, in substance, to the method of precipitation by ammonium oxalate. Within a trace the whole of the magnesium present, in a considerable quantity of solution of magnesium chloride, can be precipitated simply by successive additions of ammonium oxalate: the solution being concentrated to its original bulk after the last addition of the reagent. Yet, in working with this reagent, the rule is, that enough of it must always be added to transform all the magnesium salt into oxalate, since calcium oxalate is soluble in solution of magnesium chloride. That some magnesium salt must precipitate with the calcium salt under such conditions is obvious: and that it does so is well known, and is, though incompletely, provided for by the direction being given to repeat the process upon the precipitate first obtained. This process, therefore, is also one of fractional precipitation, and for it to approach success, the operator must know pretty nearly beforehand how much calcium, in proportion to the magnesium present, he has to deal with.

(*D*) Dr. Mohr uses microcosmic salt in precipitating magnesia after lime from an ammoniacal solution which has been kept clear by means of sal-ammoniac.

(*E*) In separating magnesium salts from lime, ferric oxide, and the alkalies, H. Hager mixes the finely powdered sample with 10 parts of glycerin and a little water, and adds 40 to 50 parts of solution of oxalic acid at 5 per cent. Calcium and magnesium oxalates are both formed, the former remaining undissolved, whilst the magnesium salt passes into solution. After standing for half an hour the calcium oxalate is collected upon a filter, washed, and determined as usual. The filtrate is boiled in a flask for five to eight minutes, filtered boiling, and the precipitate dried and weighed as magnesia.

In a solution containing calcium and magnesium salts the liquid is first mixed with glycerin, a sufficiency of ammonium oxalate is added, the liquid is strongly acidulated with oxalic acid, and the process is completed as above.

Magnesium can also be precipitated as an oxalate in presence of ferric oxide by adding glycerin, ammonium oxalate, and oxalic acid, and then boiling. In order to determine the ferric oxide in the filtrate it is heated to a boil along with ammonium carbonate, evaporated to

dryness, the glycerin extracted with alcohol, the insoluble residue treated with hot ammoniacal water, and the ferric hydroxide collected upon a filter.

For separating magnesia from the alkalies the hydrochloric solution is boiled with ammonium oxalate and oxalic acid, and filtered at a boil.

Separation of Magnesium from Potassium and Sodium

In the following method phosphoric acid can be employed under all circumstances, since its ill effects are neutralised by the complete elimination of any excess of it.

Acidulate the liquid with nitric acid, and then add excess of ammonia. To the filtered liquid add ammonium phosphate, or simply phosphoric acid, and collect the ammonio-magnesium phosphate precipitate. To get rid of the ammoniacal salts, filter, evaporate, and calcine; this causes the greater part, or even the whole, of the hydrochloric acid to be eliminated, when that acid is present, and the two bases remain united with phosphoric acid only. However, to make certain, treat the residue two or three times with concentrated nitric acid and calcine, when the whole of the hydrochloric acid being thus eliminated, only phosphoric acid, potash, and soda remain. The residue is collected in a flask and treated by a large excess of tin and nitric acid ; the phosphoric acid being thus rendered insoluble, the liquid is filtered and concentrated. The residue, composed of potassium and sodium nitrates, is calcined till completely decomposed, and as soon as the capsule is cooled the caustic alkalies are transformed into carbonates, after which they are converted into chlorides, then into sulphates, and finally ammonium carbonate is added to decompose the potassium bisulphate. With these combined elements it is possible to determine the quantity of each alkali indirectly.

The exactness of this process consists in the method of removing the phosphoric acid—a method founded on the property (discovered by A. Reynoso) possessed by stannic acid of forming a combination with phosphoric acid completely insoluble in water and in nitric acid. To render this process accurate, the hydrochloric acid must be eliminated—an object easily effected.

CHAPTER III

CERIUM, LANTHANUM, DIDYMIUM (PRASEODYMIUM, NEODYMIUM), EUROPIUM, GADOLINIUM, SAMARIUM, YTTRIUM

CERIUM; LANTHANUM; PRASEODYMIUM; NEODYMIUM

Separation and Estimation of the Cerium Metals together

THE precipitation of the cerium metals in the form of oxalates from a slightly acid solution is, unquestionably, the most satisfactory method of separating these oxides. The estimation of the oxalates upon a weighed filter is accompanied with the usual trouble and loss of time in perfectly drying the filter before and after collecting the precipitate upon it. By the following mode of proceeding Dr. W. Gibbs completely avoids these difficulties. The usual mixture of cerium, lanthanum, didymium, and samarium, when neutral, is to be rendered slightly acid by sulphuric or hydrochloric acid, and then largely diluted with water. Half a litre of water for every estimated gramme of oxide is a good working proportion. The solution is then to be boiled, and a hot solution of oxalic acid or ammonium oxalate added. On cooling, especially when the solution has been well stirred with a glass rod, or shaken, the oxalates separate in large crystalline grains of a pale rose-violet colour. The precipitate is to be filtered off and well washed with boiling water, the washing being extremely easy in consequence of the coarse granular character of the precipitate. The filter is then to be pierced and the oxalates carefully washed down into a crucible; after which the water in the crucible may easily be removed by evaporation, and the oxalates dried at a temperature of 100°. The equivalents of lanthanum and didymium are so near to that of cerium, that no very sensible error is committed by considering the mixed oxalates as consisting simply of cerium oxalate with three equivalents of water.

Volumetric Determination of Cerium.—Franz Stolba determines ceric oxalate volumetrically by means of potassium permanganate. Pure ceric sulphate, carefully dehydrated, is dissolved to the volume of a litre, and measured portions of the solution are precipitated with ammonium oxalate, the latter being determined in the known manner

with standard permanganate, the solution of the latter being standardised by means of lead oxalate.

On the other hand, portions of the solution are taken for determination as cerium oxide. Using the atomic weight Ce=141·27, the quantity of cerous oxide is ascertained from the quantities of standard permanganate consumed.

The results are concordant, and where differences appear they fall within the inevitable errors of observation. Hence, cerium, when freed from lanthanum and didymium, and separated as oxalate, may be conveniently and accurately determined as such. A corresponding quantity of sulphuric acid must be employed in titration, and warm water used. During the process, the quantity of undissolved matter diminishes, and the change of colour at the conclusion is distinctly marked.

The preparation of pure lanthanum salts has been studied by Dr. Buhuslav Brauner and Franlišek Pavliček in a paper read before the Chemical Society in 1902.[1]

They start from material obtained from cerite. Since the year 1885 much time has been devoted to the fractional crystallisation of a considerable quantity of the double ammonium nitrates of a crude mixture of lanthanum and old didymium free from cerium by the Mendeléeff-Auer method. After a long series of crystallisations lanthanum was obtained free from praseodymium, neodymium, and the whole of the elements of the samarium, gadolinium, and yttrium group.

For the further purification a second method was used, consisting in the fractional fusion of the lanthanum nitrate thus obtained with a mixture of potassium and sodium nitrates in molecular proportion (Debray-Schützenberger method). A trace of cerium and of the less basic earths was removed first by fusing for half a day at 350°; the mass was dissolved in water, filtered, and the residue washed with a saturated solution of the alkali nitrates in water in order to avoid the finely divided oxides passing into the filtrate.

The filtrate from this fraction, A2, was carefully evaporated down, and the moist residue obtained had to be dried very carefully before fusion—a tedious operation requiring a great deal of time.

On repeating the fusion &c., first at 450°–500°, and for the last fractions even at a higher temperature, the fractions A2, A3, A4, A5, and A6 were obtained. They consisted of basic lanthanum nitrate, and were perfectly white.

A *third method* of fractionation was used for the further purification of the highly purified lanthanum material, A6, which did not contain the slightest trace of an yttria earth, or of an earth yielding an absorption spectrum. Instead of using such weak bases as ammonia or magnesia, or of following Drosbach, who employed sodium hydroxide,

[1] *Chemical News*, Jan. 30, 1903.

we took the most powerful base available—namely, potassium hydroxide, which precipitates lanthanum as the hydroxide. The latter, on being digested with a hot solution of, for example, lanthanum nitrate, is converted into the basic nitrate; and in such a precipitate the *least basic* portion contained in the solution is accumulated, whereas the most basic or positive portion passes into the solution. In this way, lanthanum solutions are precipitated by lanthanum hydroxide.

The method of fractionation differed in one essential point from similar methods hitherto used, for instead of precipitating *small* fractions and leaving the greater part in solution, the *larger* part was precipitated, leaving only the *smaller* part in solution—this considered to be the fraction sought.

After calculating from a preliminary experiment the volume of a definite dilute solution of potassium hydroxide necessary for the *complete* precipitation of lanthanum, sufficient was added to the main solution to precipitate seven-eighths and to leave one-eighth in solution. The addition was made drop by drop from a large burette, and the precipitate digested for some time with the solution and then filtered.

After dissolving the precipitate in the smallest amount of dilute nitric acid, and repeating the above process of fractionation, the following eight fractions were obtained:—La0, La1, La2, La3, La4, La5, La6, La7. If lanthana is a mixture of earths, the lower fractions must contain the most basic (positive) portion, whereas the least basic (negative) portion will be accumulated in the highest fraction.

The solutions containing the above fractions were first completely precipitated by potash, the washed precipitate was dissolved in an insufficient quantity of dilute nitric acid, which was added drop by drop with stirring, and the solution filtered from a small insoluble residue consisting chiefly of silica and other negative impurities.

After this, recourse was had to repeated precipitation with ammonia, and washing of the precipitate in order to remove the alkalies completely. From the nitric acid solution of the last precipitate, lanthanum oxalate was in each case precipitated by adding a dilute solution of sublimed oxalic acid drop by drop. The crystalline, white and fine powder of the precipitate was well washed.

DIDYMIUM

Although what formerly was called didymium is now known to be a mixture of praseo- and neodymium, it is convenient here to refer to the mixture as 'didymium.' The method of separation of the two constituents is now so well known, and so little improvement has been made since Auer Von Welsbach first described his process of fractional crystallisation of the double ammonium and didymium nitrates in the presence of lanthanum nitrate, that no description of it is necessary.

Separation of Cerium from Didymium and Lanthanum

(*A*) The following method, which we owe to the researches of Messrs. Pattison and Clarke, has been found to be very effective for the separation of cerium from didymium and lanthanum. It is based upon the fact that when cerium chromate is evaporated to dryness and heated to about 110°, it is decomposed, and the cerium oxide remains as an insoluble powder, whilst the didymium and lanthanum chromates, when subjected to the same treatment, remain unchanged.

The mixed cerium, didymium, and lanthanum oxides are subjected to the action of an aqueous solution of chromic acid, aided by heat till solution is complete. The chromic acid need not be entirely free from sulphuric acid. The solution obtained is evaporated to dryness, and the residue heated to about 110°. Hot water is then added, which dissolves the lanthanum and didymium chromates and leaves the cerium oxide, which is then separated by filtering. Thus obtained, the cerium oxide is a yellowish-white powder which is almost completely insoluble in acids, but is rendered soluble by fusion with the acid potassium sulphate.

This process may also be employed for the quantitative determination of cerium, as it has been found, by careful trial, that not a trace of cerium can be detected by the best known processes in the solution after its separation as above described.

(*B*) Dr. Wolcott Gibbs has found that when a mixed cerium, lanthanum, and didymium salt is boiled with dilute nitric acid, and lead peroxide added to the solution, the cerium is quickly, and under some circumstances completely, oxidised, the solution becoming more or less deeply orange-yellow. This process affords an extremely simple and delicate test for cerium; it succeeds with all the salts which are soluble in nitric acid, though, of course, when the mixed oxalates are tested the oxalic acid is oxidised to carbonic acid before the characteristic cerium yellow appears. For the purpose of testing, it is sufficient to dissolve the salt to be examined in nitric acid diluted with its own volume of water, to add a small quantity of pure lead peroxide and boil for a few minutes, when the smallest trace of cerium can be detected by the yellow colour of the solution. When a solution containing a cerium salt dissolved in strong nitric acid is boiled for a short time with a large excess of lead peroxide, oxygen gas is copiously evolved, and, at the same time, the cerium sesquioxide formed at first is completely reduced to protoxide, the solution becoming perfectly colourless. The remarkable reaction which occurs in this case appears to be connected with the formation of lead nitrate, since, when the solution of cerium protoxide contains a large excess of this salt, the cerium is not peroxidised by boiling with nitric acid and the peroxide.

When a solution of cerium, didymium, and lanthanum is treated

with nitric acid and lead peroxide in the manner pointed out above, the deep orange-coloured liquid evaporated to dryness, and heated for a short time to a temperature sufficiently high to expel a portion of the acid, it will be found that boiling water acidulated with nitric acid dissolves only the lanthanum and didymium salts, leaving the whole of the cerium in the form of a basic nitrate insoluble in water. The insoluble matter is to be filtered off and thoroughly washed. A current of sulphuretted hydrogen passed into the filtrate removes the lead, after which the lanthanum and didymium may be precipitated together as oxalates, which, if the process has been carefully performed, are perfectly free from cerium. The mass on the filter is readily dissolved by fuming nitric acid. Sulphuretted hydrogen is then to be passed through the solution, sufficiently diluted with water, until the lead is completely precipitated. The cerium may then be thrown down by oxalic acid, ignited, and weighed as ceroso-ceric oxide or converted into sulphate and weighed as such.

Cerium proto-nitrate obtained by this process gives, when tested by the spectroscope with transmitted light, even in very thick layers, a scarcely perceptible indication of didymium.

(*C*) Another very good method of separating cerium from lanthanum and didymium is to precipitate the three metals in the state of gelatinous hydrates by adding an excess of caustic potash to their solution. These oxides are washed several times by decantation, and then a concentrated solution of caustic potash is added, and the whole submitted to a current of chlorine. The alkaline liquid being thus saturated with chlorine, the lanthanum and didymium oxides are redissolved, lemon-coloured insoluble ceric oxide remaining. This substance is washed on a filter, then redissolved, while still moist, in hydrochloric acid, precipitated by ammonium oxalate, and strongly calcined; the cerous oxalate is thus transformed into very light rose-coloured ceroso-ceric oxide.

The chlorinated liquid contains lanthanum and didymium oxides, which may be precipitated together by adding ammonium oxalate.

(*D*) For the separation of cerium from didymium and lanthanum, as in cerite, M. H. Debray melts the mixed nitrates with 8 or 10 parts of potassium nitrate in a porcelain capsule, and the fused mass is kept between 300° and 350° by means of a gas furnace. Cerium nitrate is decomposed, forming a yellowish powder of cerium oxide, which retains a little nitric acid, but didymium and lanthanum nitrates, when melted with nitre, are not appreciably decomposed, even at 350°. A thermometer, plunged into the bath of nitrate, indicates its temperature. When the escape of nitrous fumes ceases, which requires several hours, the operation is stopped. When cold the melted mass is easily detached from the capsule, and the cerium oxide is found collected at the lower part. It is dissolved in water, and there remains a powder, yellowish if it contains mere traces of didymium, but reddish if it

contains more. It is well to wash with a little weak nitric acid, which dissolves a little didymium subnitrate, produced at the same time as the cerium oxide if the capsule is too strongly heated at certain points. This is of little consequence, as the cerium oxide obtained in the first operation always requires to be purified.

It may be entirely freed from didymium by transforming it into nitrate, which is melted a second time with 8 or 10 parts of potassium nitrate. For this purpose the oxide is treated with sulphuric acid diluted with an equal volume of water, when everything dissolves if the liquid is sufficiently acid. The yellow ceroso-ceric sulphate thus obtained is reduced with sulphurous acid, and the cerous sulphate is precipitated with oxalic acid. The cerous oxalate is then readily converted into nitrate by boiling with nitric acid. This second treatment gives a yellow powder, which contains neither didymium nor lanthanum, as the nitrate of the latter earth is still more stable than that of didymium. If it is transformed into colourless cerous sulphate the spectroscope does not detect the least trace of this body, which is always easy to recognise by its absorption-spectrum. The didymium and lanthanum nitrates, which remain mixed with a large excess of potassium nitrate, are evaporated and remelted, the temperature being between 350° and 450°. The remaining trace of cerium nitrate which has escaped decomposition in the former operation is completely destroyed, and there is even formed a small quantity of didymium subnitrate. But the bulk of the didymium remains with the lanthanum in the state of a soluble nitrate.

We have thus a certain and rapid method of obtaining cerium oxide free from didymium and lanthanum, or, on the other hand, a mixture of these two oxides absolutely free from cerium.

Separation of Lanthanum from Didymium

(*A*) The nitric acid solution of lanthanum and didymium is evaporated to dryness in a flat-bottomed capsule. The dried mass is of a pale rose tint. By exposing the capsule for a few minutes to a temperature of 400° or 500° the saline mass will be fused, with disengagement of nitrous vapours. The capsule is withdrawn from the fire before the decomposition is complete, and hot water must be poured in. Lanthanum nitrate dissolves and didymium subnitrate remains insoluble in the form of greyish-white flakes. The whole is left to stand for a few hours, then boiled and filtered ; if the liquid still retains a feeble rose tint, the same operation must be repeated until a colourless liquid is obtained, containing lanthanum nitrate, free from didymium subnitrate. Lanthanum oxide is obtained by evaporating this liquid and strongly calcining the residue. The didymium oxide may also be estimated after the calcination of the subnitrate thus obtained.

This process, which was first devised by MM. Damour and Deville, is founded on the fact that didymium nitrate decomposes before lanthanum nitrate, and that the first of these salts changes to the state of subnitrate. Several precautions must be observed. The bottom of the capsule containing the mixture of the two salts must not be too much heated, nor must too large quantities of material be used, as in that case it forms a thick layer at the bottom of the capsule and decomposes unequally. It is better to recommence the operation several times than to heat too strongly in attempting to separate the two oxides at the same time. The first portions of didymium oxide obtained in this way give, with sulphuric acid, reddish-violet crystals, with traces of white needle-shaped ones, which belong to the lanthanum sulphate. The last portions give a sulphate less coloured, but, like the preceding, with the same crystalline form derived from the oblique rhomboidal prisms; the needles of lanthanum sulphate are rather more numerous. Finally, the above-described colourless solution gives, with sulphuric acid, colourless crystals derived from the right rhomboidal prism, characteristic of lanthanum sulphate.

By following this method, the estimation of didymium comes out rather too high, and, consequently, that of lanthanum rather too low.

(*B*) Dr. C. Winckler has ascertained that when cerium is separated from its solutions by mercury binoxide and potassium permanganate the cerium is not merely precipitated in the state of a peroxide, but is accompanied by didymium, whilst the lanthanum remains in solution. This is an excellent method for separating didymium from lanthanum. To obtain the didymium which accompanies the cerium in its precipitation by potassium permanganate, redissolve the precipitate in hydrochloric acid. After having well calcined it to free it from the mercuric oxide, evaporate the hydrochloric solution to dryness in the presence of sulphuric acid; dissolve the residue of sulphate in water, and add potassium sulphate to it. In twenty-four hours a triple cerium, didymium, and potassium sulphate separates, insoluble in potassium sulphate.

The precipitate must then be dissolved in water, and the sulphates changed to oxalates, which are calcined to obtain the cerium and didymium oxides; these are then separated in the usual way.

The lanthanum in the filtered liquid may be obtained thus:—First treat the filtered liquid with sulphuretted hydrogen, to separate the mercuric oxide, then precipitate the lanthanum as an oxalate, and calcine it. The lanthanum oxide then contains very little didymium.

Lanthanum and didymium may also be separated by taking advantage of the different solubilities of their sulphates. By digesting a mixture of the dry salts in cold water (5°), a saturated solution may be obtained, which, upon being heated to 30°, deposits lanthanum sulphate, whilst didymium sulphate remains dissolved. The salts may be obtained

quite pure by repeating this operation two or three times. Lanthanum sulphate is colourless, whilst didymium sulphate is of a beautiful rose-red.

Analysis of Cerite. Separation of Cerium, Didymium, Samarium, and Lanthanum.—The mineral cerite is a hydrated cerium silicate with lanthanum, didymium, samarium, and iron ; traces of some of the other rare earths are also present, as yttria, terbia, &c. As quantitative methods of any exactness for the separation of some of these earths are not yet known, the true composition of the mineral is only known approximately, and in its structure it is anything but homogeneous. Its composition agrees with the formula for the orthosilicates, $R_2SiO_4 + aq.$, and it contains from 55 to 60 per cent. of cerium oxide, about 8 per cent. of the lanthanum, didymium, and samarium oxides, 20 per cent. of silica, and 6 per cent. of water.

(*A*) To disintegrate the mineral it is finely ground, made into a thick paste with strong sulphuric acid, and heated to drive off excess of acid. The mass becomes of a white or pale grey colour. This is digested in cold water, filtered, and the residue well washed with cold water. It should be remembered that the sulphates of the cerium earths are much less soluble in hot than in cold water.

To the filtrate oxalic acid is added, which precipitates all the earths, with any lime and bismuth that may be present, as oxalates. It is sometimes advisable to ignite the oxalates so obtained and boil the residue in dilute nitric acid, by which means the didymium, samarium, and lanthanum oxides are dissolved, leaving the greater part of the cerium oxide insoluble ; this method is objectionable, however, as the cerium oxide retains obstinately much didymium, and probably also lanthanum and samarium. A better plan is to heat the dried oxalates with strong nitric acid till all dissolves, and allow to cool, or dilute, when a mixture of oxalates separates out rich in didymium and samarium, the solution containing much cerium and lanthanum oxalates.

(*B*) For the general method of separating the earths, however, it is well to proceed as follows :—The dried oxalates are boiled with strong nitric acid till completely decomposed, evaporated to dryness, and fused at the lowest temperature at which nitrous fumes come off, the residue digested in water, filtered, and washed. The insoluble residue, of a pale yellow colour, consists of cerium oxide and basic cerium nitrate, with a little didymium, whilst the filtrate contains the lanthanum, didymium, and samarium. The operation of fusing must be repeated on the earths in the filtrate many times to throw out all the cerium, whilst the cerium oxide, or basic nitrate obtained, is freed from any didymium by retreatment with nitric acid and fusion as above ; the presence of didymium in it being indicated by its brown colour or by the absorption spectrum of the solution. To free the didymium and other nitrates from the last traces of cerium it is necessary to fuse

them with three or four times their weight of potassium nitrate, very gently, at a temperature just sufficient to cause slight decomposition.

The separation of lanthanum, didymium, and samarium from each other is a most laborious process, and the amount of these earths, obtainable in anything like a pure state, small, compared with the mass of material worked up. The solution of the nitrates of these elements is made perfectly neutral, diluted to such a strength as to contain about 1 per cent. of the oxides and a very dilute solution of ammonia added, about ·1 gramme NH_3 in 500 cubic centimetres; the precipitation being conducted in large vessels, such as ordinary Winchester quart bottles. The first precipitates formed are rich in samarium and contain much didymium; these are followed by didymium, with some lanthanum and samarium; and the final precipitates consist almost wholly of lanthanum. By this method there are obtained three portions of hydrates, which must be again worked up separately by precipitation as above; the first for samarium, the second for didymium, and the third for lanthanum, the process of fractional precipitation being repeated on each portion fifty or a hundred times.

The separation of the last traces of didymium from samarium can only be accomplished by fractional precipitation, an operation so tedious that few chemists will probably be inclined to undertake it. The second portion of hydrates, consisting chiefly of didymium, is purified from the small quantities of samarium and lanthanum it contains by fusing with potassic nitrate for the samarium, as explained above for the traces of cerium; whilst to separate the lanthanum the oxalates are dissolved in warm strong nitric acid and allowed to cool, when didymium oxalate nearly free from lanthanum is obtained; repeated several times, the last trace of lanthanum remains in the solution.

To separate the small quantity of didymium from the lanthanum obtained as the final precipitate with ammonia, the only method is by a continuation of the process of fractionation; the lanthanum oxide finally obtained should be pure white, any trace of a yellowish tinge indicating that didymium is still present.

As cerite contains small quantities of the yttria earths, these may be separated from cerium, didymium, &c., by making a cold solution of the sulphate and adding finely powdered potassium sulphate in quantity more than sufficient to saturate the solution; it is then allowed to stand (with frequent agitation) for a few days and filtered, washing the precipitate with a saturated solution of potassium sulphate. The filtrate contains the yttria earths, and for their complete separation it is advisable to repeat the operation with potassium sulphate three or four times. The insoluble residue, consisting of a double sulphate of potassium, cerium, didymium, &c., is boiled with sodium hydrate, filtered, well washed, redissolved in nitric acid, precipitated with oxalic acid, and the oxalates ignited, leaving the earths—lanthana of a pure

white colour, didymia of a deep chocolate brown, and samaria of a pale brown colour.

A Simple Method for the Preparation of Sulphides, Chlorides, and Bromides of the Metals from Cerite

To prepare the sulphides, W. Muthmann and L. Stutzel [1] start with a crystallised sulphate, which is dehydrated by gentle calcination; it is then placed in a porcelain boat and heated for several hours in a combustion tube through which a current of thoroughly dry sulphuretted hydrogen is passing, raising the temperature to dull red. The colour of the product becomes darker, and in this manner we obtain perfectly pure sulphides, M_2S_3, stable in the air at the ordinary temperature, more especially if the calcination has been strong; they are only slowly attacked by boiling water, rapidly by dilute acids with the evolution of H_2S. When heated in the air, these sulphides take fire; they often appear pyrophoric; in this manner oxide and sulphate are formed.

To obtain the chlorides and bromides, heat the sulphate, prepared as has already been described, in a current of pure thoroughly dried hydrochloric or hydrobromic gas; the substance becomes discoloured, and at the end of an hour a powder consisting of pure anhydrous chloride (or bromide) is obtained. Cerous chloride and lanthanum bromide and chloride occur as white crystalline powders or masses; the chloride of neodymium is rose-coloured, that of praseodymium green. All these products greedily absorb water; they are very soluble in water and alcohol, forming a limpid solution. They are fairly fusible and slightly volatile.

Separation of the Cerium Metals from Glucinum

The separation may best be effected in the following way:—Convert the salt into sulphates, and dissolve in the smallest quantity of water. If iron be present, reduce it to the state of protosulphate, by passing a stream of sulphuretted hydrogen through the hot solution; if this precaution is not taken, the precipitated double sulphates will contain iron. Then add a saturated solution of sodium sulphate (which Dr. W. Gibbs has shown to be greatly superior to potassium sulphate for this purpose), and sufficient dry sodium sulphate in powder to saturate the water of solution. It is most advantageous to use hot solutions. The insoluble double sulphates of sodium and the cerium metals separate immediately as a white, highly crystalline powder, which is thrown upon a filter and washed thoroughly with a hot saturated solution of sodium sulphate. After washing, the double sulphates on the filter are to be dissolved in hot dilute hydrochloric acid, the solution largely diluted with water, and the cerium metals precipitated by ammonium oxalate.

[1] *Chemical News*, Jan. 11, 1901.

From the filtrate the glucinum may be precipitated at once by ammonium hydrate.

EUROPIUM

Sir William Crookes[1] has recently communicated the following note on europium to the Royal Society :—

'Europium was discovered in 1901 by Demarçay,[2] accompanying samarium, from which he separated it by fractional crystallisation of the double nitrates of magnesium and the earths. Demarçay considered that his new earth was identical with de Boisbaudran's Z_ϵ and Z_β, and was the same as I had announced in 1885[3] as giving an extremely sharp red line in the phosphorescent spectrum at wave-length 609—an earth which in 1889[4] I said was a new one, and designated by the name of S_δ.

'I detected the earth S_δ during an examination of the phosphorescent spectra given by some of the fractions of samaria and yttria, neither of the earths being pure.

'Europium is the first member of the terbium group, gadolinium being the second member. On the other side it comes next to samarium, the last member of the cerium group.

'Assuming the oxide of europium to be Eu_2O_3, the element has an atomic weight of 151·79, from the analysis of its sulphate, $Eu_2(SO_4)_3,8H_2O$.

'MM. Urbain and Lacombe[5] have sharply separated europium from samarium in the manner outlined in my note on gadolinium[6] by their method of fractional crystallisation of the double nitrates of bismuth or magnesium, with the nitrates of the rare earths. I owe to the kindness of M. Urbain a sufficient quantity of the oxide of europium to enable me to obtain a good series of its photographed spectrum.

'Exner and Haschek have measured the wave-lengths of the europium lines[7] from material supplied by Demarçay. A comparison of their lines shows that the material was by no means pure.

'Urbain's europia is not quite so free from impurities as his gadolinia. I have been able to detect in the photographs the following lines :—Gadolinium is represented by very faint lines at 3450·55, 3481·99, 3585·10, 3646·36, 3654·79, 3656·32, 3664·76, 3697·90, 3699·89, 3743·62, 3768·52, 3796·58, 3805·70, 3850·83, 3851·16, 4050·08,

[1] *Roy. Soc. Proc.* vol. lxxiv. p. 550.

[2] '*Comptes Rendus*, vol. cxxxii. p. 1484 ; *Chemical News*, vol. lxxxiv. p. 1.

[3] '*Phil. Trans.* vol. clxxvi. p. 691.

[4] '*Journ. Chem. Soc.* vol. lv. pp. 250–285.

[5] '*Comptes Rendus*, vol. cxxxviii. pp. 84, 627, 1166; *Chemical News*, vol. lxxxix. pp. 52, 179, 277.

[6] '*Roy. Soc. Proc.* vol. lxxiv. p. 420.

[7] '*Wellenlängen - Tabellen für Spektralanalytische Untersuchungen* (F. Deuticke : Leipzig und Wien, 1902).

4225·33. Yttrium is represented by the line at 3774·51, lanthanum by the line at 3988·66, and calcium by the two lines at 3933·825 and 3968·625.

'No lines of bismuth or magnesium are to be seen.

'Most of the lines of impurities are exceedingly faint, showing that the impurity is only present in very minute proportion. Indeed, I have only mentioned them if they correspond with strong lines in the gadolinium spectrum.

'Both in the europium and the gadolinium spectrum I have not attempted to give wave-lengths of all the excessively faint lines. If at some future time it becomes of interest or value to ascertain their wave-lengths, all the necessary data are present whereby they can be identified.'

Europium exists in very small quantities between samarium and gadolinium in the series of rare earths.

G. Urbain and H. Lacombe find that the magnesium salts of europium have nearly the same solubility as those of bismuth, whilst the same salt of gadolinium is considerably more soluble. Hence it is tolerably easy to separate europium from gadolinium in the tail of the fractionation. The authors find that the atomic weight of europium is definitely 151·79, and they estimate that this number differs from the real number by less than 0·06.

GADOLINIUM

C. Benedicks [1] has re-examined the subject of gadolinium, and has given methods of its separation from the accompanying earths. He finds that the quickest method for obtaining pure gadolinium is to fractionate the nitrate in concentrated nitric acid after the weaker bases have been removed, and then partially precipitate with cold dilute ammonia. (The ammonia should always be used dilute, so that precipitation takes place slowly.) By this means the terbium and samarium earths are obtained in the first precipitates; in the last, a faintly coloured and finally almost pure white gadolinium oxide is obtained. The traces of didymium which were still present after crystallisation of the nitrates are best removed by a new series of crystallisations of the nitrates. The advantage of the crystallisation process is obvious, for by this means a greater number of operations can be carried out in the same time as a single tedious potassium sulphate precipitation.

The concentrated nitric acid forms fairly easily supersaturated solutions of the nitrates, wherefore it is advantageous to add a few crystals to the solution.

[1] *Chemical News*, Feb. 2, 1900.

Atomic Weight of Gadolinium

As already mentioned, Marignac found for the equivalent weight of Ya $\overset{II}{R}O=120{\cdot}5$, which indicated an atomic weight of $\overset{III}{R}=156{\cdot}75$ for gadolinium. Lecoq de Boisbaudran obtained from Marignac's original material, after further purification, the number 155·95, or, after allowing for the probable effect of impurities, 156·15. Clève found 155 with his earth, in which Lecoq found later some samarium to be present, which had somewhat lowered the atomic weight. Bettendorff, whose determinations may be of greater value than the former, having been carried out with purer material, obtained as a mean result the number 156·33. Benedicks obtained the figures 156·38 as a mean result.

R. Marc [1] has given a method of preparing gadolinia from monazite, using a material prepared from the final chromic acid fractionations of many kilogrammes of monazite. The last fractions were again treated with chromic acid, and then the final fractions again taken. This process was repeated some few times. The last fractions were used by Marc. The material was of a decided yellow colour, and showed in the absorption spectrum the bands of the erbium components, samarium and neodymium, but no lines of praseodymium, even with the broadest layer. Three methods of fractionation were employed—the ammonia, the oxalic acid, and the potassium sulphate methods.

The Ammonia Method

The fractionation with ammonia was performed as follows:—The whole of the material (about 90 grammes) was divided into portions of 30 grammes. Each portion was dissolved in hydrochloric acid, diluted with 2 litres of water and accurately neutralised, and very dilute ammonia solution was dropped in from a separating funnel, while the liquid was kept in continual motion by means of a glass stirrer. The quantity of the ammonia was measured so that it corresponded to about half the quantity of oxide. The corresponding fractions of the separate portions of 30 grammes were again mixed, and divided by means of ammonia into 2 parts, &c. By this method the erbium accumulated in the precipitates and the yttria in the liquids.

The Oxalic Acid Method

The 10 per cent. strongly acid solution of the nitrates was heated to boiling in a little flask, and rapidly boiling oxalic acid added until a permanent precipitate or turbidity began to form. Then the flask was cooled quickly, being vigorously agitated all the time, and the

[1] *Zeitschrift für Anorg. Chemie*, xxviii. 121; *Chemical News*, May 13, 1904.

oxalates separated out as an exceedingly fine crystalline powder. The filtrate from the oxalates was concentrated to the original volume, and again treated as described above.

The Potassium Sulphate Method

The potassium sulphate method served principally to separate didymium and samarium from the remaining earths. It was first used by Mosander. Afterwards Marignac [1] investigated the solubility ratios of the double potassium sulphate salts in saturated solution of potassium sulphate.

I. If a large quantity of material had to be separated quickly into two parts, one of which would contain the greater part of the colourless earths and the other the greater part of the neodymium and samarium, then the following method was adopted :—

The neutral, or only very slightly acid, concentrated solution of the nitrates was introduced into a 4-litre flask, which was filled with a concentrated solution of potassium sulphate, the bottom being covered with crystals of this salt. The flask was filled up to the top with potassium sulphate solution, closed and sealed, and turned upside down. This was done to prevent the settling of the precipitate formed on the bottom of the flask. The separation of the double salt begins at once. As soon as the liquid has cleared, which takes one to two hours, it is drawn off. With 4 litres of liquid about 10 grammes of the earths go into solution.

The precipitate was treated as is further described below, converted into nitrate, and then another 10 grammes brought into solution by the same method. This process was repeated as long as the oxide which went into solution showed no absorption streaks of neodymium and samarium, or only showed them very faintly. Thus the material had been divided into two parts, the first of which consisted of all the earths which had gone into solution, and the second of the part which had remained undissolved.

II. But when it was a question of obtaining from a material which contained neodymium and samarium the colourless earths, quite free from these two substances, disregarding the smallness of the results and the waste of time, the following method was used :—

According to the quantity of the material, a 1 to 2 litre flask was only half filled with a concentrated solution of potassium sulphate. The bottom was covered with crystals, the concentrated neutral solution of the nitrates introduced into it, the flask closed and shaken on a shaking machine, with short interruptions, for two to three days. Almost the whole of the earth goes into the precipitate, and only 1 to $\frac{1}{2}$ gramme remains in solution. The solution was, however, always quite free from neodymium and samarium, even if they were contained

[1] *Comptes Rendus*, vol. xc. p. 899.

in the original material in considerable quantity. If the material contained no colourless earths, generally nothing, or only minute traces, went into solution. The treatment could be repeated until all the earths of the yttrium group were removed; but these operations, even with small quantities of material, would take months.

Concerning the treatment of the solutions and precipitates obtained, the following remarks must be made:—

The solutions were simply treated with ammonia, the hydroxides precipitated were filtered off, dissolved, precipitated with oxalic acid, and the oxalates ignited. The precipitates of double sulphate could not be dissolved in water. It was found best to decompose them with sodium carbonate.

About an equal quantity of sodium carbonate and a little water were added to the double salts, and the mixture was heated to boiling for some time. By this means the double sulphate is completely converted into a basic carbonate, which again, for the most part, dissolves in the excess of sodium carbonate. Hydrochloric acid is then added until carbonic acid is no longer evolved; the earths are first precipitated as carbonates, and then dissolved in the excess of hydrochloric acid. If a residue remains still undissolved, this is again heated with soda; otherwise the earths are precipitated immediately from the hydrochloric acid solution by means of ammonia, and are filtered off, dissolved, precipitated with oxalic acid, and the oxalates ignited.

The whole quantity of the material was treated with potassium sulphate by Method I., in order to separate it into two groups, the one containing the yttria, erbium, terbium, and gadolinium, and the other the neodymium and samarium. Altogether four fractionations were necessary for this purpose. The four solutions together formed the first group and amounted to 45 grammes; the undissolved residue formed the second group and amounted to 42 grammes.

The oxides of Group I. showed only very faintly the bands of neodymium and samarium. They were decomposed into two parts by a series of ammonia fractionations, and of these two parts one did not show the slightest trace of the erbium spectrum, and the other no trace of neodymium or samarium. To avoid a loss of material they were fractionated by the following method:—

The oxides were divided by means of ammonia into two equal parts, a precipitate and a filtrate, and precipitate and filtrate were each divided into two halves. In this way a series of four members was obtained. The two middle members were then further treated, and those parts which corresponded to the first or fourth members, as regards their spectra, were added to these members respectively. Thus the whole of the material was divided into two halves, separated by four fractionations. Each of these two halves was again divided. The extreme members were already separated by six fractionations, and the middle members were again treated till they were all added to the two extremes.

Thus it was possible, by a series of 36 fractionations, to divide the material into two totally different parts without the least loss. The great number of fractionations necessary for such a separation is easily understood when we consider that the number of operations necessary to bring the inner members to the same state of purity as the outer is always greater, the further the outer members are separated from one another.

The first thing to do was to find out in which part of the above-mentioned separation the gadolinium would be.

As the gadolinium is more strongly basic than erbium, it was to be assumed that it would be contained in the second part of the separation, which was shown by its spectrum to be free from erbium, and was far less yellow. This part was therefore again fractionated with ammonia according to the above scheme. Altogether about forty operations were performed, but in the last series of fractionations the separate members were not combined in two, but in three groups, according to the magnitude of their atomic weights. (In order to avoid converting from equivalent weights to atomic weights in dealing with mixtures, the expression 'atomic weight' has been retained and calculated to the formula R_2O_3.)

The oxides with atomic weight 125–139 are in the first group. They were so largely contaminated with yttrium earths that it was worth while treating for gadolinium. There were altogether 10 grammes of yellow-coloured oxides, which were almost free from absorption bands. The fractions 140–147 occurred in the middle group, amounting altogether to 10 grammes. These oxides possessed a fainter yellow colour, and showed the samarium lines clearly and the neodymium lines faintly. The third portion showed the neodymium bands very strongly, and, in addition, the samarium bands faintly. There were altogether 5 grammes of oxides of the greyish-blue colour which is peculiar to neodymium oxide.

The high atomic weight of the second group infers the presence of a high percentage of gadolinium, as it could not, in any case, be caused by the comparatively small quantity of samarium. The gadolinium was thus contaminated in this group, on the one hand by yttria, and on the other by samarium and neodymium in small quantities. It was evident that it could not be easy to isolate in a pure condition one component from 10 grammes of such a mixture. Marignac's statements[1] that yttria was soluble in less than 100 parts of potassium sulphate, gadolinium in about 200 parts, while samarium was only soluble in 400 parts, and neodymium was practically insoluble, led the author to perform the separation with potassium sulphate, according to the method given under II.

The concentrated neutral solution of the nitrate was each time

[1] *Comptes Rendus*, vol. xc. p. 889.

shaken vigorously for three days with 500 cubic centimetres of concentrated solution of potassium sulphate, when the following amounts went into solution successively :—

I.	0·46	grm.	oxide,	Atomic Weight,	for R_2O_3,	117·8
II.	0·474	,,	,,	,,	,,	121·15
III.	0·624	,,	,,	,,	,,	142·7
IV.	0·472	,,	,,	,,	,,	150·8
V.	0·45	,,	,,	,,	,,	153·7
VI.	0·44	,,	,,	,,	,,	154·78

(Free from neodymium and samarium.)

The above numbers show that the solubility of the gadolinium in a saturated solution of potassium sulphate is considerably less (about one-tenth) than that stated by Marignac (*loc. cit.*). The reason for this is, that on standing at rest strongly supersaturated solutions are formed.

All the oxides of this series were quite free from absorption spectra. The first members were decidedly yellow, the latter only faintly. The last member, with atomic weight 154·78, resembled gadolinium most closely, the following figures being given by the various authors as its atomic weight :—Marignac, 156·75 ; Lecoq de Boisbaudran, 155·9 ; Clève, 155 ; Bettendorff, 156·33 ; Benedicks, 156·38.

This preparation was doubtless still contaminated with small quantities of yttria.

The residue (7 grammes), which did not go into solution with potassium sulphate solution, was again subjected to treatment with the same solvent. But it was not possible to bring more substance free from samarium into solution. However, the small quantity of neodymium was completely removed by once applying potassium sulphate, Method I., and this removed also the greater part of the samarium. From the material (3 grammes) thus obtained, which contained a small amount of samarium, by a long series of carefully performed ammonia separations, the author obtained ½ gramme of oxide free from samarium.

Determinations of its atomic weight gave the numbers 156·3 and 156·35. These two numbers agree satisfactorily with the values 156·33 and 156·138 given by Bettendorff and Benedicks.

After strong ignition gadolinium oxide is only faintly yellow. It is difficult to say definitely whether this suggestion of a yellow colour is characteristic of gadolinium oxide or is due to the admixture of traces of a coloured earth. But it is a fact that a specimen of gadolinium which does not show this colouration had not yet been obtained. The colour disappears in a current of hydrogen.

The salts, and the solutions of the salts of gadolinium are colourless. The solutions show no absorption spectrum. Under the influence of the cathode rays neither pure gadolinium sulphate nor

oxide becomes luminescent, and no cathode luminescence spectrum is shown.[1]

There can hardly be any further doubt concerning the elementary nature of gadolinium. If gadolinium were a mixture, neighbouring earths with atomic weight higher than 156 would be known to us. However, this is not the case, the atomic weight 156 of gadolinium being, as Marignac has already noticed, the highest of the earths standing near it.

The following notes on gadolinium have recently been communicated by Sir William Crookes to the Royal Society.[2]

'Gadolinium oxide is a rare earth, occurring between yttrium and samarium. It was discovered in 1880 by Marignac, and was at first called by him Ya, a designation which he soon changed for gadolinium. Since Marignac's time, much work has been done on this earth by Lecoq de Boisbaudran, Bettendorff, Clève, Benedicks, Marc, Demarçay, Exner and Haschek, Urbain, and others.

'In the spring of 1904, M. G. Urbain gave me some gadolinia and other rare earths, which he had prepared in a state of considerable purity by means of a novel system of fractionation in which use is made of the crystallisation of double nitrates of bismuth and magnesium with the rare earth nitrates. He finds that bismuth places itself between the ceric and the terbic groups, thus sharply separating samarium, the last member of the ceric group, from europium and gadolinium, the first members of the terbic groups. I have for some time past been fractionating rare earths by Urbain's method, and can quite corroborate what he says.

'The ultra-violet spectrum of gadolinium has been measured by Exner and Haschek, who have published their results in a book, "Wellenlängen-Tabellen für Spektralanalytische Untersuchungen" (F. Deuticke: Leipzig und Wien, 1902). These observers used a material prepared by Dr. L. Haitinger, in which they say holmium, samarium and yttrium were present as impurities. They give wave-lengths of 1150 lines; I have found them to be as a rule very accurate, and in my maps I have adopted most of their wave-lengths, except in cases where my own measurements gave different figures, or where lines given by them are not to be distinguished on my photographs. In some cases also, lines ascribed to gadolinium appear to be caused by other earths as impurities.

'My photographs were taken by means of the apparatus described in my paper "On the Ultra-Violet Spectrum of Radium."[3] The arrangement is the same as there adopted in the maps of the radium spectrum. The upper half of each strip shows the iron lines used as standards,

[1] Cf. Baur und Marc, *Ber. Deutsch. Chem. Ges.* xxxiv. 2460–66.

[2] *Roy. Soc. Proc.* vol. lxxiv. p. 420.

[3] '*Proc. Roy. Soc.* August 1903, vol. lxxii. p. 295; *Chemical News*, 1903, vol. lxxxviii. p. 202.

with their wave-lengths according to Rowland's latest measurements. The lower half contains the gadolinium lines, with their wave-lengths recalculated or verified from the iron standards, according to the method given in detail in the paper just quoted. The other lines are either platinum lines or lines due to traces of impurity in the gadolinium oxide. These are very few, and their faintness speaks well for the accuracy with which M. Urbain has separated other earths from the gadolinium, for in my experience I have seldom found a so-called "pure" salt of an ordinary metal anything like so free from impurities as this earth proves to be. Moreover, it must not be taken as certain that some of the impurities assumed to be present on the strength of a strong line are really there, because in some instances I have not been able to detect the presence of another equally characteristic line of the same impurity.

'The rare elements allied to gadolinium, or occurring with it, which I have thus found to be present, are :—

Yttrium,	represented	by	the lines at	3774·51 and 4177·68
Europium	,,	,,	,,	3972·16, 4129·90, and 4662·08
Samarium	,,	,,	line at	3230·65
Ytterbium	,,	,,	lines at	3289·52 and 3694·35
Scandium	,,	,,	,,	3572·71, 3613·96, and 3630·86

The other elements which are present are :—

Bismuth,	represented	by	the line at	4259·85
Magnesium	,,	,,	lines at	2796·62 and 2802·80
Calcium	,,	,,	,,	3933·81 and 3968·60

Of these, the bismuth and magnesium are present from the salts used in the fractionation,[1] while calcium is represented by the great H and K pair which are almost always present in earthy spectra.

'I have also examined the phosphorescent spectrum of Urbain's gadolinium by means of photography. In 1896 I communicated a paper to the Royal Society[2] on the visible spectrum of phosphorescing Yα (gadolinia), given to me by Marignac, and also prepared by myself; and later in the year[3] I said that the gadolinium I was then working with showed, on the evidence of its phosphorescent spectrum, the presence of samarium and other impurities. Since that time I have used the photographic method of examining the phosphorescent spectra, and in 1899 I brought before the Royal Society[4] a preliminary notice of a new element, victorium, the existence of which I was led to infer from

[1] In a still purer specimen from M. Urbain, recently received, these impurities are absent.

[2] '*Proc. Roy. Soc.* February 1886, vol. xl. p. 236'; *Chemical News*, 1886, vol. liii. p. 133.

[3] '*Proc. Roy. Soc.* June 1886, vol. xl. p. 503.

[4] '*Proc. Roy. Soc.* May 1899, vol. lxix. p. 237'; *Chemical News*, 1899, vol. lxxix. p. 212.

its chemical properties, and from some bands in its phosphorescent spectrum. These bands consist of a strong group high up in the ultra-violet spectrum, having wave-lengths of 3117–3120, 3060, 3064, and 3219.

'The specimens of gadolinia prepared by myself in 1886, as well as that sent me by Marignac, gave these victorium bands faintly, and the gadolinia given me by M. Urbain also showed the same bands in greater strength than the other lines and bands I have ascribed to samarium and yttrium. M. Urbain has recently sent me a specimen of gadolinium which he considers quite pure, and on testing it in the vacuum tube for its phosphorescent spectrum I find the victorium bands photograph stronger than they came out in the other specimen. At the same time, I do not think that victorium is gadolinium. All the evidence from chemical and phosphorescent data tends to the conclusion that victorium is only present as an impurity in the gadolinium, and the strength with which it reveals its presence is mainly due to the excessive delicacy of the test.'

A General Method for the Separation of Certain of the Rare Earths

G. Urbain and H. Lacombe[1] have given a method for the exact separation of some of the rare earths.

Fractional crystallisation of two salts which are not isomorphous can never result in the production of either the least soluble or the most abundant in a good state of purity. If the solution has a certain composition to start with, the two salts crystallise simultaneously, forming a eutectic mixture, and never, however often crystallisation is repeated, can they be absolutely separated.

In the case of isomorphous salts the phenomena are quite different. By a series of fractional crystallisations properly carried out, a mixture of isomorphous salts can be separated into its constituents in the order of their solubility.

After a sufficient number of fractionations each one will be obtained pure. It will also be noticed, indeed, that in a mixture of isomorphous salts a more soluble member of the series diminishes the solubility of a less soluble member. The true solubility of each salt when in a pure state is profoundly modified by the presence in the solution of a homologous salt of the series in such a manner that during separation by fractional crystallisation the individual solubility of each salt appears of less importance than the tendency of the salts to replace each other in the crystalline deposit.

It is this tendency to replace one another in the deposit which enables us in certain cases to separate the least soluble salts in a pure state from those which accumulate in the mother-liquor. So exact is

[1] *Chemical News*, Dec. 18, 1903.

the separation that even the most delicate tests fail to discover a trace of the least soluble salts at the opposite end of the fractionation.

To separate elements whose proportions vary very slightly from one member to another of the series, as in the family of the rare earths, this remarkable property of isomorphous salts can be utilised. It is by crystallisations of relatively very soluble salts that the best results are obtained. Double salts, where the differences of solubility between the members are usually greater than those of simple salts, can be most conveniently separated by this method. Fractionation methods are still, and are likely to remain for a long time, the only means which allow of the separation of the rare earths among themselves. Cerium alone has a series of stable higher oxides, which can always be utilised for its separation from other rare earths.

In all cases the great difficulty of fractional methods for the separation of the rare earths is the presence of intermediate portions, which, though they can often be considerably reduced, can never disappear altogether, except in the following case :—When an element, usually separated with no difficulty from the rare earths, presents a case of isomorphism. Also if the solubility of the salt of the common element is intermediate between that of the two members of the series.

An example of such a case is the isomorphism of double nitrate of magnesium and bismuth with the double nitrates of magnesium and the rare earths. In a preliminary examination MM. Urbain and Lacombe compared this bismuth compound with the corresponding salts of the samarium-gadolinium group, and they thought at the beginning of their researches that if they added to the magnesium nitrates of these earths, whose fractionation was described by Demarçay with such brilliant results, a certain proportion of bismuth magnesium nitrate, the element bismuth will, little by little, be inserted between the two rare earths, gradually separating the elements. A simple precipitation by sulphuretted hydrogen will then eliminate the bismuth, and we should obtain a rigorous separation in the rare earth series for the first time.

Experiment has fully confirmed this prediction, and the results obtained have passed our expectations.

The authors have fractionated in presence of magnesium nitrate (1) earths rich in samarium, (2) earths rich in gadolinium. In both cases they have added a considerable quantity of bismuth magnesium nitrate to the rare earth magnesium nitrates.

After thirty-five series of fractionations, each resulting in ten fractions, they made the following observations :—Neodymium concentrates at one end, and is only mixed with bismuth. Samarium comes next. The oxide extracted from Fraction 2 shows the slight yellow colouration characteristic of samarium. This colouration diminishes in the following fractions. In the same way the yellow colouration and the absorption spectra of the solution decrease from one fraction to

the next. The proportion of rare earths decreases at the same time as the proportion of bismuth increases. In the first experiment with a substance rich in samarium the Fractions 11 and 12 contain no trace of rare earths. In the second experiment, when an earth containing very little samarium was used, Fractions 4, 5 and 6 contain only bismuth. In the following fractions the rare earths appear again, and their proportion increases up to the end of the series, whilst the proportion of bismuth decreases. The solutions show no absorption spectrum except the last fraction, when faint bands of dysprosium may be distinguished. The colour of the oxide starts from white gadolinia up to the last fraction, when the earth is brick-red.

These observations apparently show that bismuth inserts itself between samarium and gadolinium.

M. Demarçay's europium exists only in minute quantities as compared with gadolinium and samarium in the rare earths, and later researches have enabled MM. Urbain and Lacombe to assign a place to this element in the separation. They find that by examination of the absorption spectrum of europium and of its spark spectrum, bismuth inserts itself exactly between samarium and europium.

Bismuth apparently divides the two large groups of the rare earths, and from this we see that europium can be considered as the first term of the series of the yttria earths. The authors have therefore utilised, for a new type of separation, the property of the isomorphism of bismuth magnesium nitrate with the same salt of the rare earths. The principle of this method is deduced from the following facts :—

When a series of isomorphous salts gives non-crystallisable mother-liquors, the proportion of salt capable of crystallisation retained in the mother-liquors depends on the mass of the non-crystallisable salt accompanying it. Reciprocally, when a large quantity of salt capable of crystallisation is in the presence of a small quantity of non-crystallisable salt in a state of purity, a measurable quantity of this latter is retained in the crystallisation, *a fortiori* very soluble salts, but nevertheless susceptible of separate crystallisation. Thus the non-crystallisable mother-liquor of magnesium nitrate always retains a proportion of gadolinia, which can be as much as a third of the contained earths. Demarçay considered the fractionation of the double sodium sulphates to eliminate yttria as one of the most satisfactory methods.

In the present method we do not require the multiple treatments which the above method of fractionation necessitates.

If the same weight of magnesium nitrate of bismuth is added to the non-crystallisable mother-liquors, the added salt retains the gadolinium during its crystallisation. The operation should be repeated until the soluble earths give no spark spectrum of gadolinium.

This method of retention recalls the method proposed by Auer Von Welsbach to extract from neodymium the last traces of praseodymium by the addition of pure lanthana. But if, in the present separation,

the bismuth plays an analogous *rôle* to that of the lanthanum in Auer Von Welsbach's method, it is not so inconvenient, since the bismuth can with such great facility be separated from the rare earths in the subsequent operations.

This method of extraction of the gadolinium earths can equally well be used to eliminate gadolinium from crude yttria earths in which this element is present only in small proportion, as in the earths from xenotime.

The methodical fractionation of the bismuthic gadoliniferous nitrates in the same order in which they have been obtained allows of the rigorous separation of the ceric and yttric earths. The insolubility of the magnesium nitrates of the earths which precede samarium in the solution of the double nitrate of bismuth allows of the separation of these earths from soluble samaria with an almost quantitative yield.

SAMARIUM

For the preparation of samarium R. Marc [1] uses intermediate products of fractionation. He had the choice of the neodymium preparations, rich in samarium, or the middle preparations, less rich in samarium but quite free from neodymium. He decided to use the latter, as it is far more difficult to separate samarium from neodymium than from erbium, and it was important to get a preparation quite free from neodymium.

The material for the preparation of the samarium consisted of only 10 grammes of atomic weight 125 to 139. It possessed a well-marked yellow colour; its spectrum showed, besides decided quantities of samarium, small quantities of erbium, but no neodymium. The separation of the samarium from the erbium is performed comparatively easily.

Ammonia was used for the separation; it was arranged so that only as much ammonia was added as corresponded to 1 gramme of the oxide. Even after the first three fractionations the remaining liquid appeared quite free from erbium. To make quite sure, two more fractionations were performed; and the remaining 5 grammes, which were quite free from erbium, were treated in such a manner that those oxides which showed the samarium spectrum most strongly were united, purified, and further fractionated. After rather a long series of fractionations there was finally obtained, as the richest in samarium, 0·2 gramme of a yellow preparation which was quite free from absorption bands of foreign earths.

From the material on the right-hand side, by repeated fractionation with ammonia, Marc also obtained preparations very rich in samarium, but these retained the last traces of neodymium with extraordinary energy.

[1] *Chemical News*, May 13, 1904.

He also succeeded in preparing from the extreme fractions 9 grammes of almost perfectly pure neodymium, which contained only very small quantities of samarium.

Demarçay has given an excellent method for the separation of samarium from neodymium by fractional crystallisation of the double magnesium nitrates in concentrated nitric acid. This method enables us easily to get rid of the properly called ceric earths from the yttria earths, from yttrium to samarium included. It can be substituted with great advantage for the fusion methods described by Auer Von Welsbach. However, the double nitrates of magnesium do not easily lend themselves to the separation of the components of the *old* didymium.

Demarçay has satisfied himself that no intermediate element exists between neodymium and samarium.

However, in his method there are eight to ten fractions between samarium and europium, and he could scarcely affirm on this evidence that no unknown earth exists between these two elements.

G. Urbain and H. Lacombe have prepared pure samaria, free from europia and gadolinia, by their method of fractional crystallisation with bismuth-magnesium nitrates.[1]

In the hope of obtaining an easier separation, H. Lacombe has endeavoured to find a salt whose solubility was less than that of the double alkaline nitrates, and greater than that of the double nitrates of magnesium. The double nitrate of manganese, corresponding to the type $2Di(NO_3)_3+3Mn(NO_3)_2+24H_2O$, is the one that has given the best results. The experiments have been carried out successively on earths rich in neodymium and on earths rich in praseodymium.

In both cases the double nitrates of didymium and manganese are best fractionated in nitric acid of density 1·3.

The proportion of mother-liquors ought to be kept practically constant, and always in small quantity compared with the crystals. During the concentrations we sometimes observe a slight decomposition of the nitrate of manganese with the formation of the brown peroxide.

In such a case it suffices to add a few drops of fuming nitric acid to the warm liquor, and it immediately becomes clear by the reduction of the peroxide of manganese, which is then dissolved instantly. To prevent supersaturation and to cause a slow crystallisation, it is as well to start the crystals with a nucleus of the double nitrate of bismuth and manganese, a salt isomorphous with those of the rare earths.

This separation of samarium is still more rapid and more decided than that proposed by Demarçay. It enables us to separate samarium from neodymium as easily as the use of the double nitrates enables us to separate nickel and cobalt, for example. Moreover, it has incontestable advantages over that of Auer Von Welsbach, so far as the

[1] *Chemical News*, vol. lxxxviii. p. 295; vol. lxxxix. p. 52.

separation of neodymium and praseodymium is concerned, since it enables us to reduce the portions intermediate between these two elements to very small quantities in proportion to the elements obtained in a state of purity.

'THE DETECTION AND WIDE DISTRIBUTION OF YTTRIUM [1]

'Introduction

1. 'In March, 1881, I sent to the Royal Society a preliminary notice of some results I had obtained when working on the molecular discharge in high vacua.[2] When the spark from a good induction coil traverses a tube having a flat aluminium pole at each end, the appearance changes according to the degree of exhaustion. Supposing atmospheric air to be the gas under exhaustion, at a pressure of about 7 millimetres a narrow black space is seen to separate the luminous glow from the aluminium pole connected with the negative pole of the induction coil. As the exhaustion proceeds this dark space increases in thickness, until, at a pressure of about 0·02 millimetre (between 20 and 30 M.),[3] the dark spark has swollen out till it nearly fills the tube. The luminous cloud showing the presence of residual gas has almost disappeared, and the molecular discharge from the negative pole begins to excite phosphorescence on the glass where it strikes the side. There is a great difference in the degree of exhaustion at which various substances begin to phosphoresce. Some refuse to glow until the exhaustion is so great that the vacuum is nearly non-conducting, whilst others begin to show luminosity when the gauge is 5 or 10 millimetres below the barometric level. The majority of bodies, however, do not phosphoresce till they are well within the negative dark space. This phosphorogenic phenomenon is at its maximum at about 1 M., and unless otherwise stated, the experiments now about to be described were all tried at this high degree of exhaustion.

'Under the influence of this discharge, which I have ventured to call radiant matter, a large number of substances emit phosphorescent light, some faintly and others with great intensity. On examining the emitted light in the spectroscope, most bodies give a faint continuous spectrum, with a more or less decided concentration in one part of the spectrum, the superficial colour of the phosphorescing substance being governed by this preponderating emission in one or other part of the spectrum.

'Sometimes, but more rarely, the spectrum of the phosphorescent

[1] 'The Bakerian Lecture, by William Crookes, F.R.S. Delivered before the Royal Society, May 31, 1883.

[2] '*Proceedings of the Royal Society*, No. 213, 1881.

[3] 'M = one-millionth of an atmosphere.

light is discontinuous, and it is to bodies manifesting this phenomenon that my attention has been specially directed for some years past, considerable interest attaching to a solid body whose molecules vibrate in a few directions only, giving rise to spectrum lines or bands on a dark background.

'The Citron-Band Spectrum

2. 'For a long time past I have been haunted by a bright citron-coloured band or line appearing in these phosphorescent spectra, sometimes as a sharp line, at others as a broader nebulous band, but having always a characteristic appearance and occurring uniformly in the same spot. This band I first saw in the summer of 1879, and from that date down to a comparatively short time ago all my efforts to clear up the mystery proved in vain. By chemical means it was not difficult to effect a partial separation of a certain mineral or earthy body into two parts, one giving little or no citron band, the other giving one stronger than the original band; and by again treating this latter portion by appropriate chemical means, the citron-band-forming body could frequently be still more concentrated; but further than this for a long time it seemed impossible to go. I soon came to the conclusion that the substance I was in search of was an earth, but on attempting to determine its chemical properties I was baffled. A more Proteus-like substance a chemist never had to deal with. In my preliminary note, above referred to, speaking of the possibility that some of these spectrum-forming bodies might be new chemical elements, I said: "The chemist must be on his guard against certain pitfalls which catch the unwary. I allude to the profound modification which the presence of fluorine, phosphorus, boron, &c., causes in the chemical reactions of many elements, and to the interfering action of a large quantity of one body on the chemical properties of another which may be present in small quantities."

3. 'This warning was not unnecessary. No Will-o'-the-Wisp ever led the unwary traveller into so many pitfalls and sloughs of despond as the hunt for this phantom band has entrapped me. I have started with a large quantity of substance which, from preliminary observations, promised to be a rich mine of the desired body, and have worked it up chemically to a certain point, when the citron band vanished, and could not be again detected in either precipitate or filtrate. Half a dozen times in the last four years the research has been given up as hopeless, and only a feeling of humiliation at the thought of a chemist being beaten by any number of anomalies made me renew each time the attack. Likewise, the tedious character of the research made a long continuance of failures very disheartening. To perform a spectrum test, the body under examination must be put in a tube and exhausted to a very high point before the spectroscope can be brought to bear on it.

Instead of a few minutes, many hours are occupied in each operation, and the tentative gropings in the dark, pre-eminently characteristic of this kind of research, have to be extended over a long period of time.

4. 'I soon found that the best way to bring out the band was to treat the substance under examination with strong sulphuric acid, drive off excess of acid by heat, and finally to raise the temperature to dull redness (10). The anhydrous sulphate thus left frequently showed the citron band in the radiant matter tube, when before this treatment the original substance showed nothing (75).

'Examination of Calcium Compounds

5. 'My first idea was that the band might be due to a compound of lime. Much chemical evidence tended to support this view. I have already explained that the chemical extraction was rendered very difficult by the fact of the citron band so frequently turning up both in the precipitate and the filtrate. By neglecting the portion showing the least citron band, and removing all the elements present which gave little or none, I could generally concentrate the citron band into a solution which—according to our present knowledge of analytical chemistry—should contain little else than the earths, alkaline earths, and alkalies. Ammonia added to this solution would precipitate an earth (11, 14), and in the filtrate from this oxalic acid would precipitate an insoluble oxalate (7, 13).

'The citron band hovered between these two precipitates, being sometimes stronger in one and sometimes in the other. It was also to be detected, but more faintly, in the residue left after evaporating to dryness and igniting the filtrate from the oxalate.

'I frequently obtained no precipitate with ammonia, and then the oxalate gave the band brilliantly; and occasionally the ammonia precipitate when formed gave little or no citron band. I was, however, generally sure to find it in the insoluble oxalate, and sometimes it was very brilliant, being accompanied by two bright green bands and a fainter red band.

6. 'At this time one of the minerals which showed the citron band most strongly was a phosphorescent apatite from Ireland; and knowing the difficulties of separating the last traces of phosphoric acid from the earths, I explained the foregoing facts by the presence of small quantities of phosphoric acid, which gave rise to the ammonia precipitate; the bulk of the citron body not being precipitated by ammonia, but coming down as oxalate; whilst a little of this oxalate would remain dissolved in the ammoniacal salts present, and so appear with the alkalies.

'I tested this hypothesis in every imaginable way, by mixing small quantities of phosphoric acid with salts of lime and other earths, in the endeavour to imitate the conditions occurring in the native minerals,

and so educe the citron band; but I was unable to get any precipitate giving the citron band when I started with materials which did not originally give it.

7. 'A sufficient quantity of precipitated oxalate (5) having in course of time been accumulated, I attempted its purification. It was ignited, dissolved in dilute hydrochloric acid, and rendered slightly alkaline with ammonia and ammonium sulphide. The liquid was boiled down to a small bulk, keeping it alkaline, and was then set aside in a warm place: a slight flocculent precipitate formed. This was filtered, and the filtrate reconcentrated. The clear strong solution should now contain nothing but barium, strontium, and calcium, with traces of elements from previous groups which might be soluble in the precipitants employed or in the ammoniacal salts present (for we know that the word *insoluble* applied to a precipitate is not an absolute term, and in minute analysis allowance must be made not only for the slight solubility of precipitates in the reagents present, but also for the power possessed by most precipitates of carrying down with them traces of soluble metallic salts from solution). Besides these, it was possible that a hitherto unrecognised element might be present, to which the citron band was due. By the ordinary process of analysis I could, however, only detect the presence of calcium and strontium.

8. 'The concentrated ammoniacal solution was added to an excess of a boiling solution of ammonium sulphate, and the whole was set aside for twenty-four hours; the precipitate which had formed was filtered off and washed with a saturated solution of ammonium sulphate. The precipitate was found to consist of strontium sulphate. On testing this in a radiant matter tube the citron band was very decided, although much fainter than in the original oxalate. The filtrate was diluted largely, heated, and precipitated with a hot solution of ammonium oxalate; it was then allowed to stand for some time, when a bulky white calcium oxalate came down. This was filtered and washed. Tested in the radiant matter tube, after ignition and treatment with sulphuric acid, it gave the citron band, far exceeding in brightness the spectrum of the original oxalate.

9. 'So far all the chemical evidence went to show that the band-forming substance was calcium, and further tests tried with the purified oxalate confirmed this inference. Every analytical test to which it was subjected showed lime, and nothing but lime; all the salts which were prepared from it resembled those of lime, both physically and chemically; the flame spectrum gave the calcium lines with extraordinary purity and brilliancy; and finally, the atomic weight, taken with great care, came out almost the same as that of calcium, 39·9 as against Ca 40.

10. 'I now sought for the citron band amongst other calcium minerals. The preliminary testing was simple. The finely powdered mineral was moistened with strong sulphuric acid, the action being assisted by heat, and the mass was raised to dull redness (4). It was

then put into a radiant matter tube and the induction spark passed through after the exhaustion had been pushed to the required degree.

'Treated in this manner most native compounds of lime gave the citron band. A perfectly clear and colourless crystal of Iceland spar converted into sulphate gave it strongly, native calcic phosphate less strongly, and a crystal of arragonite much more brightly. A stalactite of calcium carbonate from the Gibraltar caves gave the band almost as well as calcite, as also did cinnamon stone (lime alumina garnet), iron slag from a blast furnace, commercial plaster of Paris, and most specimens of ordinary burnt lime.

'The Citron Band not due to Calcium

11. 'Evidence stronger than this in favour of the view that the citron band was an inherent characteristic of calcium could scarcely be; but, on the other hand, there was evidence equally conclusive that the band was not essential to calcium. The ammonia precipitate (5) sometimes gave the citron band with great strength and purity, and although I had not yet obtained this in quantities sufficient for a detailed examination, it was easy to decide that it contained no phosphoric, silicic, or boric acid, fluorine, or other body likely to cause the precipitation of lime in this group. This precipitate must therefore be an earth, and the more carefully I purified it from lime and other substances, the more brilliantly shone out the citron band, and the more intense became the green and red bands.

'Another stubborn fact was this:—Starting with a lime compound which showed the citron band, I could always obtain a calcium oxalate which gave the band stronger than the original substance; but if I started with a lime compound which originally gave no citron band, I could never by any means, chemical or physical, constrain the lime or the earthy precipitate to yield a citron band.

12. 'Among the minerals tried was eudialite, a zirconium, iron, calcium, and sodium silicate, containing about 10 per cent. of lime. No citron band could be detected on testing the original mineral or any of the constituents separated from it on analysis. This and a lump of common whiting (levigated chalk) were for some time my only sources of lime which gave no citron band.

13. 'The only explanation that I could see for this anomaly was that the elusive citron band was caused by some element precipitated with the calcic oxalate, but present in a quantity too small to be detected by ordinary chemical means. I then thought that were I to fractionally precipitate the solution of lime, the band-forming body might be concentrated in one or the other portion. Accordingly the calcium oxalate (7, 8, 9) was ignited and dissolved in hydrochloric acid, and fractionally precipitated in three portions with ammonium oxalate, the first and third portions being comparatively small. They

were dried, ignited with sulphuric acid, and tested in the radiant matter tube. All three portions showed the citron band, but the portion which came down first gave the band decidedly the strongest, and the third portion precipitated showed it weakest. This therefore pointed to a difference between calcium and the body sought for. The process, however, was not satisfactory, and I was driven to seek some other method.

14. 'A portion of an ammonia precipitate, found to give the citron band very well (5, 11), was dissolved in dilute sulphuric acid, and the solution evaporated down. Crystals were formed which were difficultly soluble in hot water, but appeared more soluble than calcic sulphate.

'A large quantity of the calcic oxalate (7, 8, 9) was ignited with sulphuric acid at a dull red heat, and the resulting calcium sulphate was finely ground and then boiled in a very small quantity of water—not sufficient to dissolve the one-hundredth part of it. The mass was thrown on a filter, and a small quantity of clear liquid which came through was precipitated with ammonium oxalate. The resulting white precipitate was ignited with sulphuric acid, and tested in the radiant matter tube. For the sake of comparison a portion of the calcium sulphate remaining on the filter was also put in a radiant matter tube. The sulphate from the aqueous extract gave the citron band far more brilliantly than the calcium sulphate from the filter. I found, however, that it was impossible, by any amount of washing or boiling out, to deprive the calcium sulphate of all power of giving the citron band, although it was possible in this way to weaken its intensity considerably.

'Experiments with Calcium Sulphate

15. 'Supposing that the substance giving the citron band formed a sulphate more soluble in water than calcium sulphate, it was anticipated that repeated washings with cold water would extract some of it, which might then be detected more easily. About 4 lbs. weight of commercial plaster of Paris, which showed very faint traces of the citron band, were mixed with water and rapidly poured on a large filter. Before the mass solidified a slight saucerlike depression was made in the upper part, and a few ounces of water were poured on. This ran through slowly, and it was then poured back and the exhaustion repeated several times. The aqueous extract was then evaporated to dryness, ignited with sulphuric acid, ground in a mortar with small successive quantities of water, the liquid boiled, filtered, and precipitated first with ammonia, and the filtrate with ammonium oxalate. These precipitates both showed the citron band very fairly, far more intensely than it was seen in the original calcium sulphate. The green and red bands were also visible.

'The same mass of plaster of Paris was then washed, as before, with

a little dilute hydrochloric acid passed through several times, and this extract was treated in the same way by evaporation and extraction with water, and the filtrate precipitated, first with ammonia, and then with ammonium oxalate. In these precipitates the citron band, together with the green and red bands, were much more brightly manifest than in the precipitates from the aqueous extract.

'Wide Distribution of the Citron-Band-forming Body

16. 'These experiments are conclusive in proving that the citron band is not due to calcium, but to some other element, probably one of the earthy metals, occurring in very minute quantities, but widely distributed along with calcium, and I at once commenced experiments to find a more abundant supply of the body sought for. Amongst other substances tested I may note the following as giving a more or less decided citron band in the spectrum when treated with sulphuric acid in the manner indicated above (10) :— Crystallised barium chlorate, heavy spar, common limestone, strontium nitrate, native strontium carbonate, crystallised uranium nitrate, commercial magnesium sulphate, commercial potassium sulphate, Wagnerite (magnesium phosphate and fluoride), zircon, cerite, and commercial cerium oxalate.

'Examination of Zircon for the Citron Band

17. 'Some specimens of zircon treated in the above manner appeared sufficiently rich to make it probable that here might be found an available source of the citron-band-yielding body. I found it in crystals from Green River, North Carolina, from Ceylon, from Espailly, from Miask (Oural), and from Brevig, and having a good supply of North Carolina zircons I started working up these in the following manner :—

'The finely powdered zircons were fused with sodium fluoride, and the cooled melted mass powdered, boiled with sulphuric acid, and filtered. The solution was precipitated with excess of ammonia, the precipitate well washed and dissolved in hydrochloric acid, and the solution made nearly neutral. A little zirconium oxychloride sometimes separated on evaporation ; this was filtered off. An excess of sodium thiosulphate was now added, and the whole boiled for some time until a portion of the filtrate gave no further precipitate on boiling again with sodic thiosulphate. The precipitated zirconium thiosulphate was worked up for zirconia ; it was found to be quite free from the substance giving the citron band. The solution filtered from the zirconium thiosulphate was precipitated with ammonia, and the brown gelatinous precipitate was well washed. The filtrate was precipitated with ammonium oxalate, which brought down much calcium oxalate. This showed the citron band, but not strongly. The brown gelatinous precipitate was

dissolved in nitric acid. Silver nitrate was added to separate chlorine, and the filtrate from the silver chloride was boiled down with nitric acid and excess of metallic tin to separate phosphoric acid. The clear solution, separated from the stannic oxide, phosphate, &c., was boiled down with hydrochloric acid to remove nitric acid, and then saturated with hydric sulphide to separate silver and tin.

18. 'The filtrate from the sulphides was freed from hydric sulphide by boiling, and was then mixed with tartaric acid and excess of ammonia, to precipitate any yttria that might be present, together with Forbes's zirconia β (jargonia?).[1] On standing for some hours this gave a small quantity of a precipitate, which was separated by filtration; it was tested in the radiant matter tube, and found not to give the citron-band spectrum (44). To the filtrate ammonium sulphide was added to precipitate the iron. The black precipitate was filtered off and the filtrate evaporated to dryness, and ignited to destroy the organic matter. The residue, heated with sulphuric acid and ignited, gave the citron spectrum very brightly. This would probably be the earth which Forbes calls zirconia γ.[2]

19. 'For many years chemists have suspected that what is known as zirconia might be a compound. Svanberg [3] found that zircons from different localities varied in specific gravity, and the earth or earths obtained by fractional precipitation with oxalic acid had not the same properties, the hydrogen equivalents of the metals of the earths of the different fractions varying from 17·01 to 27·3, the metal of the earth hitherto recognised as zirconia being 22·4.[4] He considered zirconia to contain two different earths, the oxalate of one being less soluble in acid than that of the other, and their sulphates differing in crystalline form and solubility. He proposed the name "noria" for one of the earths, retaining that of zirconia for the other. The researches of Berlin, on the other hand, seem to disprove this.

20. 'Remembering the remarkable result produced in the absorption spectrum of some jargons by the presence of a minute trace of uranium,[5] I tried numerous experiments with this metal, adding small quantities of it to zirconia, lime, thoria, ceria, &c., but in no case could I produce the citron-band spectrum by this means.

'I may condense a year's work on zircon—more than 10 lbs. weight of crystals from North Carolina having been worked up—by stating that the result was comprised in about 300 grains of an earthy residue (18), and about two ounces of oxalate, chiefly calcium; the former gave the

[1] Par. 98, and '*Chemical News*, vol. xix. p. 277.

[2] Par. 98, and '*Loc. cit.*

[3] '*Poggend. Annal.* vol. lxv. p. 317.

[4] Svanberg's numbers for these earths are 938 to 1320 (M_2O_3), the earth hitherto recognised as zirconia being 1140; oxygen being 100. For the sake of uniformity I have recalculated his equivalents for the metals on the O = 16 scale, taking the formula as M_2O (see note 1, par. 40).

[5] '*Chemical News*, vol. xix. pp. 121, 142, 205, 277; vol. xx. pp. 7, 104; vol. xxi. p. 73.

citron band very well. The process as detailed above is given, since by this means a very large quantity of zircons was worked up, affording me the material which ultimately enabled me to solve the problem, which at one time seemed almost hopeless.

'The zirconia prepared from these zircons when tested sometimes showed the citron band, especially after precipitation as an oxychloride. Zirconia precipitated as thiosulphate did not yield the citron band (28). A zirconia rich in citron band, fractionally precipitated by ammonia, yielded precipitates of increasing richness, the last fraction showing the citron band strongly.

21. 'The calcium oxalate obtained from zircon gave unsatisfactory results, so attention was directed to the earthy residue (18). This was found to be of a highly complex character, containing thoria (which had escaped precipitation as thiosulphate), ceria, lanthana, didymia, yttria, and probably some of the newly discovered rarer earths.

'Examination of Cerite for the Citron Band

22. 'The position of the citron band in the spectrum falls exactly on the strongest absorption band of didymium, so that a piece of didymium glass or a cell of solution of the nitrate entirely obliterates the citron band. This naturally suggested that the band was due to didymium.

'Cerite was accordingly the next mineral experimented on. The powdered mineral, tested in the tube in the original way, gave a good citron band. It was made into a paste with sulphuric acid, and after all action had ceased it was extracted with cold water. The earths were then precipitated with ammonium oxalate, and the oxalate ignited. The fawn-coloured powder was then converted into sulphate, dissolved in water, and the cerium metals precipitated by long digestion with excess of potassium sulphate. When no didymium bands could be detected in a considerable thickness of the supernatant liquor, it was assumed that all the cerium metals were down, and the liquid was filtered.

23. 'The precipitated double sulphates were dissolved in hydrochloric acid, and the earths precipitated as oxalates. After ignition and treatment with sulphuric acid, the mixed ceria, lanthana, and didymia were tested in the radiant matter tube, but the merest trace only of citron band was visible.

24. 'This experiment proved the inadequacy of the didymium explanation (22), and further tests showed that not only could I get no citron band in pure didymium compounds, but the spectrum entirely failed to detect didymium in many solutions of the earth which gave the citron band brilliantly.

25. 'Attention was now turned to the solution filtered from the insoluble double sulphates from cerite (22). Potash in excess was

added to the filtrate, and the flocculent precipitate was filtered off, and after well washing was converted into sulphate, and tested in a radiant matter tube. The spectrum, of extraordinary brilliancy, was far brighter than any I had hitherto obtained. Unfortunately, however, the quantity was too small to be subjected to very searching chemical analysis.

' Examination of Thorite and Orangite

26. ' Search was next made amongst other minerals rich in the rarer earths. Thorite, another disputed mineral, was finely powdered, treated with sulphuric acid, and tested in the radiant matter tube. It gave the citron spectrum most brilliantly—equal, in fact, to the mixture of earths obtained from zircons (18, 21) at sô great an expenditure of time and trouble. Orangite treated in the same manner gave almost as good a spectrum. Pure thorium sulphate prepared by myself was found not to give the citron band, but three specimens prepared and given to me by friends all gave it ; so it was not unlikely that in thorite and orangite might at last be found a good source of the long-sought element—that in fact the body I was hunting for, if not thorium, might possibly be Bahr's hypothetical wasium. Having obtained about 2 lbs. of orangite and thorite, they were worked up as follows :—

27. ' The finely powdered mineral was heated for some time with strong hydrochloric acid, and when fully gelatinised and all action had ceased it was evaporated to dryness to render the silica insoluble ; then extracted with water slightly acidulated with hydrochloric acid, boiled, and filtered. Hydric sulphide was passed through the filtrate for some time. The flask then corked was set aside for twenty-four hours and filtered. The filtrate was evaporated to a small bulk, nearly neutralised with ammonia, and then boiled for some time with excess of sodium thiosulphate. This precipitated the thoria, alumina, zirconia, and titanic acid, whilst it left in solution the metals of the cerium and yttrium groups. The filtrate was boiled down to a small bulk, when a further precipitation took place : this was filtered off and added to the first thiosulphate precipitate. To the clear filtrate excess of ammonium oxalate was added, and the whole allowed to rest twenty-four hours. The precipitated oxalates were filtered, washed, ignited, dissolved in hydrochloric acid, and the excess of acid evaporated off. The aqueous solution was then mixed with a large excess of freshly precipitated barium carbonate, and set aside for twenty-four hours with frequent shaking (29). This would precipitate much of the cerium, and any iron or alumina which might have escaped previous treatment. The liquid was filtered from the precipitate by barium carbonate, and the clear solution, which would contain nothing but barium, and some of the yttrium and cerium metals, was treated as described farther on (30).

28. ' The thiosulphate precipitate tested in the radiant matter tube gave no citron band, nor did it seem possible to detect this band on

testing the purified thoria obtained from this precipitate nor from the alumina or zirconia from the same precipitate. This confirmed the results obtained when working up zircons, that sodium thiosulphate did not precipitate the citron-band-forming body.

29. 'The barium precipitate (27) was dissolved in hydrochloric acid the baryta separated with sulphuric acid, and the solution precipitated with ammonium oxalate. The ignited precipitate, which amounted to 0·223 per cent. of the mineral taken, contained the cerium metals. On testing in a radiant matter tube it gave the citron band only moderately well—not nearly so strong as the original thorite and orangite. The iron and alumina in the filtrate from the cerium oxalates were likewise precipitated and tested ; they showed a faint trace of citron band.

30. 'The solution (27) filtered from the barium precipitate was freed from baryta by sulphuric acid, precipitated with ammonium oxalate, and the precipitate washed and ignited ; it amounted to only 0·125 of the mineral taken. Tested in the radiant matter tube, it showed the citron band about as well as the corresponding earth from the barium precipitate.

'This was disheartening, for after having started with a mineral which gave the citron band well, and having hunted the citron band, as it were, into a corner, the only result was two trifling precipitates showing the citron band less intensely than did the raw material itself. The experiment, however, proved one thing : the band-forming substance was not thoria. The occurrence of this spectrum must therefore be due to some other element present in small quantity in thorite and orangite.

31. 'The two mixtures of earth—the one from the barium precipitate (29) and the other from the barium filtrate (30)—which showed the citron line moderately well, were dissolved in sulphuric acid, the solution neutralised as nearly as possible with potash and digested for several days with excess of potassium sulphate. The solution, which at first showed the didymium bands, was then found to be free from didymium.

32. 'The insoluble double sulphates were filtered and washed with a cold saturated solution of potassium sulphate. The precipitate was boiled for some time in ammonia, filtered, dissolved in hydrochloric acid, and precipitated with ammonium oxalate. This precipitate was ignited and tested in the radiant matter tube. It gave scarcely a trace of citron band (23). The earth was further purified by the potash and chlorine method, and was found to consist principally of cerium oxide.

33. 'The solution filtered from the insoluble potassio-cerium sulphate (31) was boiled with ammonia and ammonium sulphide. A small quantity of a white flocculent earth came down—too small a quantity to weigh. Tested in a radiant matter tube, it gave the citron band better than either of the above precipitates, showing that by this treatment the body had been concentrated (25).

34. 'It seemed possible that the earth sought for might be present in larger quantity in the thorite, but that it had been gradually carried down mechanically or by mass-action rather than chemically, by the numerous operations it had undergone before getting it to the final stage. Therefore a fresh quantity of thorite was extracted with hydrochloric acid. The solution was precipitated with potassium sulphate, taking the usual precautions to secure complete precipitation. A bulky precipitate ensued, which contained the thoria and cerium earths. These were separated and tested, and found to give only a faint citron band.

35. 'The solution of earthy sulphates soluble in potassium sulphate was precipitated with ammonium oxalate. The precipitate ignited with sulphuric acid, and tested in a radiant matter tube, gave the citron spectrum with great brilliancy (25, 33).

'Chemical Facts connected with the Citron Body

36. 'Certain chemical facts concerning the behaviour of the sought-for element which came out during the course of the tentative trials already described had considerably narrowed the list amongst which it might probably be found. All the evidence tended to show that it belongs to the group of earthy metals, consisting of aluminium, glucinum, thorium, zirconium, cerium, lanthanum, didymium, and the yttrium family, together with titanium, tantalum, and niobium. The sought-for earth is insoluble in excess of potash (25); this excludes aluminium and glucinum. It is not precipitated by continued boiling with sodium thiosulphate (17, 27); this excludes aluminium, thorium, and zirconium. Fused with acid potassium sulphate, the resulting compound is readily soluble in cold water; this excludes tantalum and niobium. Evaporating to dryness with hydrochloric acid and heating for some time does not render the body insoluble in water (27); this excludes titanium and silicium. It is easily soluble in an excess of a saturated solution of potassium sulphate (25, 33, 34); this excludes thorium, the cerium group, some of the numerous members of the yttrium group, and zirconium. The only remaining elements among which this elusive body would probably be found are those members of the yttrium family which are not precipitated by potassium sulphate.

37. 'On the other hand, the body giving the citron-band spectrum did not behave like one of the known earths. A rich residue was fused with sodium carbonate, and the mass extracted with water. The insoluble residue, on testing in the usual way, was rich in citron band, but subsequent treatment of the aqueous solution gave me an earth which also gave the citron band strongly.

'An acid solution of the citron body was precipitated by ammonia and ammonium chloride. The earth was not completely precipitated,

but after a long boiling some remained in solution. (I have since ascertained that the detection of the citron-band body in solution under these circumstances is only owing to the marvellous delicacy of the test, which carries our powers of recognition far beyond the resources of ordinary chemistry.)

38. 'Besides obtaining indirect evidence that the citron band was not due to certain elements, I tried special experiments with each substance, brought to the highest possible state of purity. In many cases I detected more or less traces of citron band; but I had come to the conclusion, abundantly warranted by facts, that this citron band was an extraordinarily sensitive test of the presence of the element causing it; and the minute chemistry of many of these earthy metals being insufficiently known, it was not surprising that traces of one of them should adhere to another in spite of repeated attempts to purify it out. With each successive fractional precipitation the citron band became fainter, showing that with perseverance the last trace would probably disappear. The time this process would have occupied, in my opinion, seemed not worth the little additional evidence it would have afforded.

39. 'Taking into consideration the extremely small quantity of phosphorescent material which had so far been obtained, all these experiments justified me in assuming that the body sought for not only belonged to the group of earths, but also most probably to the subgroup, not precipitated by potassium sulphate, to which yttria belongs. As, however, the number of these metals has increased so much within the last few years, and as the quantity of material which I had up to the present at my disposal was too small to admit of a satisfactory chemical examination being made of it, search was commenced among other sources known to be rich in these metals. Besides, not only did the majority of the substances I had up till now obtained in anything like quantity indicate the citron-band earth to belong to the yttria group (33, 34, 36), but also that either the earth itself showed an absorption band in the spectroscope, or was invariably accompanied by one which did. On the other hand, I had a certain amount of evidence that the earth sought for did not show a band in the spectroscope (24); but remembering the extremely small quantity of very impure substance experimented with, the evidence on this point was not at all conclusive.

'The Sought-for Body one of the Yttrium Family

40. 'The yttria earths form a somewhat numerous family. Fortunately for chemists, a mineral rich in yttria earths—samarskite—has been found in large quantity in Mitchell County, North Carolina, and to this mineral I accordingly now directed my attention.

'The annexed list of elements of the yttrium and its allied families,

said to occur in samarskite and similar minerals, may be considered complete to the present time.

Name.	Absorption Spectrum.	Hydrogen equivalent of Metal.[1] (Type of Oxide M_2O.)	Name.	Absorption Spectrum.	Hydrogen equivalent of Metal.[1] (Type of Oxide M_2O.)
Cerium . .	No	47·1 [2]	Samarium . .	Yes	50·0 [14]
Columbium [3] .	Yes	—	Scandium . .	No	14·7 [15]
Decipium . .	Yes	57·0 [4]	Terbium . .	No	49·5 [16]
Didymium . .	Yes	48·5 [5]	Thorium . .	No	58·4
Didymium β .	Yes	47·0 [6]	Thulium . .	Yes	56·5 [17]
Erbium . .	Yes	55·3 [7]	Ytterbium . .	No	57·9 [18]
Holmium [8] . .	Yes	54·0 [9]	Yttrium . .	No	29·7 [19]
Lanthanum . .	No	46·0 [10]	Yttrium α . .	No	52·2 [20]
Mosandrum . .	No	51·2 [11]	Yttrium β . .	Yes	49·7 [21]
Philippium [12] .	No	—	Zirconium . .	No	22·5
Rogerium [13] . .	Yes	—			

[1] As it is at present doubtful whether the oxides of several of the metals in this table belong to the type M_2O, M_2O_3, or MO, I have, for the sake of uniformity and simplicity, in calculating the values from the composition of their salts, by which these metals are chiefly discriminated, taken the type of oxide to be M_2O.

[2] 'Bührig, *J. Pr. Chem.* ser. 2, vol. xii. p. 209.

[3] 'Dr. J. Lawrence Smith, in a paper read before the United States National Academy of Sciences in 1879, announced the discovery in samarskite of two new elements, which he named Columbium and Rogerium (*Nature*, vol. xxi. p. 146). I have failed to find any further notice of these elements. This columbium must not be confounded with the well-known columbium, sometimes called tantalum.

[4] 'Delafontaine, *Comptes Rendus*, vol. lxxxvii. p. 632, vol. xciii. p. 63. *Chemical News*, vol. xxxviii. p. 223, vol. xliv. p. 67.

[5] 'Clève, *Bull. Soc. Chim.* ser. 2, vol. xxi. p. 246. Brauner, *Comptes Rendus*, vol. xciv. p. 1718; *Chemical News*, vol. xlvii. p. 175.

[6] 'Clève, *Comptes Rendus*, vol. xciv. p. 1528; *Chemical News*, vol. xiv. p. 273. Brauner, *Comptes Rendus*, vol. xciv. p. 1718; *Chemical News*, vol. xlvi. p. 16.

[7] 'Clève, *Comptes Rendus*, vol. xci. p. 381; *Chemical News*, vol. xlii. p. 199. Lecoq de Boisbaudran, *Comptes Rendus*, vol. lxxxix. p. 516; *Chemical News*, vol. xl. p. 147.

[8] 'Called by Soret, the first discoverer, *X*. Subsequently Clève discovered the same metal and called it holmium. Soret has now adopted Clève's name. *Comptes Rendus*, vol. lxxxix. p. 708, and vol. xci. p. 378; *Chemical News*, vol. xl. p. 224, and vol. xlii. p. 199. Lecoq de Boisbaudran, *Comptes Rendus*, vol. lxxxix. p. 516; *Chemical News*, vol. xl. p. 147.

[9] 'Clève, *Comptes Rendus*, vol. lxxxix. p. 478; *Chemical News*, vol. xl. p. 125.

[10] 'Brauner, *Comptes Rendus*, vol. xciv. p. 1718; *Chemical News*, vol. xlvi. p. 16.

[11] 'Lawrence Smith, *Comptes Rendus*, vol. lxxxvii. pp. 145, 146, 148. Marignac, *ibid.* vol. lxxxvii. p. 281. Delafontaine, in October 1878 (*ibid.* vol. lxxxvii. p. 600), considers mosandrum a mixture of terbium, yttrium, erbium, didymium, and philippium. Subsequently, however, Lawrence Smith, in November 1878 (*ibid.* vol. lxxxvii. p. 831), adduces chemical and other reasons to show that his mosandrum is not a mixture, but a true element. A year later, September 1, 1879 (*ibid.* vol. lxxxix. p. 480), Lawrence Smith repeats the claim for mosandrum to be classed with the elements.

41. 'Some of these claimants will certainly not stand the test of further scrutiny. Thus samarium and yttrium β are in all probability identical; and I should scarcely have included philippium, as Roscoe [1] has conclusively proved that this is a mixture of terbium and yttrium, and my own results (61) confirm those of Roscoe. Moreover, others of these so-called elements will probably turn out to be mixtures of known elements. But in the confessedly very imperfect state of our knowledge of the chemistry of these metals it is not safe for me in this research to assume that any one of them will surely not survive. The complete list as it stands will therefore be taken to contain all hitherto claimed as new, although it is almost certain to include too many.

'The Sought-for Body has no Absorption Spectrum

42. 'In the second column, p. 92, "Yes" or "No" indicates whether the solutions give an absorption spectrum when examined by transmitted light. Now, could I definitely settle whether solutions of the citron-band body gave an absorption spectrum or not, I could at once eliminate a whole class of elements.

'This was not difficult to determine. I have already said (22, 24) that spectroscopic examination entirely failed to detect didymium in many solutions of the earth which gave the citron band strongly. This was not always the case. In the early days of this research I frequently obtained absorption bands innumerable when the citron-band body was

[12] 'Delafontaine, *Comptes Rendus*, vol. lxxxvii. p. 559; *Chemical News*, xxxviii. p. 202; *Journ. Chem. Soc.* vol. xxxvi. p. 116.

[13] 'See note 3 to columbium, *ante*.

[14] 'Lecoq de Boisbaudran, *Comptes Rendus*, vol. lxxxviii. p. 322, and vol. lxxxix. p. 212; *Chemical News*, vol. xxxix. p. 115, and vol. xl. p. 99. Brauner, *Chemical News*, vol. xlvii. p. 175. Clève, *Comptes Rendus*, vol. xcvii. p. 94; *Chemical News*, vol. xlviii. p. 39.

[15] 'Nilson, *Comptes Rendus*, vol. xci. p. 118; *Chemical News*, vol. xlii. p. 83. Clève, *Comptes Rendus*, vol. lxxxix. p. 419; *Chemical News*, vol. xl. p. 159.

[16] 'Marignac, *Ann. Chim. et Phys.* ser. 5, vol. xiv. p. 247; *Journ. Chem. Soc.* vol. xxxvi. p. 113. Delafontaine, *Ann. Chim. et Phys.* ser. 5, vol. xiv. p. 238. *Journ. Chem. Soc.* vol. xxxvi. p. 114.

[17] 'Clève, *Comptes Rendus*, vol. lxxxix. p. 478, and vol. xci. p. 328; *Chemical News*, vol. xl. p. 125, and vol. xlii. p. 182. Thalen, *Comptes Rendus*, vol. xci. p. 376; *Chemical News*, vol. xlii. p. 197.

[18] 'Marignac, *Comptes Rendus*, vol. lxxxvii. p. 578; *Chemical News*, vol. xxxviii. p. 213. Nilson, *Comptes Rendus*, vol. lxxxviii. p. 642, vol. xci. p. 56; *Chemical News*, vol. xlii. p. 61.

[19] 'Clève, *Comptes Rendus*, vol. xcv. p. 1225; *Chemical News*, vol. xlvii. p. 4; *Bull. Soc. Chim.* vol. xxxix. p. 120; *Chemical News*, vol. xlvii. p. 143.

[20] 'Marignac, *Comptes Rendus*, vol. xc. p. 899; *Chemical News*, vol. xli. p. 250.

[21] 'This is almost certainly identical with Lecoq de Boisbaudran's samarium. See Marignac, *Comptes Rendus*, vol. xc. p. 899; *Chemical News*, vol. xli. p. 250; Soret, *Comptes Rendus*, vol. xci. p. 378; *Chemical News*, vol. xlii. p. 199.

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[1] *Journ. Chem. Soc.* vol. xli. p. 277.

known to be present; but as I became better acquainted with the chemical reactions of the new earth I gradually succeeded in eliminating one after the other those metals yielding absorption spectra. The earth from zircons (18, 21) gave the most satisfactory results in this respect. This, after removing the little didymium present, gave but a trace of an absorption spectrum, which from its general appearance was probably due to erbia. The earth obtained from cerite (25), which gave the citron spectrum with great brilliancy, on the other hand yielded no absorption spectrum; and generally I may say that, whenever I started with a sufficient quantity of an earth giving both citron-band spectrum and absorption spectrum, I could, by appropriate chemical means, always separate it into three portions—one which gave the citron-band spectrum with great brilliancy, and showed in concentrated solution a very faint absorption spectrum, and frequently none at all; another which gave very little citron-band spectrum, but a good absorption spectrum; and a third intermediate portion—about four-fifths of the whole—which gave both citron-band and absorption spectrum. This portion, by repetition of the treatment, could again be split up in the same way, and the operation repeated as often as the stock of the material held out.

43. 'Having definitely settled the question that the element giving the citron-band spectrum was not one of those giving an absorption spectrum, the possible elements become materially narrowed to the following list:—Cerium, lanthanum, mosandrum, scandium, terbium, thorium, ytterbium, yttrium, yttrium α, and zirconium.

'Of these the potassium sulphate reaction (36) excludes cerium, lanthanum, scandium, thorium, yttrium α, and zirconium, so there are left only the following:—

Mosandrum,	Terbium,
Ytterbium,	Yttrium

44. 'Certain chemical reactions for a long time made me dismiss yttrium from the list of likely bodies. In my analysis of zircons (18), towards the latter part of the process, I used the following process to separate the iron:—The solution, mixed with tartaric acid and excess of ammonia, was allowed to stand for some time. A small quantity of a precipitate gradually formed, which was filtered off, and it was this filtrate, after separating the iron with ammonium sulphide, that yielded the greatest quantity of substance giving the citron band. Now one of the methods of separating yttria from alumina, glucina, thoria, and zirconia, is to precipitate it as tartrate in the presence of excess of ammonia, the other earths remaining in solution. Fresenius says: "The precipitation ensues only after some time, but it is complete."

'The precipitate thus obtained with tartaric acid and ammonia should therefore contain all the yttria: *it gave no citron band whatever in the radiant matter tube*; whilst the residue, which should be

free from yttria (18), proved for a long time the only source of material wherewith to investigate the chemical properties of the body giving the citron-band spectrum.

45. 'Another reason which made me, at this stage of the research, pass over yttria was that I had already tested this earth in the radiant matter tube. In a paper on "Discontinuous Phosphorescent Spectra in High Vacua," read before the Royal Society, May 19, 1881,[1] I said, "Yttria shows a dull greenish light giving a continuous spectrum" (75).

'For these reasons I for a long time omitted yttria from my list of possible bodies, and considered that the earth, if not a new one, might turn out to be either mosandra, terbia, or ytterbia.

'Analysis of Samarskite

46. 'A large quantity (about 15 lbs. weight altogether) of samarskite was worked up, partly by the hydrofluoric-acid method of Lawrence Smith,[2] and partly by fusion with potassium bisulphate. The niobic and tantalic acids after purification were found to give no citron-band spectrum.

'These methods both gave as a result a large quantity of mixed earths containing most, if not all, of the bodies enumerated in par. 40. Tested in the radiant matter tube, this material gave the citron spectrum very brilliantly. It was dissolved in hydrochloric acid, neutralised as nearly as possible with ammonia, and boiled with sodium thiosulphate. This precipitated the thoria, zirconia, and alumina. In this precipitate some of the scandia might also be found if present in quantity, but as scandium thiosulphate is not completely precipitated, and the earth is present only in minute traces, not much scandia, it is probable, was thus carried down.

'This thiosulphate precipitate, treated in the usual way with sulphuric acid, gave no citron band in the radiant matter tube.

47. 'The filtrate from the thiosulphate was precipitated hot with excess of ammonia, and the precipitate after washing treated with sulphuric acid, dried, and heated till all fumes of sulphuric acid disappeared. The sulphate, whitish with a very pale rose tint, was finely ground, and dissolved with frequent agitation in the smallest possible quantity of cold water—an operation which required much time. The solution was then precipitated with potassium sulphate, taking all necessary precautions to keep the liquid well saturated with potassium sulphate. This operation was allowed to go on for about ten days, when the precipitated double sulphates were filtered off and slightly washed with a saturated solution of potassium sulphate. The precipitate contained cerium, lanthanum, didymium, didymium β, decipium, samarium,

[1] '*Proc. Roy. Soc.* No. 213, 1881.

[2] '*Comptes Rendus*, vol. lxxxvii. p. 146.

scandium, yttrium α, yttrium β, together with any thorium and zirconium which might have escaped the thiosulphate treatment.

48. 'The filtrate from the double sulphates was precipitated hot with ammonia, which brought down the erbia, holmia, mosandra, terbia, thulia, ytterbia, and yttria. The small quantity of manganese in solution was in this operation completely thrown out.

49. 'The insoluble double sulphates (45) were dissolved in hydrochloric acid, precipitated hot with ammonia, washed till free from potassium salts, redissolved, precipitated as oxalates, ignited, and set aside for further examination. On testing in the radiant matter tube this mixture of oxides was found to be practically free from citron band.

50. 'The ammonia precipitate from the sulphates soluble in potassium sulphate (46) was well washed till free from potassium salts, and dissolved in excess of nitric acid. The concentrated solution gave an absorption spectrum showing lines belonging to erbium and allied metals. Having already proved that the body sought was not one of those metals which gave an absorption sepctrum (42, 43), my first object was to find some method by which I could roughly separate this mixture of earths into two portions, one giving absorption bands, and the other having no action on the transmitted spectrum. This was found to be possible by taking advantage of the different solubility of the oxalates in nitric acid.

51. 'The highly acid solution of the nitrates was fractionally precipitated in the following manner:—

'To the boiling liquid a solution of ammonium oxalate was added drop by drop. The precipitate at first formed redissolved on stirring. The cautious addition of ammonium oxalate was repeated until the precipitate refused to dissolve entirely, but left the hot liquid somewhat milky. It was then rapidly cooled with constant stirring, which brought down a heavy crystalline oxalate. This was filtered off, and called oxalate A. The filtrate, again heated to boiling, was precipitated in exactly the same way with a further quantity of ammonium oxalate till the hot liquid became opalescent. On cooling and stirring a further quantity of oxalate came down. The filtrations and precipitations were repeated until no more precipitate could be obtained. Usually I could get twelve or thirteen fractionations in this manner; towards the end the solution did not get milky, and it had to stand sometimes twenty-four hours before much oxalate came down.

52. 'The fractions first precipitated by oxalic acid gave very strong absorption bands when the concentrated solutions of the oxides were examined by transmitted light. The fractions last precipitated showed the absorption bands only faintly.

53. 'These operations gave me oxalates from A to L. These, ignited, with free access of air, were then each dissolved in nitric acid,

and again separately fractionated as oxalates. The result was about 150 precipitates, ranging from A_1 A_2 . . . A_{12}, B_1 B_2 . . . B_{12}, to L_1 L_2 . . . L_{12}.

'These, after ignition, were separated into five lots according to order of colour, and the fractionation of each of the five lots repeated as already described; the series of operations now closely resembling those of Pattinson's process for desilvering lead. This gave me about sixty lots. This time the hydrogen equivalent of the metal of each lot was taken by converting the oxalate into sulphate and estimating the sulphuric acid, assuming M_2O to be the type of oxide (40, note 1). The result was a series of earths having hydrogen equivalents (M) ranging from about 48 to 33. The earths were now sorted into high, low, and intermediate, those giving intermediate H equivalents being re-fractionated with repeated H equivalent estimation, the highest and lowest being each time separated and added to the former high and low lots.

54. 'The ultimate result of about five hundred fractional precipitations gave me a mixture of earths having an H equivalent M=48, and showing a strong absorption spectrum (56); a mixture having an H equivalent M=33, having no absorption spectrum (65); and intermediate earths.

'In the radiant matter tube all these fractions gave the citron-band spectrum well, but that of the earth of lowest equivalent was much the brightest, and that of the highest equivalent the least intense.

55. 'Three methods are available for the partial separation of these earths and for the complete purification of any one of them. The formic-acid process (56, 57) is best for separating terbia, as terbic formate is difficultly soluble in water, the other formates being easily soluble.

'Fractional precipitation with oxalic acid (63, 64, 65) separates first erbia, holmia, and thulia, then terbia, and lastly yttria. This is the only method which is applicable for the separation of small quantities of terbia from yttria.

'Fusing the nitrates (60, 68, 69) separates ytterbia, erbia, holmia, and thulia from yttria. It is not so applicable when terbia is present, and is most useful in purifying the gadolinite earths. This process is the only one known for separating ytterbia from yttria.

'Selection must be made of these methods according to the mixture of earths under treatment, changing the method as one earth or the other becomes concentrated on one side or thrown out on the other. Each operation must be repeated many times before even approximate purity is attained. The operations are more analogous to the separation of members of homologous series of hydrocarbons by fractional distillation than to the separations in mineral chemistry as ordinarily adopted in the laboratory.

'Preparation of Pure Terbia

56. 'The mixture of high equivalent earths (54) richest in terbia, erbia, holmia, and thulia was treated as follows:—

'The earths were dissolved in dilute formic acid, and the solution heated for some time. A white powder of terbium formate separated. This was filtered off, the solution containing the more easily soluble formates evaporated to dryness, and ignited. In this way the M=48 earths were separated into two lots, one rich in terbia and the other rich in erbia, &c. The treatment with formic acid was again repeated on both lots, and the crude terbia finally purified as follows:—

57. 'The crude terbia from all the operations was systematically treated by the formic-acid process, keeping the liquid so dilute that only a portion of the terbium formate separated out each time. The syrupy solution of formates was treated as described further on (60). The hydrogen equivalent of the terbium was taken each time; latterly it kept pretty constant at 49·5. The terbia was also tested in the radiant matter tube. At first the citron spectrum was very strong; gradually, however, it got fainter and fainter under the repeated formic treatment, until finally the spectrum became so weak as to satisfy me that it was due only to impurity in the terbia, and that, had the material been sufficient to stand against the extravagant process of purification adopted, I should finally have got a terbia giving no citron-band spectrum. (Subsequent examination (87) showed me that this terbia did not contain more than $\frac{1}{5000}$ part of yttria.)

58. 'A concentrated solution of the purest terbia obtained in this way, when examined by the spectroscope, showed no absorption lines whatever: proving the absence of erbium, holmium, and thulium.

59. 'The hydrogen equivalent (49·5) would not definitely show the absence of ytterbium (57·9) and yttrium (29·7); but these would have been separated by the formic-acid treatment, terbium formate requiring 30 parts of water for its solution, whilst yttrium and ytterbium formates dissolve in less than their own weight of water. Moreover, it was not probable that the terbia contained an appreciable quantity of any of these earths as an impurity, for neither the oxalic acid, the fusing nitrate, nor the formic-acid process of fractionation produced any change in the atomic weight, 49·5.

'Preparation of Mixed Erbia, Holmia, and Thulia, free from other Earths

60. 'The filtrate from the terbium formate (57), rich in erbia, and containing besides terbia, holmia, thulia, and yttria, was now treated by converting it into nitrates, evaporating to dryness, and submitting the mass to careful fusion, stopping the operation when the liquid mass began to evolve nitrous fumes. The erbium, holmium, and thulium

nitrates decomposing before the yttrium nitrate, extraction with water gave an insoluble residue rich in erbia, holmia, and thulia, and a filtrate rich in yttria. The insoluble residue was dissolved in nitric acid, again evaporated to dryness, and fused. These operations were repeated eight or ten times, with the result of raising the H equivalent of the erbium metals to about 56·8, but the citron-band spectrum remained strong for some time after. It, however, ultimately disappeared. A concentrated solution of this erbium, &c., nitrate showed a beautiful and intense absorption spectrum. I did not attempt any separation of erbium, holmium, and thulium from each other, as the evidence here obtained was sufficient to show that the element giving the citron-band spectrum is not one of these three metals. Likewise I had far too little material to enable me to enter on a work of such difficulty with any prospect of success.

'Philippia

61. 'The so-called philippia was sought for in the portion of earths intermediate between the terbia and yttria (54). These were dissolved in dilute formic acid, and the solution, filtered from some terbium formate which would not dissolve, was carefully evaporated down to a small bulk, filtering off the terbium or other difficultly soluble formates as they deposited. The clear concentrated solution was then set aside over sulphuric acid to crystallise. In the course of a few days brilliant rhombic prisms crystallised out, having exactly the appearance described by Delafontaine.[1] The finest of these crystals were picked out, dried on blotting-paper, and analysed. The hydrogen equivalent was found to be M=38·2. The citron-band spectrum in the radiant matter tube was very brilliant. The solution decanted from these crystals was evaporated to a syrupy consistency, filtered from insoluble terbium formate which deposited, and treated for yttria (65).

'Some of the best rhombic crystals were added to cold water acidulated with formic acid, and gently heated, but all attempts to dissolve and recrystallise them failed. A large quantity of an insoluble formate separated, and the mother-liquor on concentration again deposited shining rhomboidal crystals. On attempting to recrystallise these, they again deposited an insoluble white powder. The mother-liquor was found to contain a large quantity of yttria, and the white insoluble formate on ignition gave an earth having the atomic weight and chemical behaviour of terbia. This entirely corroborates Professor Roscoe's conclusions,[2] that Delafontaine's philippia is nothing but a mixture of yttria and terbia.

[1] '*Comptes Rendus*, vol. lxxxvii. p. 599; *Chemical News*, vol. xxxviii. p. 202; *Journ. Chem. Soc.* vol. xxxvi. p. 116.

[2] '*Journ. Chem. Soc.* vol. xli. p. 277.

'Mosandra

62. 'The chemical characters of this earth are so little known that I could not attempt to search for it. But as the citron-band-forming earth always appeared concentrated amongst those whose double sulphates were most soluble in potassium sulphate—and, of these, amongst those having the palest colour and lowest atomic weight—it was scarcely conceivable that the earth I was in search of should ultimately prove to be one whose properties did not in any case correspond to these—one of a dark orange-yellow colour, forming a difficultly soluble double potassium sulphate, and having the very high equivalent of M=51·2: these being the properties ascribed to mosandra by the discoverer, Professor Lawrence Smith.

'Separation of Terbia and Yttria from Erbia, Holmia, and Thulia

63. 'The mother-liquors, from which as much terbium formate as possible had been separated by the process above described (56, 57), were now evaporated down with nitric acid till all the formates were decomposed, and the highly acid solutions of nitrates were fractionally precipitated with oxalic acid (51, 52, 53).

64. 'The erbium, holmium, and thulium oxalates come down first; then the terbium oxalate; lastly, the yttrium oxalate (53). After repeated fractional precipitations I at last succeeded in obtaining a mixture of yttria and terbia of a golden colour, which gave a very brilliant phosphorescent spectrum in the radiant matter tube, but showed no trace of absorption band when the concentrated solution of the nitrates was examined in the spectroscope.

'Separation of Terbia and Yttria

65. 'The crude yttria was now added to the mixture of earths (54) having a hydrogen equivalent to M=33, and the whole submitted again to fractionation with oxalic acid in a somewhat modified manner.

'An excess of strong nitric acid was added to the solution of mixed terbium and yttrium nitrates, and the solution was heated to the boiling-point. Strong oxalic-acid solution was added drop by drop till a faint permanent precipitate was produced. Strong nitric acid was now added, a drop at a time, till the solution again became clear, and the whole was allowed to cool very slowly without agitation. On cooling, an oxalate crystallised out in brilliant prisms. These contained nearly all the terbia with some of the yttria, whilst the mother-liquor contained most of the yttria with a little terbia. The filtrate was treated with more oxalic acid, a fresh crop of crystals being produced,

when the crystals were ignited, and the resulting earths re-treated with nitric acid and oxalic acid. After repeated fractionations I finally obtained in this manner a perfectly white yttria, and a terbia containing a small quantity of yttria. This terbia was added to the crude terbia from previous operations, and purified as already described (57).

'These operations gave me two earths—yttria and terbia—which, from the constancy of their H equivalents, were taken to be pure. The earths giving absorption spectra and having H equivalents other than 29·7 and 49·5 include erbia, holmia, and thulia. This portion was not further examined for the purposes of this investigation.

'Ytterbia

66. 'Before considering it finally proved that the substance forming the citron-band spectrum was yttria, it was necessary to prepare ytterbia and ascertain its behaviour in the radiant matter tube, this earth and yttria being the only remaining earths to which the citron spectrum could possibly belong.

'The two metals have hydrogen equivalents—ytterbium 57·9 and yttrium 29·7. The chemical reactions are also sufficiently different to render their separation a matter of no very great difficulty.

67. 'Gadolinite is said by Nilson to contain most ytterbia, so this mineral was chosen in preference to samarskite. The crude earths were first purified from all the earths whose sulphates are difficultly soluble in potassium sulphate (22, 25, 31 to 36), then by the formic-acid process from terbia (56, 57), and lastly by fractional precipitation with oxalic acid from the erbia earths (65). There remained an almost white yttria, which gave the citron-band spectrum very brilliantly. Now, gadolinite contains only about 0·1 per cent. of ytterbia, and about 35 per cent. of yttria; therefore the ytterbia to yttria in this mixture was somewhat in the proportion of 1 to 350, and it gave the citron-band spectrum as brilliantly as I had ever seen it. The probability was that the earth forming nearly the whole was the one giving the spectrum.

68. 'Ytterbium nitrate decomposes on fusion almost as easily as erbium nitrate (60), whilst yttrium nitrate resists decomposition much more energetically.[1] Fusion of the nitrates is also the best process for throwing out the erbia, holmia, and thulia, and is therefore the best for purifying gadolinite yttria, as this mineral is rich in the erbia earths and contains little terbia.

'The gadolinite yttria was converted into nitrate, fused for a short time, and extracted with water. The portions soluble and insoluble in water were again separately submitted to this treatment, until at

[1] 'Marignac, *Comptes Rendus*, vol. xc. p. 902.

last a colourless earth was obtained, the nitrate of which decomposed easily on fusion, and another whose nitrate resisted decomposition when exposed for a long time to nearly a red heat (70).

'The earth from the easily decomposed nitrate gave at first a faint citron-band spectrum, evidently due to impurity. On repeating the operation several times I at last succeeded in obtaining a white earth which gave only the merest trace of citron-band spectrum. Its hydrogen equivalent, 58·0, and its chemical properties showed that it was probably Marignac's ytterbia. Subsequent experiments satisfied me that this earth did not contain more than $\frac{1}{10000}$ part of yttria (84, 87). The extreme tediousness of the chemical operations necessary to obtain this high degree of purity, and the long time they require, prevented me from pushing these results beyond what was necessary to prove the special point at issue.

'Purification of Yttria

69. 'The white earth obtained in the operation described at par. 65 might still contain traces of terbia, together with erbia, holmia, and thulia. I had relied on the absence of an absorption spectrum as proving the absence of erbia, holmia, and thulia, but this test is not a very delicate one, and a final purification was therefore attempted. The decomposition of the fused nitrates was now the process relied on for this final purification, the yttrium nitrate resisting nearly a red heat without decomposition, whilst the erbium, holmium, and thulium nitrates are decomposed at a much lower temperature. The operation was carried on as described at par. 60.

'The yttrium nitrate left undecomposed, after repeated fusions, was now fused at a higher temperature, extracted with water, filtered from insoluble residue, and the operation repeated on the filtrate. After several such operations the H equivalent of the yttria was taken at every succeeding operation, and the spectral appearance in the radiant matter tube was also examined. The equivalent gradually got down to 31·0, but the spectra did not vary very much; that from the earth of lowest equivalent being, however, the most brilliant.

70. 'The yttrium nitrate, prepared from gadolinite and freed from ytterbia by the fusion of the nitrates (68), was converted into oxalate and ignited. The resulting yttria was quite white, and on testing in the radiant matter tube gave a spectrum absolutely identical with that given by the zircon (18), cerite (25), thorite and orangite (33, 34), and samarskite (64, 69) yttrias. Pure yttria was also prepared from yttrotantalite, euxenite, allanite, tyrite, and also from plaster of Paris (15) and common limestone. In no case could I detect any difference in the position or intensity of the lines shown by their phosphorescent spectra.

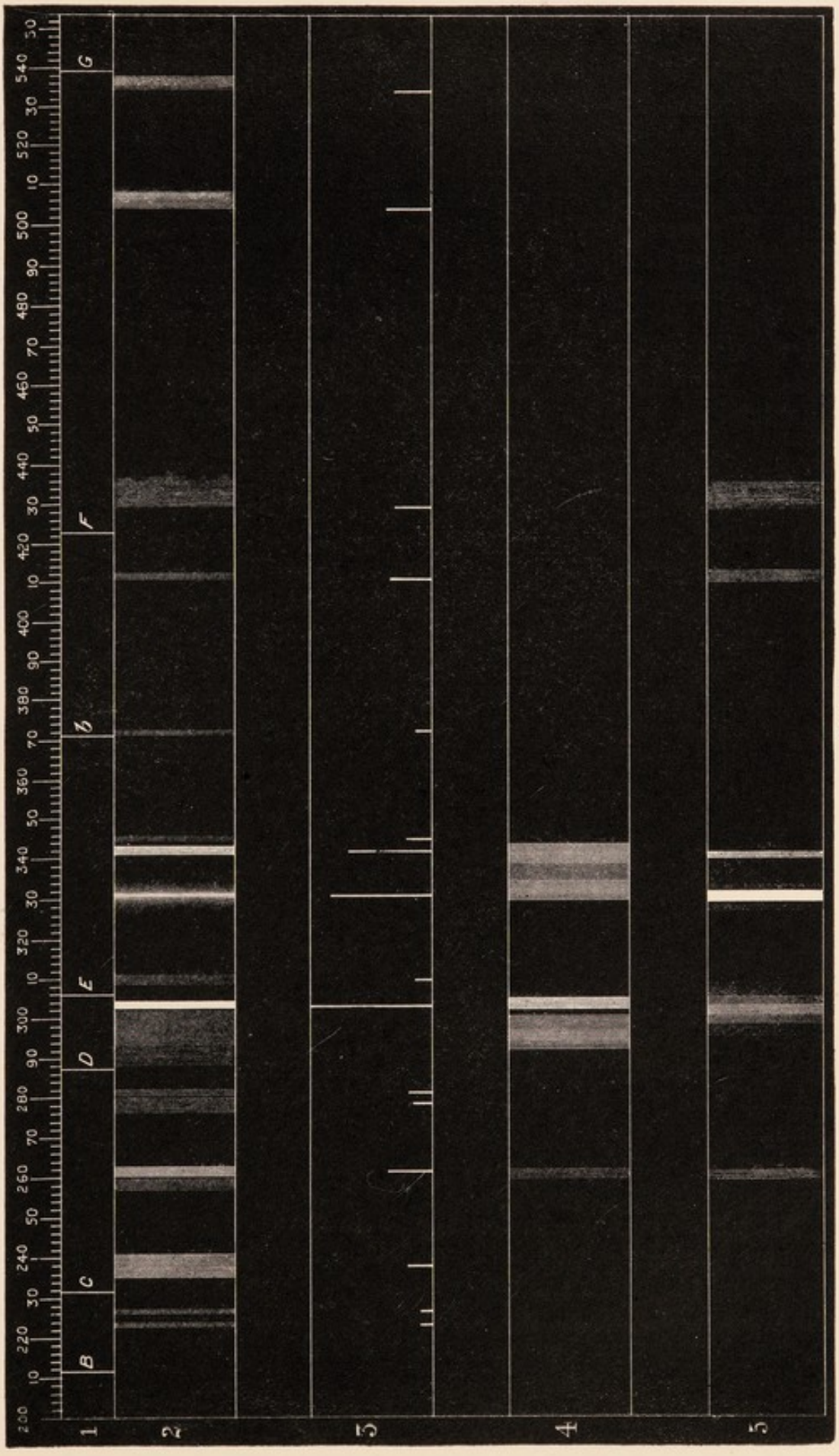


FIG. 2.

'The Phosphorescent Spectrum of Yttria

71. 'The spectrum shown by pure ignited yttrium sulphate in a radiant matter tube is one of the most beautiful objects in the whole range of spectroscopy. The lines are not so sharp as those given by spark spectra, but are more like the flame spectra of the alkaline earths. The spectrum is best seen under low dispersion and not too narrow a slit. The accompanying cut gives an accurate map of the spectrum. I have given in line No. 1 the position of the principal Frauenhofer lines for comparison of position. Line No. 2 gives the position of the bands, and No. 3 the relative intensities represented by the heights of the ordinates. The numbers along the top refer to a scale of squared oscillation frequencies, or of the squared reciprocals of wave-lengths.

72. 'Commencing at the red end, two narrow faint bands are seen at 2245 and 2275, followed by a stronger and broader red band extending between 2355 and 2415. Another faint band occurs between 2577 and 2610, followed after a very narrow black interval by a stronger reddish-orange band extending to 2627. Another faint orange band occurs at about 2800, with edges too indistinct for measurement. At about 2940 a faint yellow band appears, extending to about 3025. The strong citron-coloured band follows closely from 3028 to 3049; and a little farther on, between 3100 and 3120, a much fainter citron band is seen. Two characteristic green bands follow after a dark interval: the first, very bright, extending between 3312 and 3320, but shading off each side; the second somewhat fainter, but more sharply defined than the first, extending from 3420 to 3440; there is also a third faint green band, between 3460 and 3467. At 3730 is the centre of a narrow and faint bluish-green band; at 4110 to 4125 is a blue band; and at 4296 another blue band commences, and, extending a short distance, fades away so gradually as to render measurement of the farther side impossible. At 5052 and 5351 are two violet lines, but they are not sufficiently sharp to enable accurate measurements to be taken.

'I have carefully compared the spark spectrum given by yttrium chloride with the phosphorescent spectrum, and have not found any similarity between them, neither have I detected any discontinuity of spectrum on examining the faint light shown by yttrium compounds in Becquerel's phosphoroscope.

73. 'The above description applies to the spectrum shown either by pure yttria or by an earth tolerably rich in yttria. When traces are present the citron band only is seen. A little more yttria brings out the first and then the second green band, and finally, as the proportion of yttria increases, the red and blue bands appear (80 to 86).

'Circumstances modifying the Yttria Spectrum

74. 'In the early days of this investigation I frequently found that an earthy mixture which by one mode of treatment gave no spectrum would give a good citron band by a modification of the treatment, and I gradually found that I was most likely to get the spectrum when the body had been treated with sulphuric acid and then ignited to dull redness (4). Not knowing the circumstances governing the appearance of the citron band, it would not then have been safe to alter this mode of treatment. Now, however, having ascertained the earth to which the spectrum was due, and having a considerable quantity at my disposal, experiments were tried on other methods of treating yttria before exposing it in the radiant matter tube.

75. 'Pure yttria precipitated by ammonia from the sulphate was dried at a temperature below redness and tested. It did not phosphoresce in the slightest degree, and, necessarily, no citron-band spectrum was to be seen. The yttria was removed from the tube, converted into sulphate, heated to redness, and again tested. It now gave the citron band magnificently. This shows what apparently trivial circumstances will alter the whole course of an investigation. In 1881, when searching for discontinuous phosphorescent spectra, I tried a similar experiment with pure precipitated yttria (45), and entirely missed its citron-band spectrum. Had I first treated the yttria with sulphuric acid, instead of testing the earth itself in the radiant matter tube, the results would have been very different, and this research would probably have never been undertaken.

76. 'Yttria was now prepared by igniting the precipitated oxalate at a red heat. On testing in the radiant matter tube it phosphoresced with feeble intensity, the light being about one-twentieth of that given by the ignited sulphate under similar conditions. The citron band was almost as sharp as the sodium line, and was shifted one division towards the blue end, now occupying the position 3050 to 3060, its former place 3028 to 3049 being quite dark. The appearance is shown in line No. 4. On superposing this spectrum and that from the ignited sulphate the displacement of the citron bands was clearly observed; with a very narrow slit the two bands were seen not to touch. The two green bands were visible, but very hazy and indistinct, and only to be resolved into bands with difficulty. The yttria was now removed from the tube, ignited to a bright red heat, and re-tested. The spectrum was a little stronger than that given by the yttria ignited at a lower temperature, but in other respects the general appearance and measurements were unchanged. No alteration was caused by subsequent ignition to a white heat.

77. 'Pure yttrium sulphate ignited to a bright white heat gave a spectrum corresponding to the oxide (76); the sulphate having been decomposed by the high temperature.

78. 'Yttrium phosphate was precipitated, washed, and dried at a heat below redness, and introduced into the radiant matter tube. It phosphoresced faintly, giving the citron band hazy and faint, extending from about 3010 to 3060. The red bands were faint, and the green bands, especially the first one, were stronger than usual. The salt was now removed from the tube and heated to redness. It became of a grey colour, and now phosphoresced with a beautiful green light. The citron band was still broad and faint, but the green bands were very bright and distinct, and the red band between 2610 and 2627 was also stronger. The spectrum No. 5 shows the appearance.

'Heating the phosphate before the blowpipe made little change in the character of the phosphorescence. It was moistened with sulphuric acid, heated to a dull redness, and then tested, but no further change was produced in the spectrum. This experiment shows that the citron-band test for yttrium is far less delicate in the presence of phosphoric acid than in its absence.

'Occurrence of Yttria in Nature

79. 'It is an old and probably a true saying that every element could be detected everywhere had we sufficiently delicate tests for it. Early observations (10, 16) had prepared me for the wide distribution of the element giving the citron band, and no sooner had the exquisite sensitiveness of this spectrum test forced itself on my notice than I sought for yttrium in other minerals. Facts which I had noticed in connection with the variation of the appearance of the citron spectrum, according to the quantity of yttrium present, showed that it might be possible to devise a process for the rough quantitative estimation of yttrium, and after several experiments this was ultimately carried out in the following manner :—

'Some calcium carbonate which was found to give no citron band (12) was boiled in a quantity of nitric acid insufficient to dissolve it. The solution was filtered from the insoluble residue, diluted to a convenient bulk, and standardised : 14·91 grains of solution contained 1 grain of calcium. This operation was performed in a room in which had been no yttria compound, and the chemicals and apparatus were new, and had not been taken into the general laboratory. A portion of the standard solution was precipitated with ammonium oxalate, and the calcium oxalate ignited and treated with sulphuric acid. Tested in the radiant matter tube it gave no citron band.

'Pure yttrium sulphate was dissolved in water to such a strength that 3000 grains of solution contained 1 grain of yttrium.

80. 'The solutions were mixed together in the proportion of 1 of yttrium to 100 of calcium, evaporated to dryness, and ignited with sulphuric acid, and the residue tested in a radiant matter tube. The

spectrum was bright, the citron band, the two green bands, the blue and the red bands showed distinctly.

81. 'A mixture was now prepared in the proportion of 1 of yttrium to 500 of calcium, and tested as above. The citron band was strong, but the green bands were fainter; the blue bands were still visible.

82. 'A mixture containing 1 of yttrium to 1000 of calcium was next prepared. In the radiant matter tube the citron band was almost as strong as in the last experiment, but the edges were not so sharp, the blue bands were faint, and the green bands had disappeared.

83. 'A mixture containing 1 of yttrium to 5000 of calcium tested in the radiant matter tube showed the citron band still very bright, but hazy about the edges. No other bands were seen.

		Parts.
Pink coral (one particular specimen)	One part of yttrium in	200
Strontianite	One ,, ,,	500
Stilbite	One ,, ,,	500
Hydrodolomite, from Vesuvius	One ,, ,,	500
Witherite	One ,, ,,	1000
Aragonite	One ,, ,,	2000
Chondrodite (Humite), from Vesuvius	One ,, ,,	4000
Egyptian syenite (Cleopatra's Needle)	One ,, ,,	7000
Calcite	One ,, ,,	10,000
Natrolite	One ,, ,,	10,000
Ox bone	One ,, ,,	10,000
Meionite (Vesuvius)	One ,, ,,	10,000
Meteorite (Alfianello, Feb. 16, 1883)	One ,, ,,	100,000
Brevicite	One ,, ,,	200,000
Prehnite	One ,, ,,	500,000
Thomsonite	One ,, ,,	500,000
Vesbine, mixed with lava, from Vesuvius	One ,, ,,	700,000
Dolomite	One ,, ,,	1,000,000
Tobacco ash	One ,, ,,	1,000,000
Leucite, from Vesuvius	Less than one ,,	1,000,000
Nepheline, from Vesuvius	None	
Meteorite (Dhurmsala, 1860)	None	
Analcite	None	
Phenakite	None	
Chrysolite	None	
Haüynite	None	
Turquoise	None	

84. 'A mixture of 1 of yttrium and 10,000 of calcium was now tried. The citron band was still decided, but not at all sharp.

85. 'One of yttrium to 100,000 of calcium was next prepared and tested. The citron band was faint, but easily seen. It could not, however, be obtained at all sharp, and appeared broader than usual.

86. 'A mixture of 1 of yttrium and 1,000,000 of calcium was lastly prepared, and tested in the radiant matter tube. The citron band was very faint, but there was no mistaking its presence, and with care I have no doubt a smaller quantity than 1 in 1,000,000 could be detected. This, however, appears to be near the limit of the test.

87. 'These seven tubes were mounted on a board, so that connection with the induction coil could rapidly be made to either of them; and various minerals, &c., were prepared and tested in radiant matter tubes (10). By comparing their spectra with those of the standard tubes I could, after a little practice, determine roughly the proportion of yttrium present, supposing the test not to be interfered with by the presence of phosphoric acid (78).

88. 'In the table given on the preceding page are some of the most interesting results obtained in this way.

'Indications of other Spectrum-yielding Elements

89. 'Throughout the course of this paper I have devoted myself only to the citron-band spectrum. I do not, however, wish it to be thought that no other spectra were obtained. On the contrary, I have repeatedly seen indications of another very beautiful spectrum characterised by a strong red and a double orange band, and, more rarely, of a third spectrum distinct from the other two. These I am investigating, but not yet having obtained definite results I forbear from saying any more about them. I hope that they may bear sufficiently good fruit to be worthy of presentation at some future time to the Royal Society.'

Separation of the Yttrium Metals from Glucinum

These metals may be separated by mixing the precipitated hydrated oxides with sugar, drying, and then heating to redness in a covered crucible. The black carbonised mass is then introduced into a piece of combustion-tubing, and heated to redness, whilst a slow current of dry chlorine is passed over. The chlorides of the yttrium metals are non-volatile, whilst glucinum chloride volatilises and may be collected in any appropriate condenser.

Separation of the Yttrium Metals from those of Cerium

The yttrium metals behave the same as glucinum, in respect to sodium sulphate. The double sulphates of sodium and the yttrium metals, being readily soluble in sodium sulphate solution, may be separated from cerium, lanthanum, and didymium in the way detailed on a previous page.

SAMARIUM[1]

90. 'In the concluding sentence of the Bakerian Lecture which I had the honour to deliver before the Royal Society, May 31, 1883,

[1] Extracts from a paper read before the Royal Society, June 18, 1885, by William Crookes, F.R.S.

I said that the new method of radiant matter spectroscopy there described had given me not only spectrum indications of the presence of yttrium as an almost invariable, though very minute, constituent of a large number of minerals, but had likewise revealed signs of another spectrum-yielding element. I stated that I had repeatedly seen indications of another very beautiful spectrum characterised by a strong red and a double orange band. That this second spectrum was not then new to me is shown by a paper sent to the Royal Society in 1881,[1] in which I described a double orange band occurring in the phosphorescent spectrum of an earth less frequently met with than the "pale yellowish coloured earth" (since identified as yttria) which gave me the "red, orange, citron, and green bands."

91. 'The method adopted to bring out the orange band is to treat the substance under examination with strong sulphuric acid, drive off excess of acid by heat, and finally to raise the temperature to dull redness. It is then put into a radiant matter tube, of the form shown

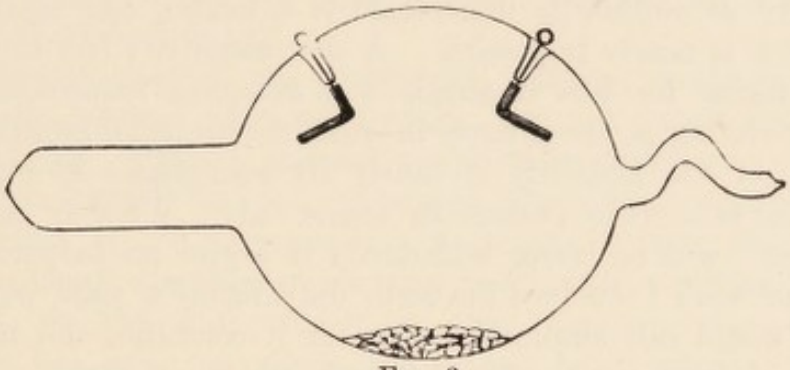


FIG. 3.

in fig. 3, and the induction spark is passed through it after the exhaustion has been pushed to the required degree. The anhydrous sulphate thus left frequently shows the orange band in the radiant matter tube, though before this treatment the original substance shows nothing.

. . . . . .

'Mixed "Citron" and "Orange" Spectra

96. 'Since the date of my last paper I have devoted myself to the task of solving the problem presented by the double orange band first observed in 1881. With the yttrium experience as a guide it might be thought this would not be a difficult task, but in truth it helped me little beyond increasing my confidence that the new, like the old spectrum, was characteristic of an element. The extreme sensitiveness of the test is a drawback rather than a help. To the inexperienced eye one part of "orange band" substance in ten thousand gives as good an indication as one part in ten, and by far the greater part of the chemical work undertaken in the hunt for the spectrum-forming element has been performed upon material which later knowledge shows does not

[1] *Proc. Roy. Soc.* vol. xxxii. (1881), p. 206.

contain sufficient to respond to any known chemical test. It is as if the element sodium were to occur in ponderable quantity only in a few rare minerals seldom seen out of the collector's cabinet. With only the yellow line to guide, and seeing the brilliancy with which an imponderable trace of sodium in a mineral declares its presence in the spectrum, I venture to think that a chemist would have about as stiff a hunt before he caught his yellow line as I had to bring my orange and citron bands to earth.

'Chemistry, except in few instances, as water-analysis and the detection of poisons, where necessity has stimulated minute research, takes little account of "traces"; and when an analysis adds up to 99·99, the odd 0·01 per cent. is conveniently put down to "impurities," "loss," or "errors of analysis." When, however, the 99·99 per cent. constitutes the impurity and this exiguous 0·01 is the precious material to be extracted, and when, moreover, its chemistry is absolutely unknown, the difficulties of the problem become enormously enhanced. Insolubility as ordinarily understood is a fiction, and separation by precipitation is nearly impossible. A new chemistry has to be slowly built up, taking for data uncertain and deceptive indications, marred by the interfering power of mass in withdrawing soluble salts from a solution, and the solubility of nearly all precipitates in water or in ammoniacal salts when present in traces only. What is here meant by "traces" will be better understood if I give an instance. After six months' work I obtained the earth didymia in a state which most chemists would call absolutely pure, for it contained not more than one part of impurity in five hundred thousand parts of didymia (131). But this one part in half a million profoundly altered the character of didymia from a radiant-matter-spectroscopic point of view, and the persistence of this very minute quantity of interfering impurity entailed another six months' extra labour to eliminate these final "traces" and to ascertain the real reaction of didymia pure and simple (131).

'For a long time the "citron-band" and the "orange-band" spectra were confounded. That they were due to two different states or kinds of matter was not easily decided, since in all the early experiments I was dealing with a mixture; consequently the spectra obtained were not only mixed but differed considerably in the relative intensities and faintness of the different lines.

97. 'At last, having separated yttria and obtained its spectrum pure (71), the characteristic lines in the other spectrum or spectra could be provisionally mapped out by difference, and a systematic hunt was instituted for the new "orange-band" substance, which, to avoid periphrasis, was termed x. Naturally my thoughts turned to samarskite and the yttria earths. A wide, prolonged survey over every available substance had convinced me that the number of bodies giving a discontinuous phosphorescent spectrum is extremely limited, and to be

counted on the fingers of one hand; and having satisfactorily mated one of these spectra to yttria it became in the highest degree probable that the twin spectrum should belong to one of the nearest chemical associates of yttria.

'Chemistry of the "Orange-band" Forming Body

98. 'At first it was necessary to take stock, as it were, of all the facts regarding x which had turned up during the search for the orange band. In the first place x is nearly as widely distributed as yttria, generally occurring with the latter earth. Sometimes, however, the orange band was strong where the citron band was absent. It is almost certainly one of the earthy metals, as it occurs in the insoluble oxalates, in the insoluble double sulphates, and in the precipitate with ammonia. It is not precipitated by sodic thiosulphate, and moreover it must be present in very minute quantities, since the ammonia precipitate is always extremely small, and as a rule x is not found in the filtrate from this precipitate.

99. 'At this stage of the inquiry the chemical reactions of x were much more puzzling than with yttria. At the outset an anomaly presented itself. The orange band was prone to vanish in a mysterious manner. Frequently an accumulation of precipitates tolerably rich in x was worked up for purposes of concentration, when the spectrum reaction suddenly disappeared, showing itself neither in precipitate nor filtrate (3, 101, 108, 115); whilst on other occasions, when following apparently the same procedure, the orange band became intensified and concentrated with no apparent loss. The behaviour of the sulphate to water was also very contradictory; on some occasions it appeared to be almost insoluble, whilst occasionally it dissolved in water readily (115).

100. 'For some time I debated whether the orange-band spectrum might not be merely a modification of the yttrium spectrum induced by the presence of some extraneous body. We know that yttria *per se* has little or no phosphorescence (75), that this power chiefly resides in the ignited sulphate. Might it not happen that some other earth with molecules peculiarly sensitive to the longer vibrations would confer upon yttria some of its sensitiveness to the red end of the spectrum?

'It would be too much like a repetition of my paper on the yttrium spectrum quest were I to detail the numerous experiments and false starts with samarskite, orangite, thorite, strontianite, cœlestine, perofskite, cerite, coral, &c.; but I may be permitted to extract from an enormous mass of chronicles which must remain unpublished some few experiments which will usefully emphasise what I may call the nodal points in this research.

'X from Samarskite

101. 'It was to be expected that samarskite would contain x. It occurred, however, very little in the yttria group, but was found with the decipia residues (47, 49) or the earths forming, with potassium, insoluble double sulphates—ceria, lanthana, didymia, decipia, samaria, together with a little thoria and zirconia. These residues were dissolved in hydrochloric acid, precipitated with ammonia, washed till free from potassic salts, redissolved, and precipitated as oxalates. The filtrate was set aside in Winchester quart bottles, and after standing for some weeks a further quantity of insoluble oxalates was found deposited at the bottom of the bottles. These were collected and appeared to be very rich in x; but on attempting to work them up vexatious anomalies constantly started up: suddenly the orange band would disappear, and after being lost sight of for a week or two, would return in a manner equally unaccountable (3, 99, 108, 115).

'Thorite and Orangite

102. 'Early in my research thorite and orangite (26) had given a brilliant spectrum, afterwards identified with that of yttria (70). When hunting for x some of the insoluble double sulphates from these minerals (32) were treated like the samarskite double sulphates to remove potassium (101), and examined in the radiant matter tube. Here also was found the orange-band spectrum, quite different from the yttrium spectrum of the soluble sulphates; but, as usual, it behaved in a most capricious manner.

'Perofskite

103. 'An American friend, Mr. George F. Kunz, with great kindness sent me some pounds weight of the rare mineral perofskite (calcic titanate), in fine crystals, from Magnet Cove, Arkansas, together with a large number of specimens of associated minerals from the same locality. The perofskite was found to be richer in x than any mineral yet examined. At great sacrifice of material a small portion of an earthy body was obtained giving the orange-band spectrum more brilliantly than I ever had seen it before. Analysis failed to detect anything in it but lime (5, 9), the flame spectrum showed lime, and the atomic weight came out RO=55·3, CaO being 56.

'Calcite

104. 'Mr. Lettsom, understanding I was engaged in quest of an unknown body supposed to be associated with calcium, most kindly sent me specimens of rare and curious minerals; and through his good offices Professor Albin Weisbach presented me with an extensive

set of calcites; these, prior to the invention of the spectroscope, had been measured by Professor A. Breithaupt, who, owing to discordant measurements, held what is known as "calcium" to consist of two or more allied elements, which as yet chemists were unable to separate.

'These calcites were treated as usual and examined most carefully in the radiant matter tube. In one of them only was a trace of yttria found, but the orange-band spectrum was very faintly seen in six of the thirteen specimens. The others shone with the usual greenish-blue phosphorescence of calcic sulphate, giving no lines or bands in the spectrum.

'I am also indebted to Mr. Lettsom for a specimen of calcite from Branchville, S. Carolina, which when heated has the curious property of glowing strongly with a golden-yellow light showing a faint continuous spectrum. In the radiant matter tube the phosphorescence was very brilliant, but there was no discontinuity in the spectrum, only a concentration of light in the red portion.

'Dolomite

105. 'Another curious mineral, for which I am also indebted to Mr. Lettsom, is a granular dolomite from Utah. When scratched with a knife or struck with a pick it emits so strong a phosphorescent red light that the miners call it "hell-fire rock." By itself in the radiant matter tube it brightly phosphoresces with a reddish light, showing no bands, but a concentration of light in the red. Treated with sulphuric acid in the usual manner, and then examined in a vacuum tube, a similar continuous spectrum is observed. Chemical analysis showed that it was a nearly pure double calcic and magnesic carbonate, with a little iron, alumina, and phosphoric acid.

'Amongst other minerals found to give the orange-band spectrum I may mention zircon, euxenite, tyrite, fergusonite, rhabdophane, cerussite, apatite, galliferous blende, argentiferous galena, anglesite, harmotome, allanite, cerite, magnesite, oolite from Bath, &c.

'Coral

106. 'In my former paper (88) I mentioned that a specimen of pink coral contained about a half per cent. of yttria, judging from the very strong yttrium spectrum it gave in the vacuum tube. Professor Martin Duncan has identified this specimen as a *Gorgonia* of the genus *Melithæa*. Another recent coral, *Mussa sinuosa*, gave equally strong indications of yttrium. By the kindness of Professor Duncan I have since been enabled to submit a large number of corals to spectrum examination in the radiant matter tube. Nearly all showed more or less discontinuity in their phosphorescent spectra, but as in the yttrium spectrum research I obtained only two specimens giving a brilliant

yttrium spectrum, so in the present quest I have found only two corals giving a strong orange-band spectrum. One is a *Pocillopora damicornis*, from Singapore and most of the Pacific Islands which have reefs, one of the old group of tabulate corals. A fragment of this coral, treated with sulphuric acid and examined in the radiant matter tube, gave as brilliant an orange-band spectrum as I had ever seen. The other is of the species *Symphyllia*, close to *Mussa*, a reef-builder from the same locality as the *Mussa* which gave so much yttria.

'Sea-water

107. 'These results induced me next to try sea-water. Ammonic oxalate and hydrate gave a white precipitate, which was filtered off and washed. The oxalate was then ignited, dissolved in nitric acid, and the solution supersaturated with ammonia and boiled. The resulting precipitate, tested in the radiant matter tube, showed the orange-band spectrum very well.

'*X* in Strontium Minerals

108. 'The orange-band spectrum in the radiant matter tube at first sight bore a close resemblance in the red region to the flame spectrum of strontium; the two spectra therefore were examined together, and on comparing them a near coincidence was observed between two lines in the orange. Was it possible that the sought-for element was strontium?

'This led to an examination of the strontic nitrate used in the flame reaction. When converted into sulphate and tested in the radiant matter tube the experiment succeeded only too well. The orange-band spectrum came out brilliantly.

'Other commercial strontium compounds were now tested. Yttria was found almost universally, but the orange band was capricious; the nitrate generally showed it well, caustic strontia sometimes, chloride as a rule not at all. These were from different makers. The source was inquired for, and in a few weeks my laboratory was filled with large specimens of Gloucestershire, Italian, and Sicilian cœlestine, and Scotch, Italian, and German strontianite, together with waste products, mother-liquors, and every commercial salt of strontium. The kindness of the manufacturers was great, and I regret that the outcome was not more notable.

'Italian cœlestine showed a good orange-band spectrum when crushed and examined in the tube without any chemical treatment. After getting the mineral into solution by fusion with sodic carbonate, &c., the x could be concentrated by fractionally precipitating with alkaline carbonates (coming down in the first fractions). The sulphate produced from this precipitate also showed the desired spectrum.

'This sulphate was digested for some time in warm ammonic

carbonate, and now the old distressing anomalies recommenced. On most occasions, when working roughly on a scale of a few grammes, all the *x* was found in the filtrate on evaporation and ignition. When, however, I took identically the same material, and worked it up more carefully, in pounds or hundredweights, it sometimes gave nothing at all, sometimes only a *ridiculus mus* on the smallest sized filter, got from a mountain of raw material. This was at first accounted for by the want of homogeneity of the mineral. The real explanation, however, was not discovered till long after (115).

'A quantitative estimation was attempted of the amount of *x* substance got from Italian cœlestine. 620 grammes gave 1·525 gramme, or 0·24 per cent. Analysis showed this to be chiefly strontic sulphate, and the atomic weight of the metal was close to that of strontium.

'Is *X* a Mixture?

109. 'For a considerable time strontium minerals and salts only were worked upon, these being considered the cheapest and most fruitful sources of *x*. A considerable quantity of material was thus accumulated, showing the desired spectrum with great brilliancy. When, however, attempts were made to separate the spectrum-forming body from the accompanying elements, as strontium, calcium, &c., all the foregoing anomalies were displayed. Ultimately two portions of substance were produced—a precipitate (113) containing the supposed new element, and a filtrate containing the strontium, calcium, and other impurities. Neither the precipitate nor filtrate tested in the usual manner showed the orange band anything like so well as the material before such separation, and indeed at this stage of the experiments it frequently vanished altogether.

'Some of the filtrate and precipitate were now mixed together, treated with sulphuric acid, and tested as before: they gave the orange-band spectrum as brightly as did the original substance. The ammonia precipitate was too small for analysis, but judging from its origin it might contain any or all of the rare earths. Chemical analysis showed nothing but a calcium salt in the filtrate.

110. 'Could it be that the union of two bodies was necessary to give this spectrum, and that calcium was one of these? Could the other constituent be of the nature of an acid such as boric, or a halogen like fluorine?

'Many experiments were tried to test this hypothesis. Pure Iceland spar was dissolved in acid, a little of the above-described precipitate added, and the mixture tested in the usual way. The orange band appeared again.

'Every conceivable mixture was now made of lime with other bodies, but whilst I frequently obtained faint indications of orange band there was never sufficient to satisfy me that I had artificially

formed the spectrum-bearing body; the traces observed were evidently due to the all-pervading presence of the sought-for body.

'So far all had been contradictory and disheartening. Analogy with the yttrium results failed to throw light to guide through the gloom. The hypothesis that the body sought was an earth, widely diffused in minute quantities only, and that its anhydrous sulphate gave a phosphorescent spectrum in the radiant matter tube, had guided me a certain distance and then led me widely astray. A new factor must now be taken into account—the presence of a calcium compound appeared to be necessary. An earthy body which, when treated and tested in the usual manner, fails to show the faintest glow of an orange-band spectrum, can by admixture with calcic sulphate be made to yield a pure and brilliant spectrum, rivalling in clearness and beauty that given by yttric sulphate.

111. 'Of the two components of the phosphorescing body—calcium and x—which is the necessary and which is the variable factor?

'This question did not appear difficult to answer. In the first case the calcium must be kept the constant, and x be made the variable quantity.

'A piece of pure colourless Iceland spar—the sulphate from which had been proved to phosphoresce normally with a greenish-blue light, without bands or concentration in any part of the spectrum (164)—was dissolved in hydrochloric acid, and mixed with about 10 per cent. of various metallic sulphates. Sulphuric acid was added, the mixture evaporated to dryness, ignited, and tested in a radiant matter tube. The bodies thus used to replace x, in addition to the more common earths, were the earths from samarskite—enumerated in the first part of this paper (40)—in as pure a state as I could get them, together with various earthy precipitates, oxalates, &c., obtained from different minerals during the preceding operations.

'These experiments resulted in an *embarras des richesses*. Whereas, hitherto, I had considered the orange-band-forming body rare and sparsely distributed, I now found it sharing with yttrium the attribute of ubiquity. The answer to my question was too full, and left me again in doubt as to whether calcium or x was the variable quantity.

'The yttrium spectrum turned up in this series of experiments about as frequently as the orange-band spectrum. I knew that in such cases yttrium was present as an impurity; might it not be that the almost universal occurrence of the orange-band spectrum was equally caused by a minute but varying quantity of x in the earths under test?

112. 'I took them one by one and submitted them to further severe chemical treatment, fractionally precipitating them, in cold dilute solution, with weak ammonia, or fractionally crystallising their oxalates from nitric acid. As the purification progressed the orange-band

spectrum generally lessened in intensity till in the case of many earths it faded out altogether, and in most of them it gave evident indications of being extraneous to the earth itself. In some instances, however, the spectrum increased in intensity; moreover, when the purified earth showed any diminution of the orange band the eliminated impurity always showed the orange band in an exalted degree. I drew from these experiments the inference that x was a definite element, as widely distributed, or nearly so, as yttrium, but requiring admixture with a calcium compound to bring out its phosphorescent properties.

113. 'Next I had to ascertain if the calcium could be replaced by any analogous body. In this case, therefore, the x was kept constant whilst the calcium was replaced. An ammonia precipitate (109) from a rich accumulation of orange-band substance was chosen as the x. Tested in the usual manner, by itself, it showed nothing, but mixed with lime it gave the orange-band spectrum very bright and pure.

'The metals used to mix with it were in the form of sulphates—strontium, barium, glucinum, zirconium, thorium, magnesium, zinc, cadmium, lead, copper, silver, cerium, lanthanum, didymium, aluminium, manganese, tin, bismuth, antimony; also silicic, titanic, tantalic, tungstic, molybdic, and niobic acids. More than half of these bodies possessed the property of conferring "orange-band" phosphorescence on the precipitate under examination, although by themselves they evinced no power of giving a phosphorescent spectrum.

'Explanation of foregoing Anomalies

114. 'In this manner the remarkable fact was established, that the x I sought was an earth which of itself could give little or no phosphorescent spectrum in the radiant matter tube, but became immediately endowed with this property by admixture with some other substance, which substance likewise by itself had no power of phosphorescing with a discontinuous spectrum.

'Of the great number of bodies used to mix with the earth x in these experiments, which acted best? It was not easy to try comparative experiments at this early stage; ultimately I came to the conclusion that lime, if not the best, was as good as any.

115. 'These results afford a full explanation of the anomalies which had so long hampered my endeavours to repeat on a large scale experiments which, when working with small quantities, had given good results (99, 101, 108). The preliminary experiments were intended to ascertain whether the desired orange band was present or not. Natural impatience led to hurried operations and defective washing of precipitates, and thus some of the necessary *lime* was left with the phosphorescing body. The subsequent larger operations were performed in a

more systematic manner with the object of securing as large a yield of substance as possible. The precipitates were thoroughly washed, the lime was more completely thrown cut, and the sought-for earth, although obtained, refused to reveal itself by the spectroscope and radiant matter tube.

'The contradictory behaviour of the sulphate to water (99) was now easily explained. The insoluble crystals, which from the brilliancy of their phosphorescent spectrum I had at first mistaken for the nearly pure sulphate of x, were merely calcic or strontic sulphate contaminated with perhaps not more than the one ten-thousandth part of x sulphate which it had carried down with them on crystallising.

'X in Cerite

116. 'In the corresponding yttrium research I was aided materially by the fact that the sought-for earth did not give an absorption spectrum (42). This enabled me to throw out a large number of obscurely known elements, and I therefore early endeavoured to ascertain whether the supposed new earth, x, did or did not give an absorption spectrum. At first I could not decide one way or the other. I frequently obtained a good orange-band spectrum when the solutions gave no trace of absorption spectrum, whilst on other occasions the solution showed good didymium and other bands. Gradually, however, it was noticed that whenever the didymium absorption bands were strong the orange-band spectrum was also particularly brilliant. Moreover, amongst the earths enumerated in par. 113 as mixed with lime in the quest for x, I have mentioned that some of them gave the orange-band spectrum with increased intensity; the earths of the cerium group were the most noteworthy, and these considerations made it probable that here would be found the location of x.

117. 'On a former occasion, when searching for the citron-band-yielding earth, and examining cerite (22 to 25), I made use of the potassic-sulphate method of separating the two great sub-groups, viz. the cerium and the yttrium earths; the former giving insoluble, and the latter soluble, double sulphates. I said (23):—

'"The precipitated double sulphates were dissolved in hydrochloric acid, and the earths precipitated as oxalates. After ignition and treatment with sulphuric acid, the mixed ceria, lanthana, and didymia were tested in the radiant matter tube, but the merest trace only of citron band was visible."

'A repetition of the above experiment produced similar results. The contents of the tube were now removed, mixed with lime and excess of sulphuric acid, ignited, and again tested in the tube. This time the orange-band spectrum came out very brilliantly, showing in a striking manner the necessity of supplementing x with some other earth to bring out its phosphorescing properties.

'The cerium group, to which x was now almost certainly traced, consists of cerium, lanthanum, didymium, samarium, and perhaps yttrium-α (136). The other metals, enumerated in par. 101 as being precipitated by potassic sulphate, were found not to phosphoresce with a discontinuous spectrum, either alone or when mixed with lime.

'Analysis of Cerite

118. 'The first necessity was to get the earths ceria, lanthana, and the mixture hitherto called didymia in a pure state, for my so-called pure earths of this group all showed the orange band in more or less degree.

'About 14 lbs. of cerite were finely ground, made into a thick paste with strong sulphuric acid, and heated to drive off excess of acid. The mass became of a white or pale grey colour. This was digested in cold water, filtered, and the residue well washed with cold water.

'To the filtrate oxalic acid was added, which precipitated all the earths, with any lime, &c., that might be present, as oxalates. It saves time at first only to aim at a partial separation of the mixed earths, and for this purpose it is well to proceed as follows:—The dried oxalates are boiled with strong nitric acid till completely decomposed, the nitrates are evaporated to dryness, mixed with three times their weight of nitre, and fused at the lowest temperature at which nitrous fumes come off; the residue is digested in water, filtered, and washed. The insoluble residue, of a pale yellow colour, consists of ceric oxide and basic ceric nitrate, with a little of the other oxides, whilst the filtrate contains the bulk of the lanthanum, didymium, and samarium.

. . . . . .

123. 'As cerite contains small quantities of the yttria earths, these must be separated from cerium, didymium, &c., by making a cold solution of the sulphates and adding finely powdered potassic sulphate in quantity more than sufficient to saturate the solution, allowing the mixture to stand (with frequent agitation) for a few days; filtering, and washing the filtrate with a saturated solution of potassic sulphate. The filtrate contains the yttria earths, and for their complete separation it is advisable to repeat the operation with potassic sulphate three or four times. The insoluble residues, consisting of a double potassic sulphate with either cerium, didymium, or other member of this group, are boiled with sodic hydrate, filtered, well washed, redissolved in nitric acid, precipitated with oxalic acid, and the oxalates ignited, leaving the earths lanthana, didymia, or samaria to be finally purified as described further on.

124. 'The ceric oxide obtained in the manner just described was white. A considerable thickness of a strong solution did not show a trace of absorption spectrum.

The atomic weight of the metal was taken and yielded

the number	= 141·1
The number given by BÜHRIG [1]	= 141·2
„ „ ROBINSON [2] . . .	= 140·2

'Many older determinations [3] range from 138 to 139.

'This ceric oxide gave no orange-band spectrum in the radiant matter tube, either with or without the addition of lime.

'Purification of Lanthana

125. 'The lanthana obtained in the manner described above was more difficult to purify than ceria. Long after the lanthana appeared pure, it gave in the radiant matter tube a good orange-band spectrum when mixed with lime and treated as usual, although without lime it gave no spectrum.

'So long as the lanthana showed the didymium absorption bands I could not be certain whether the orange-band spectrum belonged to it or to didymium, therefore the tedious process of fractionation with very weak ammonia in cold dilute solutions was repeated for some weeks. The first precipitates were lanthana containing most of the didymia, whilst the final precipitates were lanthana almost if not quite free from didymia, according to the quantity originally present. After several hundred fractional precipitations repeated over and over again a little lanthana was got which failed to show the didymium absorption bands. As the purification progressed the phosphorescent orange-band spectrum became fainter, until finally a lanthana was obtained which, mixed with lime and treated in the usual manner, gave no orange-band spectrum whatever. This lanthana was snow-white, and had an atomic weight of 138·3. MARIGNAC gives for lanthana 138·6, BRAUNER 138·28, CLÈVE 138·22.

'Purification of Didymia

126. 'The earth formerly called didymia is now known to be a mixture of didymia and samaria. The didymia which I prepared by the method described above, when mixed with lime and sulphuric acid and tested in the radiant matter tube, gave the orange-band spectrum as brightly as I had ever seen it. It was not, however, quite free from the accompanying samaria, and systematic operations were now commenced with the object of obtaining the didymia and the samaria in a state of purity—that is to say, in such a condition that one of them should show no orange-band spectrum at all, whilst the other should give the spectrum in its highest degree of intensity.

[1] '*Journ. prakt. Chem.* [2], xii. 209.

[2] '*Chemical News*, vol. l. p. 251, Nov. 8, 1884.

[3] '*Ibid.* vol. xlix. p. 282, June 27, 1884.

'I did not attempt the two purifications simultaneously on the same material. One earth only was taken in hand at a time, and by repeated fractionations and the most profuse sacrifice of material I was at last enabled to obtain a little of the desired earth quite free from admixture.

127. 'I took didymia first. About 1000 grammes of the earth, partially purified as described, were dissolved in a large excess of strong nitric acid. To the nearly boiling liquid a hot saturated solution of oxalic acid was carefully added, and constantly stirred, until the precipitate, which at first rapidly disappeared, just refused to dissolve. A drop or two of nitric acid was now added to render the solution clear, and the liquid set aside to cool, when brilliant pink-coloured prisms of didymic oxalate (containing nitric acid) crystallised out. These crystals contained nearly all the didymium and samarium, whilst the mother-liquor contained the greater part of the lanthanum, reserved for the preparation of pure lanthana (125).

'The crystals of didymic oxalate were ignited and again converted into nitrate, and the above-described partial crystallisation as oxalate repeated five or six times, in each case rejecting the mother-liquor as contaminated with lanthanum.

128. 'The final oxalates—the ultimate accumulation of the portions least soluble in nitric acid—were next converted into nitrates, and the excess of acid driven off. The anhydrous salt was dissolved in fifty times its weight of water, and fractionally precipitated by ammonia in the following manner:—A large quantity of ammonia was first prepared of the dilution (1 to 5000) used in the previous fractionation, and 500 c.c. of this were gradually added, with constant stirring, to Winchester quarts about three-fourths full of the dilute didymic nitrate. In about half an hour another 500 c.c. of ammonia were again added, and this operation was repeated at intervals till the Winchester quarts were full. The bulk of the samaria comes down in the first precipitates, which are filtered off and set aside for the preparation of pure samaria (133).

'To the filtrate, containing didymium, with a little samarium and lanthanum, ten successive quantities of about 200 c.c. each of dilute ammonia were added to each Winchester quart at intervals of about an hour, and after violent agitation allowed to subside. The clear supernatant liquid was now poured off, evaporated to about half its bulk, and then, when cold, again poured back into the precipitate, and the operation of precipitating with dilute ammonia was likewise repeated. By this means the greater portion of the samarium present was obtained in the precipitate, whilst the didymium left in solution contained a less proportion of samarium.

129. 'After a time a balance seemed to be established between the affinities at work, when the earths would appear in the same proportion in the precipitate and the solution. At this stage they were thrown down by ammonia, and the precipitated earths set aside to be worked

up by the fusion of their anhydrous nitrates so as to alter the ratio between them, when fractionation by ammonia could be again employed.

'Samaric nitrate decomposes by heat before didymic nitrate. The nitrates were mixed with four times their weight of potassic nitrate, and the whole kept fused in a crucible till about three fourths of the earthy nitrates were decomposed. The cooled mass was then dissolved in water, filtered, and the solution evaporated to dryness, and again submitted to fusion. This was repeated several times.

'The basic nitrates insoluble in water were dissolved in nitric acid, and put through the operation of fractional precipitation with ammonia for samaria (133), in the manner just described above (128).

130. 'To remove the last traces of samarium which might have survived this treatment, the solution of nitrates which had longest resisted decomposition by fusion was now mixed with excess of potassic sulphate. The precipitated double sulphates were subjected to long washing with a saturated solution of potassic sulphate, in which the samarium salt is more soluble than the didymium salt. They were then reconverted into nitrates, and the precipitation and washing with potassic sulphate repeated several times. Finally, the didymium salt was converted into oxalate, and re-crystallised many times from nitric acid, to eliminate any trace of lanthanum that might still contaminate it. Pure didymia is of a very deep chocolate-brown colour.

'These proceedings are tedious enough even in their narration, but no mere words can enable the reader to realise the wearisome character of these operations when repeated day by day, month after month, on long rows of Winchester quart bottles.

131. 'I commenced the purification of didymia in the latter part of the year 1883, and the operations have been going on since almost daily in my laboratory.[1] At intervals of some weeks the didymia in the then stage of purification was tested in the radiant matter tube, a little lime having previously been added to bring out the discontinuous phosphorescence. During the first month the intensity of the orange-band spectrum scarcely diminished. After this it began to fade, but the last traces of orange band were very stubborn, and not till the last few weeks could I obtain a didymia to show no trace of the orange-band spectrum; and this result has not been accomplished without sacrifice. My 1000 grammes have dwindled away bit by bit, till now less than half a gramme represents all my store.

132. 'Whilst in the midst of the operations of purifying didymium and samarium I had the pleasure of receiving a visit from Professor Clève, to whom we owe so much of our knowledge of the chemistry of the samarskite and cerite metals, and especially of didymium and samarium. He gave me not only most valuable information, and

[1] This was written in 1885. The experiments on the rare earths are still going on. –[W. C. Jan. 1905.]

suggestions respecting the work I was then engaged upon, but on his return to Upsala he munificently presented me with specimens of lanthana, didymia, samaria, yttria, and erbia—specimens at that time considered to represent a state of purity. According to any chemical tests these earths would be deemed absolutely pure, but the test of the phosphorescent spectrum proved too severe a trial, and the didymia, lanthana, and samaria all showed the orange band—the lanthana faintly, the didymia more strongly, and the samaria brightest of all. A subsequent lot of "samarium-free" didymia, sent by Professor Clève, also gave a strong orange-band spectrum, though the samarium present probably did not amount to more than the one hundred-thousandth part of the didymium.

'Purification of Samaria

133. 'The foregoing experiments left little doubt that x, the orange-band-forming body, was samarium; the last problem was, therefore, to get this earth in a pure state. The general plan of operations was the same as I adopted in getting didymium free from samarium, only attention was now directed to the portions richest in samarium which had been formerly set aside (128, 129). On fractionation in highly dilute solutions with very weak ammonia the first precipitates are richer in samaria than the last. These first precipitates were re-converted into nitrates, and fractionation again proceeded with.

'Fusion of the nitrates with potassic nitrate (129), or precipitation by, and washing with, potassic sulphate (130), is of no use in the final purification of samarium. When the object is to separate a little samarium from a large quantity of didymium, fusing the nitrates will effect the purpose, but I have not found the converse to hold good. The potassic sulphate method cannot separate the last traces of didymium from samarium, for the didymic double sulphate, not being quite insoluble, would wash out along with the first portions of the samaric salt. I have found no method better than fractionation with ammonia, and Professor Clève tells me that is his experience.

'Towards the end of the operations, when the samaria is getting pure, it is useful to precipitate it as a double sulphate with potassic sulphate, and wash it well for some time, to remove any traces of earths of the yttria and other groups which might have been present and become accumulated with the samaria (123).

134. 'During fractional precipitation with ammonia an experienced eye can judge roughly what is the preponderating earth present, by the appearance of the precipitate as it comes down. When much samaria is present, with but little didymia and lanthana, the precipitate forms immediately. When there is much didymia, and little samaria and lanthana, the precipitate forms as quickly as in the first case, but does not settle so rapidly. With much didymia, and a fair quantity of

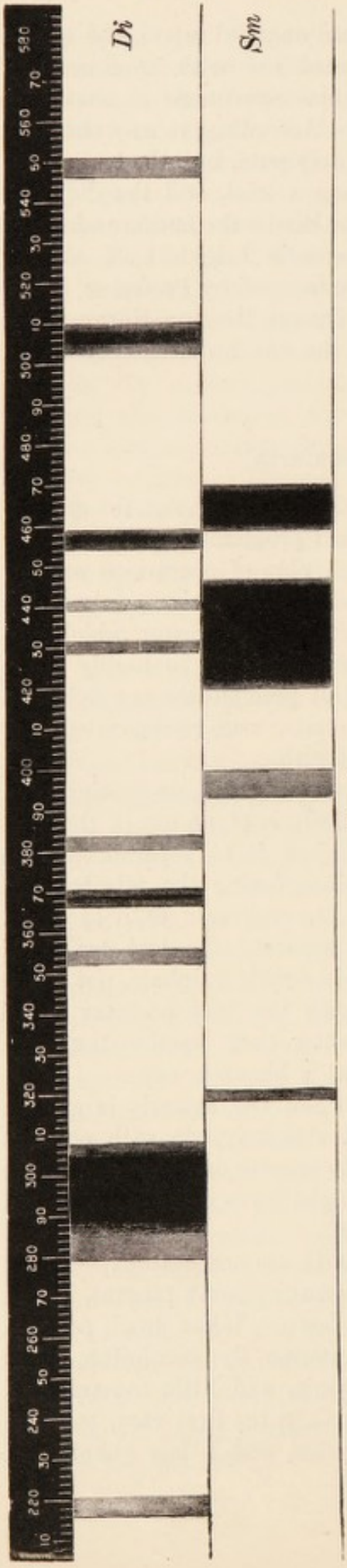


Fig. 4.

lanthana, the precipitate forms more slowly than before and settles sluggishly. When there is much lanthana and little didymia the precipitate takes a long time to settle, the liquid remaining opalescent for days. These peculiarities are due in great measure to the varying basicity of the elements, samarium being the least basic and lanthanum being the most basic, didymium occupying an intermediate position.

'In freeing samarium from the last portions of didymium the only test available to detect the presence of the latter metal is the absorption spectrum. The best plan is to provide a strong solution of the samaric nitrate in a flask, to act as a lens, and to concentrate the light of a gas-flame by its means on to the slit of a low dispersion spectroscope. Long after the light colour of the ignited oxide shows that the didymium is getting small in quantity, its absorption bands will be so strong as almost to obliterate the fainter samarium spectrum.

135. 'The fractionation should be persevered in till no didymium bands are seen in the absorption spectrum. After this point is reached I prefer to keep on fractionating for some time longer, if the material will hold out, so as to make assurance doubly sure. The colour of samaria, as pure as I have been able to prepare it, is white with the faintest possible tinge of yellow. The absorption spectrum of samarium salts is much more feeble than the spectrum of didymium salts.

'The accompanying drawing (fig. 4) shows the absorption spectra of solutions of didymic and of samaric nitrates. It will be observed that the strongest bands of the samarium

absorption spectrum are almost covered by strong absorption bands of didymium. Unless, therefore, the samarium is decidedly in excess, it will be difficult for any but a very practised observer to detect its presence. Fortunately the marvellous delicacy of the phosphorescent spectrum of samarium renders any other spectrum test of less value.

136. 'I have already mentioned (117) that the cerite earths are supposed to contain a fifth member, which has been provisionally called Yα.[1] Not much is known respecting the properties of this earth, but from the little I can glean it would appear to become concentrated with the samarium, from which a partial separation may be effected either by continuing the operation of fractional precipitation or by taking advantage of the different solubilities of their double potassic sulphates in potassic sulphate; the potassio-samaric sulphate being almost insoluble in a saturated solution of potassic sulphate, whilst the corresponding salt of Yα is soluble in 100 to 200 volumes of the same solution. By persevering in this mode of treatment I ultimately obtained a small quantity of a white earth which gave no samarium spectrum in the radiant matter tube. Whether or no it was Yα I cannot say, as the quantity obtained was insufficient to enable me to determine its atomic weight.

'The Phosphorescent Spectrum of Samarium

137. 'Pure samaric sulphate by itself gives a very feeble spectrum. Some of the pure salt was heated to redness,[2] sealed in a radiant matter tube, and carefully exhausted. The coil was adjusted so as to give a powerful spark; the room was well darkened, and the eye kept shielded from extraneous light. It was difficult to hit the exact moment of exhaustion between the disappearance of gas and non-conductivity, but by careful watching at the spectroscope a point was reached at which the phosphorescence appeared. The spectrum consists of a faint band in the red, then a sharp orange line next a wide ill-defined orange band, and finally an equally ill-defined green band.

138. 'When, however, the samaria is mixed with lime (114) before examination in the radiant matter tube, the change is very striking, and the spectrum is, if anything, more beautiful than that of yttrium. The bands are not so numerous, but the contrasts are sharper. Examined with a somewhat broad slit, and disregarding the fainter bands, which require care to bring them out, the spectrum is seen to consist of three bright bands—red, orange, and green, nearly equidistant, the orange being the brightest. With a narrower slit the orange and green bands are seen to be double, and on closer examination faint wings are

[1] Marignac, *Comptes Rendus*, vol. xc. p. 899; *Chemical News*, vol. xli. p. 250.

[2] Samaric sulphate is not decomposed at the temperature employed.

seen, like shadows to the orange and green bands. In this spectrum the sharp orange-coloured line (137) of pure samaric sulphate is absent.

139. 'The bands are best seen in a spectroscope of low dispersion, and with not too narrow a slit. In appearance they are more analogous to the absorption bands seen in solutions of didymium than to the lines

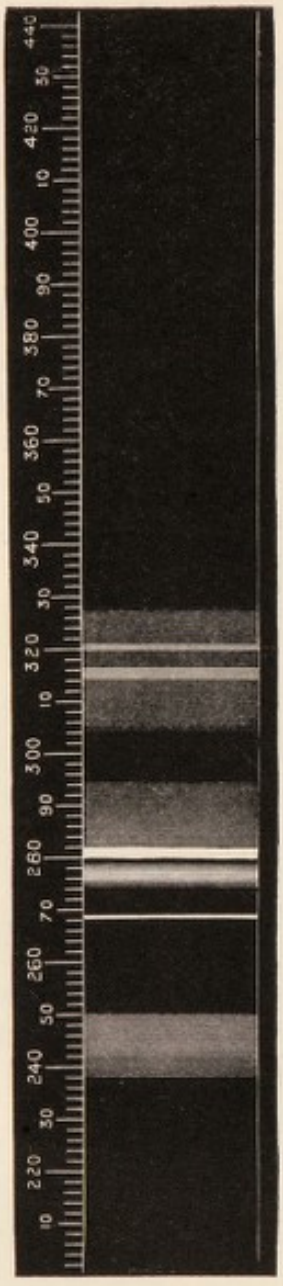


Fig. 5.

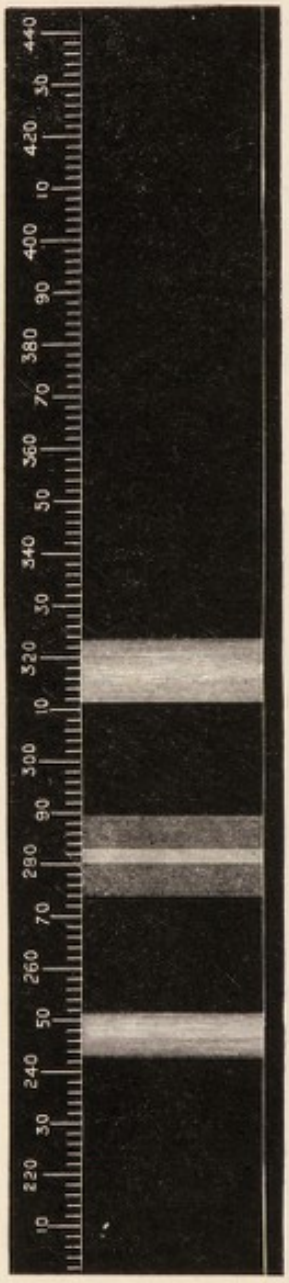


Fig. 6.

given by spark spectra. Examined with a high magnifying power all appearance of sharpness generally disappears; the scale measurements given below must therefore be looked upon as approximate only; the centre of each band may be taken as accurately determined within the unavoidable errors of experiment, but it is impossible to define their edges with much precision.

140. 'The accompanying cut (fig. 5) gives as good an idea of the

spectrum of samarium-calcium as is possible in black and white. The numbers along the top are the squared reciprocals of wave-lengths, and are on the same scale as the diagram of the yttrium spectrum (71) given in my Bakerian Lecture already quoted. The phosphorescing mixture in the tube consisted of 20 parts of pure samaria and 80 parts of lime. They were converted into nitrates in a platinum capsule, and then decomposed by excess of sulphuric acid and ignited at a dull red heat. If sulphuric acid is added in the first instance there is a difficulty in getting the earths completely converted.

'The least refrangible band seen is a very faint red, which extends from $\frac{1}{\lambda^2}$ 2310 to 2400. Here a much stronger red band begins, extending to 2494. The first component of the bright orange band begins at 2739 and ends at 2762. Between 2762 and 2798 is a dark interval, and then the second component of the orange band is seen extending from 2798 to 2818. This band is stronger and more sharply defined than the preceding band. A faint yellow wing extends from the second orange band to 2942. There is now an intensely black interval reaching to 3025; here a faint yellowish-green light is seen extending to 3149, where the green band commences and extends to 3164. Here a fainter green wing begins, and extends to 3270. On this wing a very narrow faint green band is seen, having its centre at 3190. There is then another dark space, after which three ill-defined blue and violet bands are seen, too faint to measure accurately.

141. 'Preliminary experiments (114) had shown me that lime was one of the best materials to mix with samaria in order to bring out its phosphorescent spectrum, but it was by no means the only body which would have the desired effect. More accurate observations were now taken with pure materials mixed together in definite quantities. The bodies employed were those enumerated in par. 113. Of these the following induced no phosphorescence:—zirconium, cerium, didymium, copper, silver, manganese, and tin; silicic, titanic, tungstic, molybdic, niobic, and tantalic acids.

142. 'The other substances which I tried caused the samarium to give good phosphorescence with a discontinuous spectrum. They are strontia, baryta, beryllia, thoria, magnesia, zinc oxide, cadmium oxide, lead oxide, lanthana, alumina, bismuth oxide, and antimony oxide. There is a general resemblance between these spectra, but nearly all of them differ one from another in details.

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145. 'The samarium spectra, modified by other metals as above described, may be divided into three groups. The first group comprises the spectra given when glucinum, magnesium, zinc, cadmium, lanthanum, bismuth, or antimony is mixed with the samarium. It consists simply of three coloured bands, red, orange, and green; as a typical illustration I will select the lanthanum-samarium spectrum

(fig. 6). The centres of the bands are—red 2429, orange 2808, and green 3177.

'The second type of spectrum gives a single red and orange, and a double green band. This is produced when barium, strontium, thorium or lead is mixed with samarium. The lead-samarium spectrum (fig. 7)

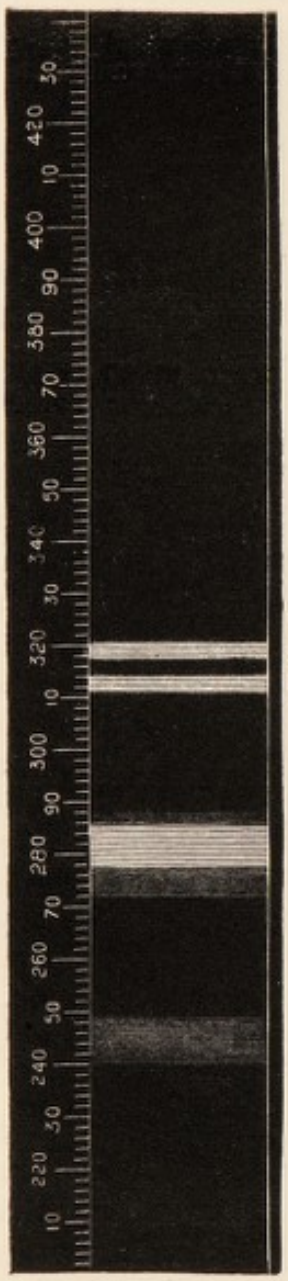


Fig. 7.

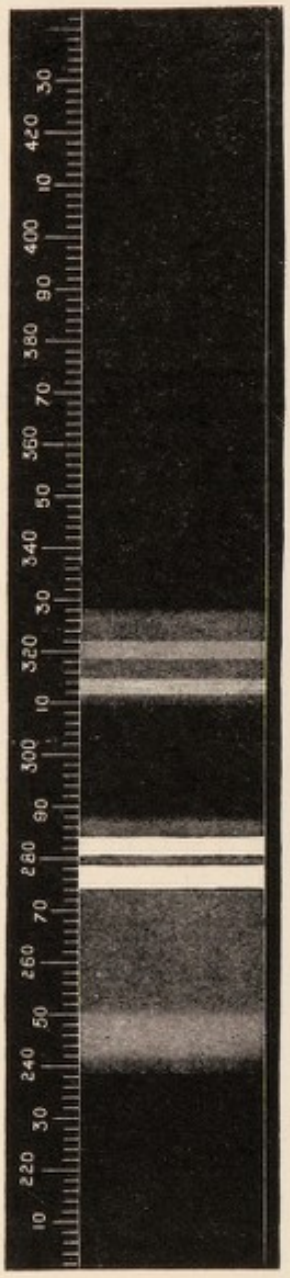


Fig. 8.

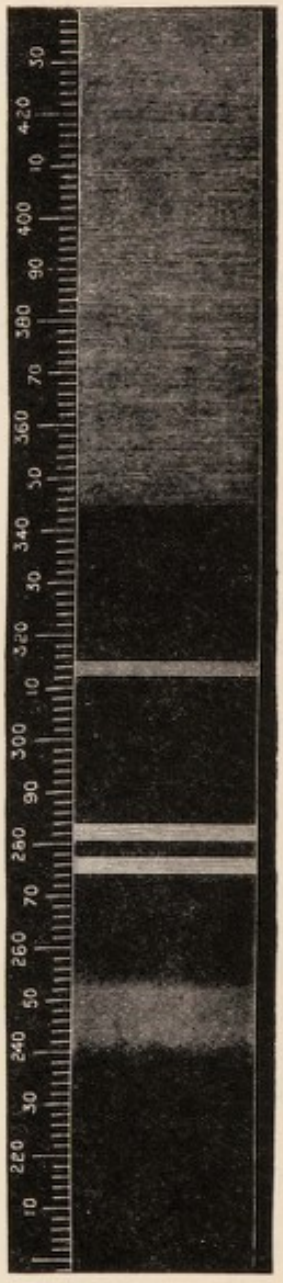


Fig. 9.

illustrates this type. The centres of the bands of this spectrum are—red 2437, orange 2830, green 3133 and 3199.

'The third kind of spectrum is given by calcium mixed with samarium. Here the red and green are single, and the orange double. Aluminium would also fall into this class were it not that the broad ill-defined green band is also doubled. The calcium-samarium spectrum, already illustrated in fig. 5 (140), is a good illustration of this type.

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156. 'The foregoing observations had prepared me for the exceeding delicacy of this spectroscopic test for samarium. I have already shown (86) that one part of yttrium can be detected spectroscopically in the presence of a million parts of calcium, and the reaction is almost as sensitive if other earths are taken instead of lime. The spectrum test for samarium is, if possible, even more delicate. Experiments were now commenced with the object of getting some approach to a

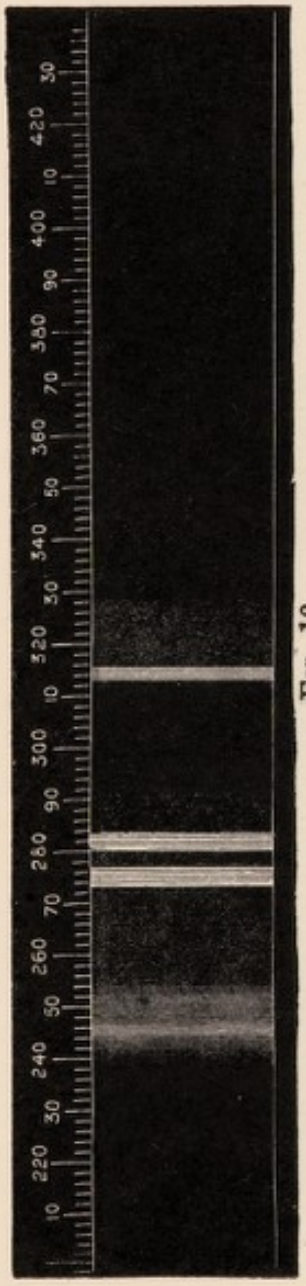


FIG. 10.



FIG. 11.

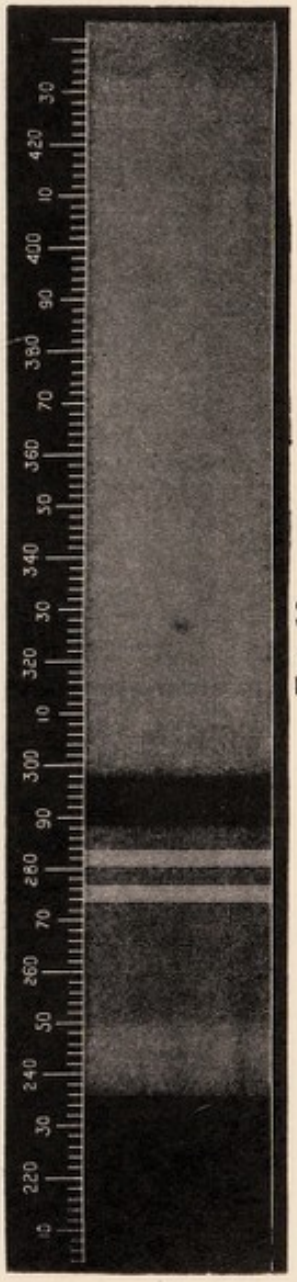


FIG. 12.

quantitative estimate of how small a quantity of samarium could be detected.

'A solution of specially purified calcic nitrate (79), which was found to contain neither yttrium nor samarium by the radiant matter test, was standardised, so that 1 part of calcium was contained in 50 parts of solution.

157. 'A standard solution of samaric nitrate was made containing 1 part of samarium in 100,000 parts of solution.

'These solutions were mixed in the proportion of 1 part samarium to 100 parts of calcium. The spectrum (fig. 8) was very brilliant, and but little inferior in sharpness to the spectrum given by a 50 per cent. mixture.

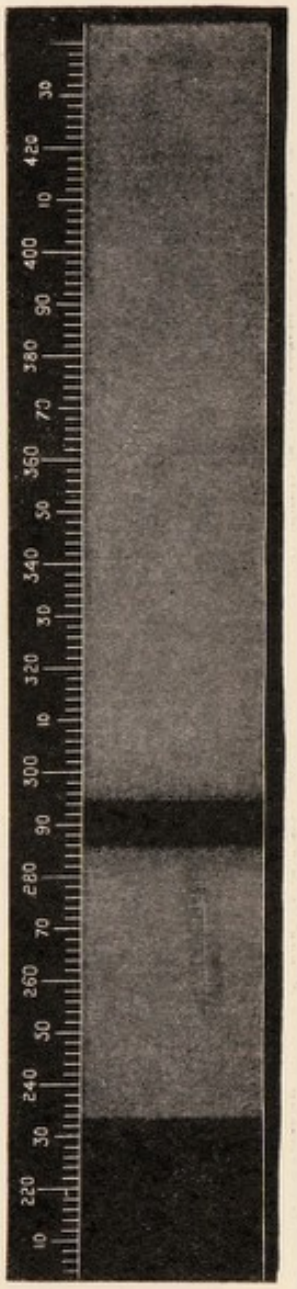


Fig. 13.

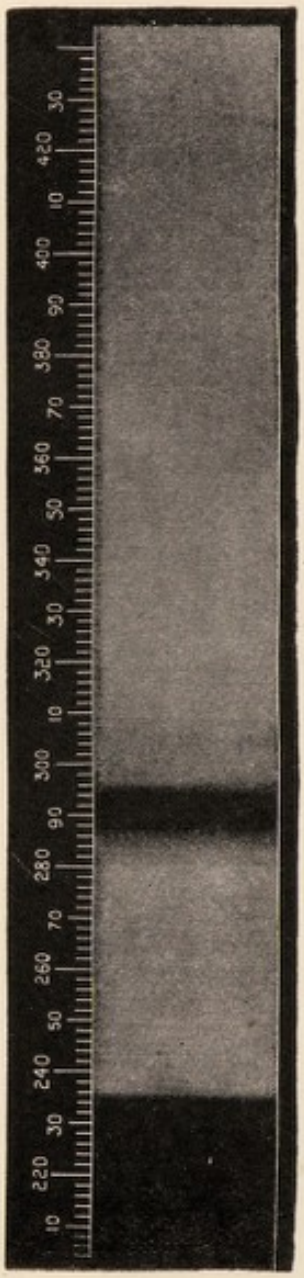


Fig. 14.

158. 'A mixture was now prepared containing 1 part of samarium to 1000 parts of calcium. Very little difference could be detected between the spectrum of this mixture and that of the last. The bands were, however, a little less sharp. Fig. 9 shows the appearance of this spectrum.

159. 'A mixture containing 1 part of samarium to 10,000 parts of calcium. The resulting spectrum is shown in fig. 10. The bands are

now getting fainter, the second green band is fading out, and the continuous spectrum of calcic sulphate is getting brighter.

160. 'The next mixture tried contained 1 part of samarium in 100,000 parts of calcium. The appearance of the spectrum is shown in fig. 11. Here the green is almost gone, being overshadowed by the continuous spectrum of calcium which has spread over it. The red band has likewise almost disappeared in the greater brightness of the continuous red of the calcic spectrum. The double orange band is still very prominent, and the black space, 2942, between it and the green is very marked.

161. 'The next mixture, 1 part of samarium to 500,000 parts of calcium, gives a spectrum which is fainter than the last, but the orange bands are still distinctly visible. The black space between the yellow and green is strongly marked, but narrower than before. Fig. 12 shows the appearance of this spectrum.

162. 'A mixture of 1 part of samarium in 1,000,000 parts of calcium was next subjected to experiment. In this the samarium spectrum is very feeble, and the orange bands are only to be seen with difficulty. Now the most striking characteristic of this spectrum is the black space which still cuts out the greater portion of the yellow. Fig. 13 represents this spectrum.

163. 'A mixture of 1 of samarium in 2,500,000 parts of calcium was now taken. In the spectrum shown by this mixture the bands of samarium have entirely gone, and its presence now is apparent only by the darkening in the yellow portion of what otherwise would be a continuous spectrum. Fig. 14 shows this appearance.

164. 'Finally the calcium spectrum by itself was examined. It is continuous, with no break, lines, or bands in it.

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167. 'In this and the former paper on Radiant Matter Spectroscopy much stress has been laid on the sensitiveness of the radiant matter test for indicating the presence of samarium and yttrium; but it might be argued, from the anomalies that arise when *both* these elements occur together, that in reality the radiant matter test, however delicate, is one not to be depended upon. For instance, it might reasonably be asked what inference is to be drawn in the case of certain minerals treated with sulphuric acid and tested in the vacuum tube, and found to give only a feeble spectrum? Does this prove the absence of all but traces of either samarium or yttrium, or does it show the presence of both these earths in considerable quantity? The answer is simple. In spite of the perplexing anomalies that have come to light, and are described in this paper, regarding the influence of these two phosphorescing earths on each other, no single instance has occurred during the work connected with this subject in which, with the experience now gained, brilliant phosphorescence and a characteristic spectrum could not be evolved from any mixture containing both or either of the earths samaria and yttria. If, after treatment with sulphuric acid

and ignition, the earthy mixture gives a pure spectrum of either yttria or samaria, and the line 2693 is absent, it is pretty safe to assume that the particular earth indicated is alone present. If, however, the spectrum is not quite characteristic, or the anomalous line 2693 is present, it is not sufficient to test the unknown mineral or mixture direct in the vacuum tube. It must first be treated chemically to separate the samaria and yttria, and lime must be added before testing in the radiant matter tube, when the spectrum immediately makes its appearance if either of these earths be present in the smallest quantity. Although I say lime is to be added, many other substances perform the same office of eliciting the spectrum, such as baryta, lead, &c.; but my chief experience has been with lime, and I have always found it to give uniform results under varied conditions.

'One important lesson taught by the many anomalies unearthed in these researches is, that inferences drawn from spectrum analysis *per se* are liable to grave doubt, unless at every step the spectroscopist goes hand in hand with the chemist. Spectroscopy may give valuable indications, but chemistry must after all be the court of final appeal.

168. 'Chemistry, however, by itself would have been helpless to solve the difficulties had it not been possible to appeal at every step to the radiant matter tube and to the spectroscope. The problems to be solved are so new as to be entirely outside the experience of laboratory work. A double orange-coloured band shows itself in a faint emission spectrum obtained under novel circumstances. On further examination the band, or one not far from it, is seen to occur in minerals of very divergent kinds and apparently irrespective of their chemical constitution or locality, as well as in laboratory reagents and chemicals of assured purity. This band is sometimes accompanied by bands in other parts of the spectrum, and occasionally shifts its place to the right or to the left. Frequently the orange band disappears and a citron-coloured band takes its place. Chemical research continued for a longer time than most chemical researches require fails to throw any light on the subject. These being the conditions of the problem, the very last explanation likely to occur to the inquirer would be that these elusive shifting bands were due to the presence of two elements almost universally distributed, and that these two elements should be yttrium and samarium—yttrium one of the rarest of known elements, and samarium, almost unknown at the time its spectrum reaction was first discerned.'

THORIUM

Preparation of Pure Thorium Nitrate

Arthur C. Neish [1] purifies crude thorium nitrate prepared from monazite in the following way:—He dissolves 200 grammes of thorium

[1] *Chemical News*, Oct. 14, 1904.

nitrate containing a small percentage of cerium, in water in thirteen beakers, each holding about 1000 cubic centimetres. To each beaker 150 cubic centimetres of hydrogen peroxide, containing about 4 per cent. hydrogen dioxide, is added (10 cubic centimetres for every 0·5 gramme thorium oxide). The solutions are heated to 85° C., and allowed to settle. The precipitates are washed by decantation, and at the end of the sixth decantation the filtrate gives no test whatever for cerium on the addition of ammonia. The precipitates are transferred to a large Büchner funnel and the washing continued, stirring the precipitate with a spatula. The precipitate is transferred to a large evaporating dish and 250 cubic centimetres of concentrated nitric acid added, which readily dissolves the precipitate when a little heat is applied. The solution is evaporated to dryness, taken up with water, diluted, and divided among the thirteen beakers so that each contains about a litre, and the thorium reprecipitated as before. The precipitate is dissolved in nitric acid, and evaporated to dryness, and dried in the air-bath for three days at 115° C. This gives thorium nitrate of the highest purity, containing no free nitric acid.

Separation of Thorium from other Earthy Metals

Professor L. Smith has discovered an exact method for separating thoria from the other earths. It consists, like the method employed for separating cerium from didymium and lanthanum, in suspending the oxides recently precipitated, in water, containing four to five times their weight of caustic potash or soda, and in passing a current of chlorine into the liquid. All the oxides are dissolved, save those of cerium and thorium, the residue being a gelatinous precipitate, like alumina.

Separation of Thorium from Cerium, Lanthanum, and Didymium

R. Chavastelon [1] pours the neutral solution of the mixed earths into an excess of hot or cold saturated solution of neutral sodium sulphite ; cerium, lanthanum, and didymium are precipitated in the form of sulphites insoluble in excess of alkaline sulphite, while practically the whole of the thoria remains in solution. The insoluble sulphites are transformed into chlorides by the addition of HCl. The hydrates are precipitated by ammonia, well washed, and then brought in contact with excess of alkaline bicarbonate, the whole being stirred by a current of carbon dioxide ; cerium peroxide alone dissolves.

A new separation of thorium from cerium, lanthanum, and didymium by metanitrobenzoic acid has been worked out by Arthur C. Neish.[2]

[1] *Comptes Rendus*, vol. cxxx. No. 12. [2] *Chemical News*, Oct., 14 1904.

The author first tried the separation of thorium from mixtures with cerium, lanthanum, and didymium, and then from mixtures of thorium with all three. The experiments showed that one precipitation would not separate thorium from an equal weight of cerium, lanthanum, or didymium, or from an equal or one-half the amount of all three. A nearly constant amount of each is carried down. A reprecipitation being necessary, many methods were tried to change the thorium metanitrobenzoate into thorium nitrate. The precipitate is readily soluble in nitric acid, but on evaporating this solution a hard insoluble skin is left, which encloses the impurities, making the second precipitation useless. The precipitate must be dissolved off the paper into the precipitation beaker with hot dilute nitric acid (1 to 5), the paper well washed with hot water, the solution in the beaker diluted and a little solution of metanitrobenzoic acid added. Methyl orange is now added until the solution becomes decidedly red, and then dilute ammonia (1 to 10) run in from a burette very slowly, with constant stirring, until the solution turns from deep red to light red or pink. The clear solution, after the addition of some ammonia, becomes opalescent, due to the reprecipitation of thorium metanitrobenzoate, and as more is added, the precipitate becomes white and flocculent, increasing with the ammonia.

When the precipitate becomes flocculent, the ammonia is added with great care, drop by drop, and the solution thoroughly stirred after every addition.

If the process of neutralisation were carried to the yellow tint, the other earths would precipitate.

The addition of ammonia is carried on until the red changes to pink; this marks the neutralisation of the mineral acid, and the weak acid (metanitrobenzoic) keeps the indicator pink. A very few drops more of ammonia would change the pink to yellow.

At this point—the pink tint—all the thorium should be precipitated, but to ensure a complete precipitation, 50 cubic centimetres more of the precipitant are added, and the beaker heated on the water-bath as before, the solution filtered, and the precipitate washed with a 5 per cent. solution of the precipitant, and either ignited and weighed or redissolved in nitric acid and the neutralisation repeated.

The behaviour of other elements towards metanitrobenzoic acid was tried, to see if their presence interfered with the separation.

Glucinum, gadolinium, yttrium, titanium, and samarium gave no precipitate, cold or hot.

Zirconium gave a white opalescence and precipitate, which increased on heating.

Erbium gave an immediate white curdy precipitate in the cold, with little change on heating; the precipitation is quantitative.

The following commoner salts were tried, although none are apt to be present in the analysis of monazite:—calcium chloride,

barium chloride, magnesium chloride, potassium-aluminium sulphate, potassium-chromium sulphate, ferrous sulphate, ferric sulphate, zinc sulphate, manganous sulphate, nickel nitrate, cobalt nitrate, bismuth nitrate, silver nitrate, lead nitrate, cadmium nitrate, copper nitrate, arsenious acid, arsenic acid, potassium-antimonyl tartrate (tartar emetic), ammonium molybdate, auric chloride, hydrochlorplatinic acid, ammonium tungstate, uranium nitrate, mercurous nitrate, mercuric nitrate, stannous chloride, and sodium stannate. With the exception of the last four, they gave no precipitate. The precipitates with mercurous and mercuric nitrates were very heavy, white and curdy in the cold, but dissolved on heating.

The composition of the precipitate was found on analysis to be $Th(C_6H_4NO_2COO)_4$.

The precipitate, when dry, presents very peculiar properties: it is snow-white, very light, and is electrified. When pressed or touched with a glass rod or a brush it acts like pith balls, being first attracted, then repelled by the rod, so that it is impossible to handle it without loss. Even the transfer of a precipitate to a platinum crucible cannot be accomplished without loss—for this reason, the precipitate is always ignited without previous drying. The thorium metanitrobenzoate is radio-active, giving, after an exposure of five days to an *X*-ray plate, a faint image; while the thorium oxide, produced from the ignition of the metanitrobenzoate, and the oxide separated from monazite sands by metanitrobenzoic acid, gave about four times the effect.

When thorium metanitrobenzoate is ignited, a large volume of gas is given off, which burns with a sooty flame, leaving, after complete ignition, thorium oxide, snow-white and in a very loose condition. This oxide, when placed in a platinum boat inside a platinum combustion tube and strongly heated with two blast-lamps, gave off white fumes, similar to those obtained by Metzger from the oxide produced by the ignition of thorium fumarate.[1] These fumes were collected in a small glass tube, but disappeared after a few minutes.

Thorium metanitrobenzoate is insoluble in water; it is easily soluble in, and prevented from precipitation by, hydrochloric, nitric, sulphuric, and acetic acids. Tartaric acid or tartrates dissolve the precipitate, from which solution the thorium cannot be precipitated either by ammonium hydroxide, potassium hydroxide, or oxalic acid. Oxalic acid dissolves the precipitate with the formation of a white crystalline precipitate of thorium oxalate. Sodium carbonate decomposes the precipitate with the production of a flocculent precipitate, soluble in excess of sodium carbonate. Potassium hydroxide decomposes it with the formation of thorium hydroxide. It is soluble in acetone; alcohol and ether have no solvent effect.

[1] *Journ. Am. Chem. Soc.* 1902, vol. xxiv. p 901.

TITANIUM

Decomposition of Titanium Minerals

In attempting to conduct the analysis of a very refractory mineral containing titanium, magnesium, chromium, &c. according to the method given by Chatard, it was found very difficult to secure complete decomposition of the mineral by the use of hydrofluoric and sulphuric acids as detailed. Repeated fusions with potassium pyrosulphate while decomposing the mineral introduced large quantities of salts, and was very tedious.

These difficulties led Mr. Jesse Jones to seek some method that would give more satisfactory results. The following was finally adopted :—2 grammes of the mineral were placed in a pressure bottle, to which was added 20 c.c. of water and 20 c.c. strong sulphuric acid. The ground-glass stopper not fitting air-tight, a small sheet of pure rubber was interposed. The bottle and contents were placed in an ordinary air-bath, and kept at 200° C. for two hours. The residue weighed 0·018 gramme and was mainly silica. On treatment with hydrofluoric acid, but 0·002 gramme of residue remained. A temperature of 200° C. was found to melt the rubber somewhat, but a longer exposure at a lower temperature gave equally good results. As the resulting solution showed a tendency to gelatinise, water was added to it, taking care not to allow it to touch the heated sides of the bottle. The refractory nature of the rock may be judged from the fact that it contained over 7 per cent. magnesia, 14 per cent. alumina, and considerable amounts of titanium and chromium. By using ammonium salts in the subsequent operations, they can be expelled by nitric acid, and potash and soda if present in the mineral can be determined.

If a pressure bottle is not at hand, one can easily be improvised. The writer found an old bromine bottle sufficiently strong.

Detection and Estimation of Titanium

(*A*) Mr. R. Apjohn proceeds as follows :—Twelve grammes of the finely powdered rock are fluxed with six times their weight of acid potassium sulphate, and the heat is continued until the greater part of the free sulphuric acid is driven off. The cooled mass is reduced to a fine powder extracted with cold water, and the aqueous solution, largely diluted, is boiled with acid sodium sulphate. As soon as the precipitation is complete, the contents of the flask are allowed to cool, and a little sulphurous acid is added to redissolve any iron or aluminium which might have been precipitated. This precipitate of titanic acid is converted into the potassium titano-fluoride in the usual manner, and the salt thus obtained is collected on a weighed filter, washed with

a few drops of cold water, dried, and weighed ; and from this weight the amount of titanic acid is deduced.

(*B*) For the detection of small quantities of titanium, especially when mixed with iron, alumina, and silica, E. Jackson adds hydrogen peroxide to the acid (hydrochloric or nitric) solution. A fine yellow or orange colour appears. Ferric chloride should not be present. An excess of hydrofluoric acid prevents the appearance of the colour unless a larger excess of hydrochloric acid is added.

Ammonium molybdate in nitric acid gives a similar colouration, but the two are readily distinguished by means of the spectroscope. The titanium solutions show no blue or green in strong solutions, only orange and red remaining, whilst with ammonium molybdate the shade of the green and some of the blue are visible.

Preparation of Pure Titanic Acid

(*A*) The following is Wöhler's plan for preparing pure titanic acid :—Fuse the rutile or titaniferous iron with an excess of potassium carbonate at a high temperature, in a fire-clay crucible. Pour the fused mass out on to a piece of sheet-iron, so as to form, on cooling, a thin cake ; next, grind this to powder, thoroughly extract with water, which leaves the greater part of the iron undissolved, and saturate the filtrate with hydrofluoric acid. A formation of potassium fluotitanate soon occurs in white scaly crystals resembling boracic acid. These may be rendered quite free from iron and silicium by a few crystallisations from hot water, and ammonia will then precipitate pure titanic acid from their hot aqueous solution.

(*B*) Another method for the preparation of pure titanic acid is to fuse the rutile or titaniferous iron with potassium carbonate, and extract the fused mass with water in the manner above described. After filtering from the insoluble portion, the liquid is slightly supersaturated with hydrochloric acid added in the cold ; it is then filtered if necessary. Acetic acid and dilute sulphuric acid are now added, and a brisk current of steam is passed in for several hours, the liquid being kept boiling all the time. Pure titanic acid will be precipitated.

(*C*) Professor Dunnington has improved Weller's method for the estimation of titanium, depending upon the production of a compound of intense yellow colour by the addition of hydrogen peroxide to the solution of titanium.

The solution of the melt obtained by fusion with acid sodium sulphate, when made with dilute sulphuric acid of 5 or more per cent., gives constant results, which tally with those made gravimetrically ; but when water only or very dilute acid is employed, one may obtain lower results. Upon one occasion a colouration was obtained which corresponded to only about one-third of the titanium which was

afterwards found to be present. Moreover, if we take a slightly acid solution of titanium sulphate, dilute it, and heat until it is partially precipitated, cool, redissolve with sulphuric acid and then add hydrogen peroxide, the yellow colouration will correspond to only a portion of the titanium present. An explanation of these facts is found in the formation of some meta-titanic acid.

It appears probable that after the fusion of titanic oxide with acid sodium sulphate, if the melt is digested in water only, the solution of the free acid may occasion sufficient heat to form some meta-titanic acid, which when redissolved by the further admixture of acid would not be coloured by the hydrogen dioxide. It is therefore concluded that in making the estimation of titanium the melt, after cooling, is to be digested in dilute sulphuric acid of such strength as will prevent the formation of a precipitate even in warm solutions of titanic sulphate; for this purpose 5 per cent. acid is found to answer.

ZIRCONIUM

Preparation of Pure Zirconia

(*A*) The zircon is first broken up in a steel diamond mortar, and next reduced to a powder in an agate mortar. It is then mixed with acid potassium fluoride, and the mixture fused. In this manner a perfect resolution of the mineral is easily obtained. The potassium fluozirconate is then dissolved out from the insoluble fluosilicate by means of hot water acidulated with hydrofluoric acid. From this solution zirconia may be precipitated by ammonia.

(*B*) In Messrs. Tessié du Motay & Co.'s patent for improvements in preparing zirconia for purposes of oxyhydrogen illumination, the following process is given. The zirconia is extracted from its native ores by transforming, by the action of chlorine, in the presence of charcoal, the zirconium silicate into the zirconium and silicium chlorides. The silicium chloride, which is more volatile than the zirconium chloride, is separated from the latter by the action of heat; the zirconium chloride remaining is afterwards converted to the state of oxide by any of the methods now used in chemistry. The zirconia thus obtained is first calcined, then moistened, and submitted in moulds to the action of a press with or without the intervention of agglutinant substances, such as borax, boracic acid, or clay. The sticks, cylinders, discs, or other forms thus agglomerated, are brought to a high temperature, and in this manner receive a kind of tempering or preparing, the effect of which is to increase their density and molecular compactness.

Of all the known earthy oxides zirconia is the only one which remains unaltered when submitted to the action of a blowpipe fed by oxygen and hydrogen. Zirconia is also, of all these earthy oxides,

that which, when introduced into an oxyhydrogen flame, develops the most intense and the most fixed light.

(*C*) E. Wedekind adopts the following method for preparing pure zirconium :—

An intimate mixture of 20 parts of zircon, 12 parts of lime, and 7 parts of carbon is heated in a carbon crucible in the electric furnace. The crucibles, which are only three-quarters full, and uncovered, are heated by means of a current of 1000 ampères and 50 volts for seven minutes. After the reaction the graphite cover is put on to prevent oxidation. After cooling, wash with cold water, then with hydrochloric acid. The carbide is then dissolved in aqua regia; filter through asbestos, and evaporate to dryness. The iron is removed from the residue, either by precipitating zirconia and iron sulphide by means of sulphide of ammonium, and then dissolving the sulphide of iron with sulphurous acid, or by precipitating the sulphide of iron with sulphide of ammonium in the presence of tartaric acid. When treated with a current of chlorine, carbide of zirconium gives the anhydrous chloride $ZrCl_4$, which dissolves in water, forming the oxychloride. This oxychloride can be obtained in a well-crystallised form by dissolving the chloride in hydrochloric acid. When heated to 100° to 110° it becomes less soluble in water.

Separation of Zirconium from Titanium

Titanic acid and zirconia, which separately may be estimated with the greatest accuracy, when together present such properties that it might be said one of these two bodies had partly destroyed the individuality of the other, since the reactions they possess when separate they no longer possess together, whilst in some cases they act quite differently. Thus, it is well known that titanic acid in the state of sulphate is completely precipitated by boiling in a diluted solution ; but that when in presence of zirconia there may be, according to the proportions of the two bodies, either incomplete precipitation or none at all. Moreover, the precipitated titanic acid always retains zirconia, although the greater part remains in solution with the rest of the titanium.

(*A*) Messrs. G. Streit and B. Franz say that when titanic acid is precipitated from a solution containing zirconia, by boiling with dilute sulphuric and acetic acids, the precipitated titanic acid is free from zirconia. The boiling should be performed by the aid of steam, and be continued for eight or ten hours. They experimented with a solution containing 4·23 grammes of titanic acid, and added thereto the sulphuric acid solution of 0·613 gramme of zirconia. To the solution was then added its own bulk of acetic acid, and the liquid boiled ; all the titanic acid was thereby precipitated, while zirconia remained in solution. From the filtrate the latter substance was precipitated by

ammonia, and, after having been collected upon a filter, washed, dried, ignited, and weighed. The quantity obtained was very near the amount required by theory.

(*B*) According to Dr. G. H. Bailey hydrogen peroxide supplies a means of separating zirconium from its associated earths. Very dilute solutions of hydrogen peroxide produce no precipitate, but with a moderately concentrated solution the precipitation is perfect. Clève has already shown that it does not throw down iron and alumina. Titanium occasions a colouration from which the formation of a higher oxide may be inferred, but there is no precipitation. From a solution containing titanium salts zirconium may, therefore, be thrown down quite free from titanium. Niobium and tantalum seem likewise to form no precipitates with hydrogen peroxide, as is also the case with tin and silicium. The above-mentioned elements are those which generally occur together with zirconium, and are difficult to separate according to the ordinary method. Hydrogen peroxide of such a strength that it yields 120 vols. oxygen throws down zirconia at once, and completely separates it from a solution of zirconium in excess of sulphuric acid.

(*C*) F. Pisani adds metallic zinc to a mixed solution of titanic acid and zirconia in sulphuric or hydrochloric acid, until the titanium is reduced to the state of titanium sesquioxide, giving the liquid a more or less intense violet colour. Titanic acid and zirconia are, under ordinary circumstances, precipitated equally by potassium sulphate; but if the titanium is previously reduced in this manner only the zirconia is precipitated. Add excess of potassium sulphate to the violet liquid, which should be small in quantity and not too acid, the zinc being still slowly attacked; leave the whole to stand for some time, then filter quickly and wash the precipitate with a solution of potassium sulphate; afterwards extract the zirconia by the usual processes. Upon dissolving this zirconia in hydrochloric acid, and adding zinc, it will be found that only a trace of titanium remains. Unfortunately, this process is not quite accurate, and cannot be used for quantitative separation.

(*D*) Titanic acid may be estimated in the presence of zirconia volumetrically. The above-described violet solution of titanium is a powerful reducing agent. On pouring potassium permanganate into this liquid, titanic acid is formed, and the solution gradually loses its colour, until it becomes of a rose tint. According to the quantity of potassium permanganate it is found necessary to add, may be calculated the quantity of titanic acid, taking for each equivalent of iron to which the permanganate corresponds one equivalent of titanic acid. The following is the mode of operating as described by Pisani, to whom this process is due :—

Titanic acid in solution in hydrochloric acid is best, because, if in the state of sulphate, it is liable to be partially precipitated by the rising of the temperature before its complete reduction has been

effected. The reduction should be effected in a flask, to which has been adapted a cork with a tube drawn out to a point, so as to keep the liquid from contact with the air. The quantity of liquid should not be great, and should be acidified until the disengagement of hydrogen becomes regular ; then heat gently to accelerate the reduction, and when the colour of the liquid ceases to increase in intensity, leave it to get quite cold, and dilute the liquid with cold water which has been previously boiled to free it from air, as it would otherwise oxidise the titanium. As soon as the liquid is diluted, decant it into a glass without taking the zinc with it, wash the flask once or twice, and then rapidly pour in the potassium permanganate. The combined weight of titanic acid and zirconia being previously known, and the titanium being estimated volumetrically, the difference gives the quantity of zirconia. The permanganate should be previously standardised by means of iron by Margueritte's process.

If potassium fluotitanate or titanic acid in hydrochloric acid to which an alkaline fluoride has been added, is reduced by zinc, the liquid is no longer violet, but greenish, probably because a titanium sesqui fluoride is then formed instead of a sesquichloride. The results of the estimation by permanganate are, however, the same in each case.

(*E*) Zirconia may be detected in titanic acid by taking advantage of its reaction on turmeric paper. A solution of zirconia in hydrochloric acid colours turmeric paper orange, especially after it has been left to dry, but titanic acid, under the same circumstances, colours it brown, which prevents zirconia from being recognised. The difficulty may be overcome by reducing the titanium by zinc, as in the state of sesquioxide titanium does not colour turmeric paper, leaving the colour of the zirconia to appear alone. The paper must not, however, be left too long to dry in the air, or the titanium, passing into the state of titanic acid, would in its turn colour the paper brown.

TANTALUM

Analysis of the Natural Tantalates containing the Yttrium Metals.—Professor J. L. Smith calls attention to the use made for their solution of concentrated hydrofluoric acid, whose action, especially upon the samarskite and euxenite of North Carolina, is as rapid and energetic as that of hydrochloric acid upon calcareous spar. If finely powdered samarskite is taken, moistened with its own weight of water, and treated with twice its weight of fuming commercial hydrofluoric acid, the attack takes place in the cold in a few seconds, the mass heats with a slight effervescence, and the decomposition is effected in from five to ten minutes. If needful, the action may be assisted by exposure to the heat of the water-bath for a few moments. The capsule is then kept at the temperature of boiling water long enough to expel the

excess of acid. The contents of the capsule are then treated with 30 to 40 grammes of water (to 5 grammes of mineral) thrown upon a filter and carefully washed, adding, if needful, one or two drops of hydrofluoric acid. The mineral is thus separated into two portions: the filtrate, containing all the metallic acids and the iron and manganese oxides, and the insoluble precipitate, containing all the earths and uranic oxide. The difficulty of the attack increases with the proportion of tantalic acid in the minerals. The most interesting constituents of samarskite are the earths. In the description already published of the North Carolina variety, the author merely arranged the earths in two classes—the yttria group and the cerium group—remarking that the latter probably did not contain cerium oxide, and that the thoria detected in the variety from the Urals was present in too small quantity to be recognised in a satisfactory manner. He has since found that the earths of the yttria group consist of about two-thirds yttria and one-third erbia.

CHAPTER IV

ZINC, CADMIUM, GALLIUM, INDIUM, ALUMINIUM, THALLIUM

ZINC

Precipitation of Metallic Zinc

When metallic magnesium, as met with in commerce, is introduced into a slightly acidulated solution of zinc sulphate (or other zinc salt), hydrogen is evolved, and a precipitation of a spongy bulky mass of metallic zinc occurs. If this sponge is washed till free from soluble salts, then dried and pressed in a steel crushing-mortar between the jaws of a powerful vice, a brilliant solid lump of zinc is produced.

Electrolytic Determination of Zinc [1]

(*A*) According to Classen,[2] zinc is separated from the solution of the zinc ammonium double salt easily and rapidly by the electrolytic method.

The reduced metal has a bluish-white colour, and adheres sufficiently well to the negative electrode, though not as finely as iron, cobalt, or nickel. For reduction we take the cold solution, pass a current equal to 5 or 6 c.c. detonating gas per minute, and ascertain the end of the decomposition with potassium ferrocyanide, applying heat. The metal deposited, which is purified by washing with water and alcohol, adheres so firmly to the capsule when dry, that it can only be dissolved with difficulty by heating with acids. There generally results a dark coating of platinum black which can be removed only by igniting the capsule, and again treating the residue with an acid. Hence it is recommended to deposit on the capsule, before weighing, a layer of copper, tin, or, by preference, of silver.

For coppering the platinum capsule we decompose a solution of copper sulphate, acidified with nitric acid, with a current of 2 to 3 c.c. detonating gas, and interrupt it after some hours. The deposit of copper is washed with water and alcohol, and the capsule is dried for a short time in the air-bath at from 90° to 100°. A coating of tin is

[1] For details of the operation see chapter on Electrolytic Analysis.

[2] Ibid.

obtained from the solution of the acid double oxalate (see Tin), and one of silver from the solution in potassium cyanide (see Silver).

(*B*) According to Von Miller and Kiliani, 4 grammes potassium oxalate and 3 grammes potassium sulphate are dissolved in water, a carefully neutralised solution of zinc sulphate or nitrate is added not containing more than 0·3 gramme zinc as a maximum, and electrolysed without heat with a current of normal density 100=0·3-0·5 ampère. The reduction is completed in two or three hours.

(*C*) Beilstein and Jawein precipitate the zinc from a solution of potassium zinc cyanide. For this purpose the liquid is mixed with soda-lye until a precipitate is formed, and potassium cyanide is added until it is redissolved. Four Bunsen elements are required for reduction. As the liquid is very strongly heated by the powerful current, the authors recommend that it should be refrigerated.

(*D*) According to Riche, zinc is deposited from an acetic solution containing an excess of ammonium acetate obtained by supersaturating with ammonia and acidulation with acetic acid.

(*E*) F. Rüdorff gives the following instructions :—To the solution containing at most 0·25 gramme zinc, there are added 20 c.c. of a 25 per cent. solution of sodium acetate and three drops of dilute acetic acid (50 per cent.). The mixture is diluted with so much water that a copper edging of from 1 to 2 cm. remains unmoistened in the coppered platinum capsule. The electrolysis is effected with a battery of 5 to 6 Meidinger elements. In order to prevent the zinc from redissolving the capsule must be cleaned as rapidly as possible. For drying the capsule the temperature of the air-bath must not exceed 60°.

Only solutions which contain the zinc as sulphate are suitable for treatment by the above-described method.

(*F*) A. Beard deposits the zinc from a solution containing sodium pyro-phosphate in excess (see Iron).

After the double salt has been formed the solution is rendered strongly alkaline with ammonium carbonate, and the decomposition is effected with a current of from 5 to 10 c.c. of detonating gas per minute.

For the complete separation of the zinc, the current is finally strengthened to from 15 to 20 c.c. detonating gas.

(*G*) G. Vortmann has made experiments on the separation of metals as amalgams. Zinc was determined as an amalgam by C. Luckow as early as 1885. Vortmann effects the separation of zinc as an amalgam either from the double ammonium oxalate or from an ammoniacal solution. In the solution of the zinc salt to be electrolysed there is dissolved a weighed quantity of mercuric chloride, and from 3 to 5 grammes ammonium oxalate. It is diluted with water and electrolysed. A current of 6 to 8 c.c. detonating gas is first passed through the liquid for some minutes, it is then reduced to one half, and is gradually raised to its original strength.

As regards the addition of mercury, care must be taken that the

proportion is 2 to 3 parts of mercury to 1 part of zinc. The amalgam obtained is washed with water, alcohol and ether, and dried in the desiccator until the weight is constant.

For separating the amalgam from an ammoniacal solution it is mixed with tartaric acid and ammonia in excess. The weight of the mercury in this case must be at least three times that of the zinc.

(*H*) In the separation of zinc from the solution of the double oxalate according to the method of Picté, the determination of the metal as an amalgam presents no practical advantages.

Zinc free from Arsenic

For the preparation of zinc free from arsenic, see Chapter VIII, under the heading ' Arsenic.'

Estimation of Zinc as Oxalate

An ingenious method of estimating zinc as well as other metals, and one which, in the author's hands, has proved very accurate, has been worked out by Mr. W. Gould Leison, of the Lawrence Scientific School. The process is as follows :—The zinc compound is obtained in the form of a sulphate, and to a neutral solution of this salt oxalic acid and then a large quantity of strong alcohol are added. Zinc oxalate precipitates in the form of an extremely fine powder. This is filtered through sand, thus : A slight funnel is ground conical near the throat. A little pear-shaped piece of glass with a long stem is then dropped into the funnel, stem upwards, so as to form a valve, impassable to sand laid upon the ball of the glass, but allowing liquids to pass freely. By means of the stem the valve can be lifted from its seat, and the sand and zinc oxalate, after washing with alcohol and careful drying, are washed together into a flask with hot dilute sulphuric acid. A few c.c. of strong sulphuric acid are then added, and the solution titrated with potassium permanganate. From the amount of oxalic acid thus found the quantity of zinc can readily be calculated.

Estimation of Zinc as Sulphide

All who have experienced the difficulty of filtering and thoroughly washing the light, slimy precipitate of zinc sulphide, as ordinarily obtained, will be glad to know of a modification of the usual mode of precipitation (due to Mr. J. H. Talbot, of the Lawrence Scientific School), whereby this difficulty is avoided. The solution of zinc, if acid, is to be neutralised as nearly as possible by sodium or ammonium carbonate. To the boiling solution, sodium or ammonium sulphide is to be added, a large excess being very carefully avoided. The white precipitate, on continued boiling, soon becomes granular, and settles

readily. The supernatant clear liquid is then to be tested with a drop of the alkaline sulphide, to be sure of complete precipitation, and the sulphide then washed with hot water. The filtrate is perfectly clear and quite free from zinc; the washing is easy and rapid. The zinc sulphide is next to be partially dried with the filter, brought into a porcelain crucible, and ignited at first gently and afterwards strongly, with free access of air. The expulsion of the last traces of sulphuric acid is much facilitated by occasionally dropping fragments of ammonium carbonate into the crucible. Pure zinc oxide finally remains, the ignition being continued until a constant weight is obtained. The results in this way are very accurate.

Estimation of Zinc in the State of Sulphide

The estimation of zinc by precipitation as sulphide and calcination of the precipitate in a current of hydrogen gives good results, but requires very careful manipulation on account of the difficulty experienced in obtaining a clear filtrate, and also on account of the long time necessary for washing. Mr. E. Murmann [1] adds to the solution a little bichloride of mercury, whereupon the finely divided sulphide of zinc is carried down with the sulphide of mercury, and deposited rapidly. The filtration and washing are also rapid; if the precipitate is not very abundant, the pores of the filter may first be filled up with a little sulphide of mercury. On calcining, the sulphide of mercury is completely volatilised.

Estimating the Value of Zinc Powder

(*A*) V. Drewsen prepares two solutions; the one of pure fused potassium bichromate—say 40 grammes per 1000 c.c.—and the other of crystalline ferrous sulphate, about 200 grammes in 1000 c.c. The iron solution must be strongly acidulated with sulphuric acid, to prevent oxidation. In order to find the respective value of the two liquids, 10 c.c. of the iron solution are measured into a beaker, a little sulphuric acid is added, and the other solution is dropped in from a burette until a drop of the mixture is no longer turned blue by potassium ferricyanide. About 1 gramme of the zinc powder is then weighed, placed in a beaker with 100 c.c. of the chromic solution, 10 c.c. of dilute sulphuric acid are added, the whole is well stirred, 10 c.c. more of the sulphuric acid are added, and allowed to act for about a quarter of an hour with vigorous stirring. When everything is dissolved except a small insoluble residue, an excess of sulphuric acid is added, and 50 c.c. of the iron solution in order to reduce the greater part of the excess of chromate; more of the iron solution is then added from a burette till a drop displays a distinct blue reaction with ferricyanide, and the mixture is then titrated back with chromate till this reaction disappears. From the total number of

[1] *Chemical News*, Feb. 2, 1900.

c.c. of the iron solution consumed the quantity is deducted which corresponds to the ferrous solution employed. The chromate contained in the remainder, if multiplied by 0·6611, shows the metallic zinc contained in the powder.

(*B*) To determine the metallic zinc present—the only valuable constituent—Fresenius mixes about 3 grammes of the powder in a flask with sulphuric acid, and passes the hydrogen gas evolved through refrigerating and desiccating tubes into a combustion-tube filled with cupric oxide. The water formed is absorbed in a U-tube two-thirds full of broken glass and containing 12 c.c. pure concentrated sulphuric acid. Nine parts of water correspond to 32·53 parts of metallic zinc.

(*C*) J. Barnes estimates the value of the zinc powder by the amount of hydrogen evolved. The hydrogen is measured by the quantity of water which it displaces. The gauge consists essentially of a narrow graduated tube placed in mercury; on the upper end of the tube a bulb is blown. The value of the graduations is determined. On exposing this bulb to the temperature and pressure at which the gas is being measured, reading off the division at which the mercury inside and outside is level, and referring to a table, a number is obtained. The observed volume of the gas is divided by this number, and the corrected volume at once obtained.

CADMIUM

Electrolytic Precipitation of Cadmium [1]

(*A*) According to Classen, cadmium may be quantitatively deposited from cadmium-ammonium oxalate or from the double potassium oxalate, the latter appearing preferable. The solution is mixed with an excess of potassium or ammonium oxalate, and the hot solution, diluted to 175 c.c., is electrolysed with a current equivalent to 0·05 c.c. of detonating gas per minute. Care must be taken that during the electrolysis no liquid is evaporated from the capsule, or water must be added from time to time, sufficient to cover the deposited metal. The precipitation of 0·2 gramme cadmium requires from four to five hours, the end of the reaction being ascertained by means of hydrogen sulphide.

(*B*) Other methods have been proposed for the determination of cadmium. Smith and Luckow recommend the separation of the metal from a solution of the chloride or sulphate, previously supersaturated with sodium acetate.

(*C*) Eliesberg, who has tested the method, finds that the reduction goes on easily on adding to the solution (about 100 c.c.) 3 grammes sodium acetate and a few drops of acetic acid, effecting the electrolysis in heat and using a current of about 0·6 c.c. of detonating gas per minute.

(*D*) In the laboratory of the Munich High School the above-

[1] For details of operation see chapter on Electrolytic Analysis.

described method is carried out by adding to the solution (previously neutralised if needful), containing as a maximum 0·5 gramme cadmium, 3 grammes sodium acetate, and acidulating slightly with acetic acid. The liquid, heated to 45°, is decomposed with a current of N.D. 100= 0·02–0·07 ampère. The metal is washed without interrupting the current, and rapidly dried at 100°.

(*E*) According to Beilstein and Garvein, the determination of cadmium is effected like that of zinc. If the solution contains free acid, it is neutralised with potash-lye, and potassium cyanide added until the liquid becomes clear. For the reduction the authors use a battery of three Bunsen elements (the strength of current not stated), and dilute the liquid to be electrolysed so that 75 c.c. may contain about 0·2 gramme cadmium. The vessel in which the precipitation is effected is refrigerated during the process.

(*F*) According to F. Rüdorff, good results are obtained by the above process by operating as follows:—To the solution, which must be as neutral as possible and which may contain up to 0·4 gramme cadmium, he adds potassium cyanide until a clear solution is obtained. He dilutes to 100 c.c. and electrolyses with a current of from three to six Meidinger elements. The metal obtained is washed with water and alcohol and dried at from 70° to 80°.

(*G*) A. Brand converts the cadmium into a pyrophosphate by means of sodium pyrophosphate and dissolves it in a large excess of ammonia. For the decomposition he uses at first for some seconds a current of from 2 to 3 c.c. detonating gas, reducing it then to 0·3 or 1 c.c. Towards the end of the reduction it is again intensified to about 5 c.c. of detonating gas.

(*H*) For determining cadmium as amalgam according to G. Vortmann we may proceed as for zinc, either using the ammoniacal solution, or the solution of the double ammonium oxalate. To one part of cadmium at least four parts of mercury are required. If the proportion of the mercury is six times that of cadmium the amalgam is so hard that it may be rubbed off with the finger without loss. If eight parts of mercury are present to one of cadmium, the amalgam is liquid.

The separation of the amalgam from the solution of the double oxalate is, on account of the slight solubility of the cadmium salt, suitable for the determination of small quantities up to about 0·3 gramme.

For separating larger quantities the liquid containing the double cadmium and mercury salt is mixed with 3 grammes tartaric acid, ammonia is added in some excess, diluted with water and electrolysed. The end of the process is ascertained by means of ammonium sulphide.

Estimation of Cadmium

A very accurate and rapid process of estimating cadmium is based upon the reaction worked out by Leison.

(*A*) Obtain the metal in the form of a strong aqueous solution as neutral as possible; add oxalic acid in excess, and then a large quantity of strong alcohol. The resulting oxalate is beautifully crystalline, and the precipitation is so complete that sulphuretted hydrogen gives a scarcely perceptible yellowish tinge in the filtrate. Wash the oxalate by Bunsen's method, and dry at 110° C., until every trace of alcohol is expelled. Then pierce the filter with a glass rod, and wash the cadmium oxalate into a flask with hot dilute hydrochloric acid. A few c.c. of strong sulphuric acid are then added, and the hot solution is titrated with potassium permanganate. The results are very accurate.

(*B*) A. Orlowski gives the following method for detecting cadmium in presence of copper in systematic qualitative analysis:—

The blue solution, after removal of bismuth hydroxide, is acidified with hydrochloric acid, mixed with sodium thiosulphate, boiled till the precipitate passes from a yellow to a dark brown (not black) and the liquid is colourless and transparent. If cadmium is present the characteristic yellow precipitate will appear on neutralising the filtrate with ammonia and adding ammonium sulphide.

Detection of Cadmium in Presence of Zinc before the Blowpipe

Professor E. J. Chapman remarks that when cadmiferous zinc ores, or furnace products derived from these, are treated in powder with sodium carbonate on charcoal, the characteristic red-brown deposit of cadmium oxide is generally formed at the commencement of the experiment. If the blowing be continued too long, however, this deposit may be altogether obscured by a thick coating of zinc oxide. When, therefore, the presence of cadmium is suspected in the assay substance, it is advisable to employ the following process for its detection. The substance, if in the metallic state, must first be gently roasted on a support of porcelain or other non-reducing body. Some of the resulting powder is then fused with borax or phosphor salt on a loop of platinum wire, and potassium bisulphate in several successive portions is added to the fused bead. The latter is then shaken off the wire into a small porcelain capsule, and heated with boiling water. A bead of alkaline sulphide is next prepared by fusing some potassium bisulphate on charcoal in a reducing flame, and removing the fused mass before it hardens. A portion of the solution in the capsule being tested with this, a yellow precipitate will be produced if cadmium be present. The precipitate can be collected by decantation or filtration, and tested with some sodium carbonate on charcoal. This latter operation is necessary, because if either antimony or arsenic were present, an orange or yellow precipitate would also be produced by the alkaline sulphide. By treatment with sodium

carbonate on charcoal, however, the true nature of the precipitate would be at once made known.

Separation of Cadmium from Zinc

Add a considerable excess of tartaric acid to the solution containing these two metals. Then add solution of caustic soda until the reaction is decidedly alkaline, and after dilution with much water keep the solution in a state of ebullition for several hours. Only the cadmium is deposited. The zinc may be separated from the filtrate by ammonium sulphide.

Electrolytic Separation of Cadmium from Zinc [1]

(*A*) The separation of these metals is founded on the same principle as the separation of copper from single metals. Eliesberg has carried out experiments on this subject and ascertained that the separation of both metals succeeds well, if the solution is constantly heated and if a current of from 0·1 to 0·15 c.c. detonating gas per minute is applied for the separation of the cadmium. The solution freed from acid is heated, with the addition of from 8 to 10 grammes potassium oxalate and from 2 to 3 grammes ammonium oxalate, diluted to 100 c.c. and electrolysed as directed. The precipitation of the cadmium is completed in six or seven hours. It is deposited on the platinum capsule, partly in a compact state and partly crystalline.

For the determination of zinc in the residual liquid, see Zinc.

(*B*) For the separation A. Yver recommends [2] mixing the solution of the acetates or sulphates with sodium acetate and a few drops of acetic acid, heating and electrolysing with two Daniell elements.

(*C*) According to Eliesberg's experiments the separation succeeds if the solution is diluted to 80 or 90 c.c. and if the strength of the current is from 0·5 to 0·6 c.c. detonating gas per minute.

(*D*) In the laboratory of the Technical High School at Munich the following conditions for this method have been ascertained. To the sulphuric solution of both metals there is added soda-lye until a permanent precipitate appears; the liquid is diluted to about 70 c.c. and the cadmium is reduced with a current of N.D100=0·07. When the bulk of the metal is precipitated the free sulphuric acid is neutralised with soda-lye, adding 3 grammes sodium acetate, when the liquid is heated to about 45° and electrolysed with a current of N.D100=0·03 ampère. The latter determination presupposes that the electromotive force of the source of current is 3·6 volts as a maximum. If greater, the tension at the electrodes is reduced to about 2·4 volts.

(*E*) E. F. Smith and Lee K. Frankel recommend for the separation

[1] For details of operation see chapter on Electrolytic Analysis.

[2] *Bull. Soc. Chim. Paris*, vol. xxxiv. p. 18.

of both metals the precipitation of cadmium from the solution of the double cyanide. If the solution is mixed with an excess of potassium cyanide so that to about 0·4 gramme of the mixed metals there may be present 4·5 grammes potassium cyanide, and the diluted liquid is electrolysed with a current of 0·3 c.c. detonating gas, the precipitation of the cadmium is completed in from eighteen to twenty-four hours. With so weak a current the zinc is not deposited until all the cyanogen is decomposed. In the liquid freed from cadmium the zinc is precipitated as given under Zinc.

GALLIUM

Detection of Gallium

To test for gallium in a blende the mineral is attacked by nitro-hydrochloric acid, excess of acid expelled by boiling, and the solution treated with pure zinc in the cold. The solution is filtered while there is still a notable evolution of hydrogen, and the filtrate boiled with zinc. The precipitate that is formed is washed, dissolved in hydrochloric acid, and the solution, as concentrated as possible, is tested spectroscopically. If necessary, the operation of boiling with zinc is repeated on the first white deposit formed.

For a blende containing the average amount of gallium, 10 grammes of the mineral are sufficient to obtain distinctly the principal lines of gallium.

Compounds of gallium—the chloride in particular—give in the spectroscope two very characteristic lines, one of which especially is sufficiently brilliant to reveal feeble traces of this element. The hydrated chloride produces in the gas flame but a very feeble and fugitive spectrum.

In order to obtain a sensitive reaction it is necessary to have recourse to the induction spark which is taken off the surface of the solution, employing a spark of 1·5 to 2 millimetres long.

The characteristic bands in wave-lengths are :—

509· . .	A nebulous band of moderate intensity, only seen with concentrated solutions of Ga_2Cl_6.
417· . .	Sharp, intense.
403·1 . .	Distinct, but much less intense than 417.

Separation of Gallium from Zirconium

The boiling solution is treated with excess of solution of potash. The precipitate of zirconia requires prolonged washings, and retains traces of gallia, which are extracted by re-solution in hydrochloric acid and reprecipitation by potash. Two or three treatments with boiling potash generally suffice. The gallium oxide is freed from potassium salts by supersaturation, first with hydrochloric acid, and

then with ammonia and prolonged boiling, or more accurately by means of cupric hydrate. Only feeble traces of zirconia pass into the alkaline solution ; these are separated from gallium by potash at the end of the analysis.

Ferrocyanide cannot be used, as it gives a canary-yellow precipitate in solutions of zirconium, even if very acid and very dilute. Ebullition even does not effect the solution of the precipitate in a liquid containing two-thirds of its bulk of concentrated hydrochloric acid. This fact is mentioned because some chemical treatises assert that potassium ferrocyanide gives a precipitate in neutral solutions of zirconium, but not in such as are acid.

Separation of Gallium from Zinc

(*A*) The hydrochloric solution, very strongly acid, is supersaturated with ammonia and boiled till it reddens litmus, the water driven off being replaced. Care must be taken that the liquid when cold does not cease to redden litmus, which will happen if traces of zinc oxide remain unattacked. If the gallium oxide retains a little zinc oxide it is redissolved by hydrochloric acid in excess, and the boiling with ammonia is repeated. Cupric hydrate separates gallium accurately from zinc. The process is conducted with the aid of heat on principles already laid down. In case of need the operation is repeated. When in addition to zinc, iron is present in the solution, it is better to reduce with metallic copper and precipitate with cuprous oxide. The separation is as exact as with cupric hydrate. The zinc being much more readily eliminated than the iron, the latter metal is the chief object of concern.

(*B*) Barium and calcium carbonates precipitate gallium oxide in the cold, but the deposits contain considerable quantities of zinc oxide, especially if barium carbonate has been used. These two reagents can only be employed when it is required to concentrate gallium into a small volume, and cannot be admitted in an exact analysis. The same observation applies to the precipitation of gallium by calcium carbonate at a boil after sulphurous reduction. There is much zinc in the deposit, however short the boiling has been, especially if the excess of calcium carbonate is considerable. The treatment with calcium carbonate in heat, after reduction with sulphurous acid, though not suitable for analysis, is very advantageous for the extraction of gallium from its ores, since by repeating the process two or three times we may eliminate almost all the zinc, the greater part of the iron and many other bodies.

Separation of Gallium from Aluminium and Chromium

The most convenient process is to precipitate the gallium with ferrocyanide from a very acid hydrochloric solution, containing at least

from a fourth to a third of its bulk of concentrated acid. When the gallium is in small proportions (less than $\frac{1}{100000}$), it must be allowed to stand one or two days for the precipitate to form. It is then received on a filter, and washed with water containing a fourth to a third of its bulk of hydrochloric acid. The filter is dried at a gentle heat and ignited. The result is a mixture of the gallium and iron oxides, which are separated as will be explained subsequently. The almost inevitable formation of a little Prussian blue in the highly acid liquid presents no inconvenience, and merely increases the proportion of ferric oxide to be afterwards separated from the gallium oxide. Ferrocyanide enables us to separate and determine gallium mixed with 2000 times its weight of aluminium or chromic oxide. Nevertheless, slight traces of gallium diffused among enormous masses of alumina or chromic oxide may escape the action of the ferrocyanide. They are then collected by entanglement in metallic sulphides (those of zinc, arsenic, or manganese) formed in alkaline or acetic solutions. Precipitation with sulphuretted hydrogen in a solution containing ammonium acetate, free acetic acid, and arsenious acid seems preferable. The galliferous arsenic sulphide, previously washed with sulphuretted hydrogen water containing a little acid ammonium acetate, is treated with aqua regia, and evaporated almost to dryness in presence of an excess of hydrochloric acid to expel nitric acid. The arsenic acid is then reduced by sulphurous acid or an alkaline sulphite, diluted with water strongly charged with hydrochloric acid, and treated with sulphuretted hydrogen. The precipitated arsenious sulphide is washed with sulphuretted hydrogen water containing hydrochloric acid. The gallium remains in the liquid, and is separated by concentration to a small bulk and boiling, after supersaturation with ammonia.

Separation of Gallium from Cadmium

(*A*) This separation is effected only in an approximate manner by means of sulphuretted hydrogen. The difficulty is that in presence of a decided excess of hydrochloric acid the cadmium is not entirely precipitated, while if the solution is scarcely acid a portion of the gallium remains in the cadmium sulphide. Nevertheless, good results may be obtained by a succession of operations, each of which yields a decreasing quantity of cadmium sulphide free from gallium. For this purpose a decidedly acid solution is treated with sulphuretted hydrogen, the precipitate is redissolved in hydrochloric acid, diluted with water, and again treated with sulphuretted hydrogen. This reaction, if repeated once or twice, enables us soon to collect the greater part of the cadmium as a sulphide free from gallium. The liquids which hold in solution all the gallium, along with a little cadmium, are concentrated to expel the large excess of acid, diluted with water, and saturated with sulphuretted hydrogen. The new deposit of cadmium sulphide

obtained is dissolved and reprecipitated once or twice to free it from gallium. The repetition of this treatment frees the gallium chloride from every sensible trace of cadmium.

An excess of boiling potash precipitates cadmium oxide and dissolves gallium oxide, of which a small quantity remains in the cadmium oxide. It is therefore redissolved in hydrochloric acid and separated again by means of potash. When the cadmium is in a somewhat large proportion, four or five treatments are needful to extract all the gallium. The alkaline liquids contain merely feeble traces of cadmium ; to separate these the liquid is supersaturated with a very slight excess of hydrochloric acid, and the gallium is removed by means of cupric hydrate. The filtered solution is mixed with a little ammonium acetate, and saturated with sulphuretted hydrogen, which precipitates copper and cadmium sulphides. These are taken up in aqua regia, evaporated with an excess of hydrochloric acid to destroy the nitric acid, and this very acid solution is then treated with sulphuretted hydrogen. The copper is thus eliminated, and we have merely to concentrate in order to obtain cadmium chloride.

The following methods of procedure are more expeditious :—

(*B*) A prolonged boiling after supersaturation with ammonia precipitates gallium and leaves cadmium dissolved, but the original liquid should be very acid in order to form a sufficient quantity of ammonium chloride. The gallium oxide thus obtained retains very slight traces of cadmium, which are eliminated by a second similar treatment.

(*C*) The separation can be effected well with potassium ferrocyanide, provided that the liquid contains about one-third of its volume of concentrated hydrochloric acid, which holds the cadmium ferrocyanide in solution.

(*D*) Cupric hydrate, with the aid of heat, precipitates gallium containing scarcely a trace of cadmium, which a second operation entirely removes. This is an excellent process.

(*E*) If it is required to remove iron at the same time as cadmium, the slightly acid liquid is reduced in heat by metallic copper, and is then mixed with a slight excess of cuprous oxide. The gallium oxide collected contains traces of cadmium which disappear on a repetition of the same treatment. The reaction of cupric hydrate and of metallic copper with cuprous oxide are the most to be recommended.

INDIUM

Separation of Indium from Commercial Zinc

Zinc from the Freiburg mines contains, besides a small quantity of lead, iron, arsenic, and cadmium, 0·0448 per cent. of indium. To separate the indium the zinc is dissolved in dilute sulphuric or hydrochloric acid, and boiled until the evolution of gas ceases. The metallic

precipitate left, when the precaution is taken to leave a little zinc undissolved, contains all the indium, together with the lead, &c. In the case of a solution containing indium—such as zinc chloride—the separation may be effected by means of sodium acetate, indium having the property, like iron, of forming an insoluble basic salt. A little dilute sulphuric acid is first added to the solution containing indium, and sodium carbonate is next added until, after stirring, a slight cloudiness remains; sodium acetate is then added, and the mixture is boiled. In this way a basic indium sulphate, containing a little iron and zinc, is precipitated. It is best to wash the precipitate by decantation, as the gelatinous precipitate rapidly clogs up the pores of filtering-paper.

From a hydrochloric or nitric solution of indium the separation may be effected by barium carbonate, which perfectly precipitates the oxide in the cold. The precipitate usually contains some iron, but no zinc.

Separation of Indium from Blende

Roast the indiferous blende and boil in dilute sulphuric acid; filter, nearly neutralise with sodium carbonate, and then put clean plates of zinc into the solution. Scrape the reduced metals from time to time from the zinc, and preserve the precipitates separately. The purification of the indium is then easier, in consequence of this fractional precipitation.

Purification of Indium

To obtain the indium pure, the precipitate containing it is dissolved in nitric acid. Most of the lead is first removed by means of sulphuric acid; sulphuretted hydrogen is then passed through the liquor until the remainder of the lead, with the arsenic, cadmium, &c., is precipitated. The excess of sulphuretted hydrogen is then got rid of by boiling, and the liquor is next oxidised by means of potassium chlorate and precipitated by excess of ammonia. In this way a good deal of the zinc present passes into solution; a small quantity, however, remains with the precipitated iron and indium oxides. The precipitate is now dissolved in dilute acetic acid, and again precipitated by sulphuretted hydrogen. A little zinc and iron still go down with the indium, and will after six precipitations; so, for the perfect purification, an additional operation is necessary. The mixed sulphides are dissolved in hydrochloric acid; in this solution the ferric chloride is reduced to ferrous chloride by the evolution of sulphuretted hydrogen. Barium carbonate is now added, and then after twelve or twenty-four hours all the indium is found in the precipitate, free from all impurities but barium.

To obtain the metal, the oxide is carefully heated in a stream of hydrogen. In consequence of the volatility, the heat at first must not

be great, and the stream of gas must be passed slowly. After the reduction the metal will be found in small silver-looking buttons, which can be fused together under potassium cyanide.

Separation of Gallium from Indium

Of all the methods tried, the following effects a prompt and accurate separation:—The solution, suitably concentrated, is treated with a slight excess of boiling potash. The boiling is kept up for some minutes, for in the cold, indium oxide is not immediately thrown down by potash. The precipitate retains merely very slight traces of gallium, which are entirely eliminated by one, or at most two, repetitions of the same treatment. The potassic solutions contain merely slight traces of indium, which may be neglected in weight if the masses of gallium and indium are small, and consequently the volume of the alkaline liquids is moderate. To extract these traces of indium the solution is supersaturated with a very slight excess of hydrochloric acid, and the gallium and indium are precipitated together by slowly boiling the liquid after supersaturation with ammonia, or, better still, by means of cupric hydrate. The gallium and indium chlorides are transformed into slightly acid sulphates; a quantity of ammonium sulphate is added, a little larger than what is necessary to transform all the gallium sulphate into gallium alum, and the liquid is then concentrated to a very small volume. After cooling, whether crystals of alum are already formed or not, the solution is mixed with four to five times its volume of alcohol at 70 per cent. The agitation causes the deposit of gallium-ammonium alum in a crystalline powder, which is washed once or twice with alcohol at 70 per cent. The alum is then taken up in a little hot water containing a trace of sulphuric acid, and the operation is repeated several times. By far the larger quantity of the gallium is in this manner transformed into ammonium alum free from indium. The alcoholic solutions containing a small quantity of indium and gallium are concentrated down to a small bulk. The oxides are thrown down by boiling with ammonia, or by means of cupric hydrate; they are dissolved in hydrochloric acid, and are then treated with boiling potash. We obtain thus a small supplementary quantity of indium free from gallium. As very little potash suffices, the slight traces of indium in the alkaline solution are absolutely unimportant, though the last residue of gallium may be separated as alum if its quantity is noteworthy. Generally the traces of indium carried by the potash along with the gallium are entirely eliminated after four alcoholic crystallisations of the gallium-ammonium alum. With gallium containing 4 per cent. of indium seven or eight recrystallisations are necessary. These operations are performed very rapidly and easily with the salt derived from less than 0·01 gramme of gallium.

ALUMINIUM

Detection of Alumina

Mr. Beckmann recommends baryta-water in preference to the caustic alkalies, as not being contaminated with alumina and silica. Solution of ammonium chloride is afterwards added as usual.

Precipitation of Alumina

(*A*) Ammonium sulphide is a more complete precipitant for alumina than caustic ammonia or ammonium carbonate, and should always be employed in preference when practicable. The small quantity of free sulphur which will be generally precipitated at the same time is driven off on ignition. It must be remembered that oxalic acid and its salts possess in a slight degree the property of most non-volatile organic acids, of impeding certain reactions of alumina; therefore, when ammonium oxalate is present in great excess, alumina is not immediately precipitated by ammonia and ammonium sulphide; although, in the course of a little time, according to its proportion, alumina is precipitated, especially if the solution be heated.

(*B*) M. Classen[1] finds that if aluminium-ammonium oxalate, dissolved with an excess of ammonium oxalate, is submitted to the action of an electric current, in proportion as the ammonium oxalate is converted into ammonium carbonate the aluminium is deposited in the state of hydroxide. When the oxalic acid is oxidised, the liquid is boiled until it smells faintly of ammonia, filtered, washed with water, and the hydroxide is converted into alumina by ignition.

Precipitation and Washing of Alumina

Messrs. S. L. Penfold and D. N. Harper have experimented on the precipitation and handling of alumina precipitates. A standard solution of aluminium chloride was first made, containing 0·1 gramme alumina and 1 c.c. pure concentrated hydrochloric acid in every 50 c.c. The precipitation of the alumina was in all cases made in a volume of about 300 c.c. by neutralising the solution with ammonia till the odour of ammonia could be distinctly obtained from the hot solution; the beaker was then placed upon a lamp-stand, and the solution brought to boiling, which was not continued more than one minute. The precipitates were in all cases washed without a pump, but suction-tubes 7 inches long were attached to the funnels, which caused a gentle suction, and, if the filter-papers were carefully fitted to the funnels, very materially hastened the filtration.

The following facts were observed:—That precipitates which were made in solutions containing large quantities of acid, either hydro-

[1] For details of operations see chapter on Electrolytic Analysis.

chloric or nitric, filtered as well as or better than those from solutions containing little ammonia salts, but on washing with boiling water the precipitates from solutions containing large quantities of ammonia salts became very sticky and washed slowly so that it was almost impossible to free them from the last traces of ammonium chloride; and that very perceptible quantities of alumina settled out from the filtrates and washings, on adding a few drops of ammonia and allowing the beaker to stand in a warm place. Further, that all of the alumina which ran through did so during the washing. The precipitates, after they had become slimy and sticky, seemed either to be quite soluble in the hot water, or else got into such a condition that they readily passed through the pores of the paper and stopped them up, thus hindering the filtration.

To make a successful precipitation and washing of alumina, it is quite essential not to have very much ammonia salts present, and even with the greatest care it is found that if the filtrates and washings are set away in a warm place, slight precipitates will almost invariably settle out. The above holds good for solutions containing ammonium chloride and nitrate. The fact that alumina passed through the filter only during the washing, suggested that if the precipitate could be washed with a saline solution which would be completely volatile and do no harm to the precipitate, the passage of the alumina through the filter might be avoided, and it might also hinder the packing of the precipitate. Ammonium nitrate suggested itself as a salt which would be volatile on ignition and do no harm, and experiments with it have been very satisfactory. The following strength of ammonium nitrate was used in all the experiments:—2 c.c. of pure concentrated nitric acid neutralised with ammonia and diluted to 100 c.c. with water; this strength has proved quite satisfactory.

Using this hot saline wash instead of hot water, the precipitation can be made in solutions containing large or small quantities of ammonium salts, and no very great care is needed in adding the ammonia. The precipitates from solutions containing a goodly quantity of ammonium salts, resulting from 4 to 8 c.c. of pure concentrated hydrochloric or nitric acid, filter and wash better than precipitates from solutions containing less saline matter. After having made a large number of precipitations, the authors can say that only in one or two cases have they found a trace of alumina in either the filtrate or washings, and that unless the precipitate becomes too dry and packs too firmly upon the sides of the funnel, the washing goes on as well at the end as at the beginning, and there is no difficulty in washing the precipitate free from all traces of chlorine.

Volumetric Estimation of Alumina in Caustic Soda

Gatenby estimates first the amount of caustic soda present with normal hydrochloric acid and phenol-phthalein as indicator. When

the phenol-phthalein is decolourised, we have the amount of caustic soda present. Then put into it a few drops of methyl orange solution and again add normal hydrochloric acid, stirring well (not heating), until a pink colour is obtained which does not vanish by stirring for a few seconds. The number of c.c. of normal hydrochloric acid required by the second titration equals the amount of alumina and alkaline soda salts present. Then add litmus solution and titrate back with normal caustic soda until a decided blue colour appears.

Each c.c. of normal caustic soda requires 0·0257 of alumina.

A sample of caustic soda bottoms from 70 per cent. white caustic soda, called by the trade 68 per cent. bottoms, tested as follows :—

Na_2O	57·1
H_2O	16·5
Na_2CO_3, &c.	2·4
Al_2O_3	11·3
Insoluble Fe_2O_3, &c.	12·5
	99·8

This process is said to be very rapid, and accurate enough for technical use. It is an interesting fact that alumina is alkaline to methyl orange, and acid to litmus solution.

Assay of Clays for Alum Making

Mr. G. Pouchet proceeds as follows :—A mean sample of 50 grammes is taken and placed in a tared platinum or porcelain capsule. It is submitted to a moderate calcination. When it has attained a dull redness, the capsule is withdrawn, allowed to cool, and weighed. The loss indicates the proportion of moisture and of volatile matters (combined water and organic matter). Upon the calcined clay are then poured 100 grammes of sulphuric acid at 60° B.; the whole is well mixed with a glass rod, and heated till it becomes solid. It is then lixiviated with boiling water, and the alumina is determined in the ordinary manner in a known part of the solution.

Separation of Aluminium from Zinc

The metals should preferably be in the form of chlorides. Dilute the solution considerably, render it neutral or nearly so, add sodium acetate in excess, and then boil for a short time, adding a drop of free acetic acid occasionally; the whole of the aluminium will be precipitated in the form of basic acetate. Filter rapidly through a ribbed filter, and keep the liquid as near the boiling-point as possible during filtration. If an absolutely complete separation is necessary, redissolve the precipitate in dilute hydrochloric acid and repeat the operation. From the solution the zinc is completely precipitated by sulphuretted hydrogen.

Separation of Aluminium from Zirconium

To separate these two metals Mr. J. Thomas Davis proceeds as follows:—Their solution in hydrochloric acid is treated with sodium carbonate until a permanent precipitate is formed. This precipitate is dissolved in the smallest possible quantity of dilute hydrochloric acid, and sodium iodate is added in excess. The solution is heated for about fifteen minutes. It is then allowed to stand twelve hours, filtered, washed down with boiling water, dissolved in hydrochloric acid, and finally precipitated with ammonia, ignited and weighed.

Three analyses of the zirconium salt proved it to be an oxy-iodate of variable composition. Several attempts were made to separate iron both in the ferrous and ferric state, but without success. This metal must be removed from the mixture of aluminium and zirconium previous to their treatment with sodium iodate.

Separation of Aluminium from Glucinum

(*A*) Dr. Wolcott Gibbs adds a solution of sodium fluoride to the one of aluminium and glucinum, when the whole of the aluminium is thrown down in the form of cryolite, while the glucinum remains in solution. From this solution ammonia precipitates the glucina.

(*B*) When sodium thiosulphate is added to a nearly neutral dilute solution containing aluminium and glucinum, and the liquid is boiled until no more sulphurous acid is disengaged, alumina is precipitated (together with some sulphur), while the glucinum remains in the solution.

The following methods are not satisfactory: precipitation of the alumina as basic acetate, some glucinum being also precipitated; precipitation of the alumina with barium carbonate; solution of the glucinum in a boiling solution of ammonium chloride; by long boiling of a solution of ammonium chloride the solution becomes slightly acid, and some alumina is dissolved, while Genth found that the glucinum was not completely dissolved. Solution of the glucinum in, and precipitation of the alumina with ammonium carbonate gives unreliable results.

(*C*) Messrs. S. L. Penfold and D. N. Harper have improved upon Genth's process of dissolving the mixed chlorides in the least possible excess of caustic soda, diluting the solution largely, and precipitating the glucina by boiling.

The method is as follows:—50 c.c. of each solution were measured into a platinum dish and evaporated to dryness, the chlorides were dissolved in the least possible quantity of water, and a rather strong solution of pure soda, made from metallic sodium, was cautiously added until the precipitate which at first formed was completely dissolved. The contents of the dish were then rinsed with cold water into a beaker

containing about 800 c.c. of boiling water, and the contents of the beaker boiled for one hour, replacing from time to time the water which evaporated. The glucinum separates out as a granular precipitate, which is easy to filter and wash. After acidifying and concentrating the filtrate, the alumina was precipitated with ammonia. The best results are obtained by dissolving the dried chlorides in the least possible quantity of water, and using as little soda as possible for dissolving the aluminium and glucinum.

(*D*) When phosphoric acid is present the same authors separate alumina from glucinum by boiling the solution of the mixed chlorides with barium hydroxide. The alumina goes readily into solution, while the precipitate containing the barium phosphate and glucinum is easy to filter and wash. After dissolving the precipitate and separating the barium with sulphuric acid, a glucinum phosphate can be precipitated with ammonia. After weighing this, the phosphoric acid may be determined by means of ammonium molybdate, and the glucinum by difference; or the precipitate may be fused with sodium carbonate, and the fusion soaked out with water, which gives almost a complete separation of phosphoric acid from glucinum. If phosphoric acid is also to be determined, it must be borne in mind that very perceptible quantities of it will be found in the barium sulphate precipitate.

Separation of Aluminium from the Cerium Metals

Bring the metals to the form of sulphates dissolved in a small quantity of water, and add sufficient powdered sodium sulphate to form a saturated solution. The cerium metals immediately separate in the form of double sulphates with sodium sulphate, as a white highly crystalline powder. Filter off and wash with a saturated solution of sodium sulphate. Precipitate the aluminium from the filtrate by addition of ammonia and ammonium sulphide, and dissolve the double sodium and cerium sulphates, &c., in dilute hydrochloric acid, and precipitate with ammonium oxalate.

Separation of Aluminium from Magnesium

(*A*) These, when in solution together, may be separated by Dr. Gibbs's plan, viz. boiling the dilute solutions with excess of sodium acetate and a little acetic acid, whereby the aluminium is precipitated as basic acetate. The details of the operation are conducted as in the Separation of Aluminium from Zinc (page 159).

(*B*) Insoluble mixtures containing aluminium and magnesium, such as spinel (magnesium aluminate), are best analysed by the process given by Wöhler. Fuse the finely levigated mineral with six times its weight of potassium bisulphate, and keep the mass fused at a red heat till sulphuric acid is no longer disengaged. Dissolve the

fused mass in water acidulated with hydrochloric acid, and decompose it with sal-ammoniac, which precipitates the alumina. To prevent any magnesia coming down with the alumina, care must be taken to keep the liquid boiling till no more free ammonia is given off. The gelatinous alumina, which the boiling liquid deposits, is filtered, but as it is almost impossible to wash in this state, it must be allowed to half dry on the filter, when it can be washed perfectly. The magnesium is precipitated from the filtrate by ammonia and sodium phosphate.

Separation of Aluminium from Calcium

The method of separating calcium from aluminium by means of ammonia has been improved by H. Rose. Instead of being careful to employ ammonia free from carbonic acid, and avoiding the presence of this gas, he heats to gentle ebullition the liquid in which the alumina has been precipitated by excess of ammonia. When the evolution of ammonia ceases, all the aluminium is in the precipitate, and may be separated by filtration without requiring any special precaution, for the simple reason that in the presence of ammoniacal salts the calcium carbonate is decomposed, the calcium entering into solution. A little sal-ammoniac may even be added, if there is a chance of there not being sufficient to favour this decomposition.

When the calcium is present in small quantities only, tartaric acid may be added, and the solution then supersaturated with ammonia. The calcium is precipitated in the form of tartrate if there is only a little aluminium present; otherwise, much remains in solution. In either case, however, ammonium oxalate will separate it perfectly in the form of calcium oxalate.

Estimation of Aluminium in the Presence of Iron, Manganese, Calcium, and Magnesium

William H. Hess and E. D. Campbell [1] have found that the well-known ammonium base, phenylhydrazine, is the most satisfactory of the many organic bases tried for the precipitation of alumina. As a base it is somewhat weaker than ammonia. It precipitates aluminium from its solutions quantitatively as the hydroxide without a trace of the precipitate being redissolved in excess of the precipitant. Phenylhydrazine is, moreover, a strong reducing agent, quickly reducing iron from the ferric to the ferrous state, thus playing a double *rôle* of usefulness in the separation of iron from alumina.

Method of Analysis

A convenient sample to be analysed is weighed out and obtained in solution, preferably as the chloride, in the usual way. To a convenient

[1] *Chemical News*, April 6, 1900.

bulk of solution—200 to 300 cubic centimetres heated to near the boiling-point—dilute ammonia is added slowly as long as the precipitate formed just redissolves with readiness. A neutral, saturated solution of ammonium bisulphite [1] is added, drop by drop, with stirring, to this hot and nearly neutral solution, until it becomes colourless, showing the complete reduction of the iron. To the hot solution, now smelling strongly of sulphur dioxide, 1 or 2 cubic centimetres of phenylhydrazine are added. If this amount of phenylhydrazine causes a permanent precipitate, then a few drops more of phenylhydrazine are added to ensure complete precipitation of the alumina. If 1 to 2 cubic centimetres of phenylhydrazine do not produce a permanent precipitate, it is economical, after adding this amount of phenylhydrazine, to add dilute ammonia, carefully, drop by drop, to a just perceptible permanent precipitate, and then complete the precipitation by adding a few drops more of phenylhydrazine. The precipitate, consisting of aluminium hydroxide and aluminium phosphate, is filtered out on an ordinary filter, and washed with warm water containing a small amount of phenylhydrazine bisulphite. This washing solution is prepared as follows :—To a few cubic centimetres of phenylhydrazine in a beaker, a saturated aqueous solution of sulphur dioxide is added gradually, until the precipitate of phenylhydrazine sulphite, which at first separates out in crystals, is redissolved to a yellow solution. If, after a few minutes, an odour of sulphur dioxide is perceptible, a few drops of phenylhydrazine are added to neutralise this excess of sulphurous acid. This concentrated solution of phenylhydrazine bisulphate, if well stoppered, will keep indefinitely. 5 to 10 cubic centimetres of this to 100 cubic centimetres of water is an efficient strength of solution for washing the precipitate of alumina. The washing with this warm solution is continued until the washings give no test for iron with ammonium sulphide. A drop or two of phenylhydrazine are added to the filtrate while stirring, to see if the precipitation has been complete. If chlorides of metals other than iron be present, the washing must be continued until the washings are free from chlorine. The presence of chlorides of volatile bases will do no harm in the ignition of alumina.

The precipitate, together with the filter, is placed in a platinum crucible, dried, and the filter charred at a low temperature ; after the filter is completely burned, the ignition is continued, at a bright red heat, to constant weight. Care is taken to weigh quickly with the cover on the crucible, since both the phosphate and oxide of aluminium are very hygroscopic. A second ignition and weighing is always necessary.

[1] This solution of ammonium bisulphite is made by passing sulphur dioxide into a cooled solution of ammonia (1 : 1) until the solution becomes yellow. It serves the purpose here not only of reducing the iron, but the excess of sulphurous acid unites with the phenylhydrazine added, to form a salt which acts as a most efficient agent for keeping the iron reduced, and thus prevents its precipitation with the alumina.

This precipitate of alumina carries all the phosphorous pentoxide, so that the weight of alumina is found by subtracting the weight of phosphorous pentoxide found in a separate sample.

Chromium is quantitatively precipitated by phenylhydrazine, and may thus be separated from iron with great readiness. Neither calcium, magnesium, manganese, cobalt, nor nickel is precipitated.

THALLIUM

Detection of Thallium in Minerals

The optical process of detecting thallium in a mineral is very simple. A few grains of the ore are crushed to a fine powder in an agate mortar, and a portion taken up on a moistened loop of platinum wire. Upon gradually introducing this into the outer edge of the flame of a Bunsen gas-burner, and examining the light by means of a spectroscope, the characteristic green line will appear as a continuous glow, lasting from a few seconds to half a minute or more, according to the richness of the specimen. By employing an opaque screen in the eyepiece of the spectroscope to protect the eye from the glare of the sodium line, thallium may be detected in $\frac{1}{2}$ grain of mineral, when it is present only in the proportion of 1 to 500,000. The sensitiveness of this spectrum reaction is so great that no estimate can be arrived at respecting the probable amount of thallium present. Before deciding whether a deposit or mineral contains sufficient of the metal to be worth extracting, it is necessary to make a rough analysis in the wet way by methods which will be subsequently described.

Thallium is a very widely distributed constituent of iron and copper pyrites. Upon examining a large collection of pyrites from different parts of the world, it was found present in more than one-eighth. It is not confined to any particular locality. Among those ores in which it occurs most abundantly (although in these cases it does not constitute more than from the $\frac{1}{100000}$ to the $\frac{1}{4000}$ of the bulk of the ore) may be mentioned iron pyrites from Theux, near Spa in Belgium, from Namur, Philipville, Alais, the South of Spain, France, Ireland, Cornwall, Cumberland, and different parts of North and South America; in copper pyrites from Spain, as well as in crude sulphur prepared from this ore; in blende and calamine from Theux; in blende, calamine, metallic zinc, cadmium sulphide, metallic cadmium, and cake sulphur from Nouvelle Montagne; in native sulphur from Lipari and Spain; in bismuth, mercury, and antimony ores, as well as in the manufactured products from these minerals (frequently in so-called pure medicinal preparations of these metals); in commercial selenium and tellurium (probably as selenide and telluride).

Thallium is likewise frequently present in copper and commercial salts of this metal. In Spain a very impure copper is prepared in the

following way:—Copper pyrites is allowed to oxidise in the air, and the resulting copper sulphate is washed out; scrap iron is now placed in the liquid, which causes the copper to precipitate in a powdery state. The metal is then collected together, dried, strongly compressed, and heated to the melting-point. It is brought over to this country in the form of rectangular cakes, weighing about 20 pounds each, and is called 'cement copper.' The thallium sulphide oxidising to sulphate along with the copper sulphide is washed out by the water, and precipitated with the copper by the iron. The two metals alloy together.

Thallium is present in tolerable quantity in lepidolite from Moravia, and in mica from Zinnwald. It has likewise been found in the deliquescent 'Sel-à-Glace' from the mother-liquors of the salt-works at Neuenheim. This consists of a mixture of the magnesium, potassium, and sodium chlorides, with relatively considerable quantities of rubidium and cæsium chlorides, and sensible traces of thallium chloride. Thallium is also met with in the mother-liquors in the zinc sulphate works at Goslar, in the Hartz.

Many samples of commercial sulphuric acid and yellow hydrochloric acid contain thallium. The source in these cases is evidently the pyrites used in the sulphuric acid works.

Preparation of Thallium

From the Flue-Dust of Pyrites-burners.—This is by far the most economical source of thallium at present known. In burning thalliferous pyrites for the purpose of manufacturing sulphuric acid, the thallium oxidises along with the sulphur, and is driven off by the heat. If the passage leading from the burners to the leaden chambers is only a few feet long, the greater portion of the thallium escapes condensation, and volatilises into the leaden chambers; it there meets with aqueous vapours, sulphurous and sulphuric acids, and becomes converted into thallium sulphate. This being readily soluble both in water and dilute sulphuric acid, and not being reduced by contact with the leaden sides, remains in solution and accompanies the sulphuric acid in its subsequent stages of concentration, &c. If, on the other hand, the passage connecting the burners and chambers is 10 or 15 (or more) feet in length, nearly the whole of the thallium is condensed, together with the multiplicity of other bodies which constitute 'flue-dust.' Accompanying the thallium have been found mercury, copper, lead, tin, arsenic, antimony, iron, zinc, cadmium, bismuth, lime, and selenium, together with ammonia, sulphuric, nitric, and hydrochloric acids. The amount of thallium in these flue-deposits is very various. In many specimens it is not present at all, and in very few it amounts to as much as $\frac{1}{4}$ per cent., although in some as much as 8 per cent. of thallium has been found.

(*A*) The following is the best plan for extracting this metal from the

dust :—The dust is first heated to very dull redness, so as to allow the excess of sulphuric acid to drive off any hydrochloric acid which may be present, and is then mixed in wooden tubs with an equal weight of boiling water, and well stirred ; after this, the mixture is allowed to rest for twenty-four hours for the undissolved residue to deposit. The liquid is then syphoned off, and the residue is washed, and afterwards treated with a fresh quantity of boiling water. The collected liquors, which have been syphoned off from the deposit, are allowed to cool, precipitated by the addition of a considerable excess of strong hydrochloric acid, and the precipitate, consisting of very impure thallium chloride, is allowed to subside. The chloride obtained in this way is then well washed on a calico filter, and afterwards squeezed dry. Three tons of flue-dust treated in this way yielded the author 68 pounds of this rough chloride.

The next step consists in treating the crude chloride in a platinum dish with an equal weight of strong sulphuric acid, and afterwards heating the mixture to expel the whole of the hydrochloric acid. To make sure of this the heat must be continued until the greater part of the excess of sulphuric acid is volatilised. After this the mass of thallium bisulphate is dissolved in about 20 times its weight of water, nearly neutralised with chalk, and then filtered. On the addition of hydrochloric acid to the filtrate nearly pure thallium chloride is thrown down ; this is collected on a filter, well washed, and then dried. The crude thallium protochloride obtained by either of the above methods is added by small portions at a time to half its weight of hot oil of vitriol in a porcelain or platinum dish, the mixture being constantly stirred and the heat continued till the whole of the hydrochloric acid and the greater portion of the excess of sulphuric acid are driven off. The fused bisulphate is now to be dissolved in an excess of water, partially neutralised with sodium carbonate, and an abundant stream of sulphuretted hydrogen passed through the solution. The precipitate, which may contain tin, arsenic, antimony, bismuth, lead, mercury, and silver, is separated by filtration, and the filtrate is boiled till all free hydrosulphuric acid is removed. The liquid is now to be rendered alkaline with ammonia, and boiled ; the precipitate of iron and alumina, which generally appears in this place, is filtered off, and the clear solution evaporated to a small bulk. Thallium sulphate will then separate out on cooling in the form of long, clear prismatic crystals. As ammonium sulphate is much more soluble than thallium sulphate, the latter can readily be separated from the small quantity of the former salt present. The two salts do not crystallise together.

(*B*) In order to avoid the inconvenience of driving off the excess of oil of vitriol in the decomposition of thallium chloride, it is less troublesome, although not quite so accurate, to proceed as follows :—Boil the thallium chloride in solution of ammonium sulphide for five minutes : decomposition takes place readily. Filter and wash with sulphuretted

hydrogen water till no more chlorine can be detected in the filtrate; then dissolve the sulphide on the filter in dilute sulphuric acid, and treat the solution with ammonia, &c., as above directed.

In order to obtain the metal when working on small quantities of material, thallium sulphate is dissolved in 20 times its weight of water; the liquid is acidulated with sulphuric acid, and a current of electricity from two or three cells of Grove's batteries is passed through it, platinum terminals being used. The appearance presented when a tolerably strong solution of thallium is undergoing reduction is very beautiful. If the E.M.F. of the current bears a proper proportion to the strength and acidity of the liquid, no hydrogen is evolved at the negative electrode, but the metal grows from it in large crystalline fernlike branches, spreading out into brilliant metallic plates, and darting long needle-shaped crystals, sometimes upwards of an inch in length, towards the positive pole, the appearance being more beautiful than with any other metal. Some of the tabular crystals, as seen in the liquid, are beautifully sharp and well defined; considerable difficulty is, however, met with in disengaging them from the electrode and removing them in a perfect state from the liquid. So long as thallium is present in the solution, no hydrogen is evolved with a moderate strength of current: as soon as bubbles of gas are evolved the reduction may be considered complete. The crystalline metallic sponge may now be squeezed into a mass round the platinum terminal, disconnected from the battery, quickly removed from the acid liquid, rinsed with a jet from a wash-bottle, and transferred to a basin of pure water. The metal is then carefully removed from the platinum, and kneaded with the fingers into as solid a lump as possible. It coheres together readily by pressure, and will be found to retain its metallic lustre perfectly under water.

(*C*) When considerable quantities of thallium are to be reduced to the metallic state, it is convenient to employ metallic zinc for the purpose. In the course of twenty-four hours, the author has reduced upwards of a quarter of a hundredweight of metal in the following way. Plates of pure zinc (which should leave no residue when dissolved in sulphuric acid) are arranged vertically round the sides of a deep porcelain dish holding a gallon. Crystallised thallium sulphate, in quantities of about 7 pounds at a time, is then placed in the dish, and water poured over to cover the salt. Heat is applied, and in the course of a few hours the whole of the thallium will be reduced to the state of a metallic sponge, which readily separates from the plates of zinc on slight agitation. The liquid is poured off, the zinc removed, and the spongy thallium washed several times. It is then strongly compressed between the fingers, and preserved under water until it is ready for fusion.

The metal is readily obtained in the coherent form by fusing the sponge. This is most conveniently performed under potassium cyanide

on the small scale, and under coal-gas when working with large quantities. In the former case the sponge, strongly compressed and quite dry, is broken into small pieces, which are dropped one by one into potassium cyanide kept fused in a porcelain crucible. They rapidly melt, forming a brilliant metallic button at the bottom. When cold, the potassium cyanide may be dissolved in water, when the thallium will be left in the form of an irregular lump, owing to its remaining liquid and contracting after the cyanide has solidified.

On the large scale, the fusion is best effected in an iron crucible. This is placed over a gas-burner, and a tube is arranged so that a constant stream of coal-gas may flow into the upper part of the crucible. Lumps of the compressed sponge are then introduced, one after the other as they melt, until the crucible is full of metal. It is then stirred up with an iron rod, and the thallium may either be poured into water and obtained in a granulated form, or cast into an ingot. Thirty or forty fusions have been performed in the same crucible without the iron being appreciably acted upon by the melted thallium.

From the Mother-Liquors of the Zinc Sulphate Works at Goslar.—Each kilogramme of these liquors is said to yield as much as $\frac{1}{2}$ gramme of thallium chloride. A sheet of zinc is plunged into the liquid, whereby the thallium, copper, and cadmium are precipitated. The metallic sponge is then removed from the zinc, washed, and treated with cold dilute sulphuric acid, which dissolves the cadmium and thallium with disengagement of hydrogen, while the copper is left behind. The filtrate from the copper is then mixed with hydrochloric acid, which precipitates the nearly insoluble thallium chloride. If only a small quantity of thallium is present, potassium iodide may be used as a precipitant, as the thallium iodide is insoluble in water.

Preparation of Pure Thallium

(*A*) Commercial thallium sulphate is dissolved in water, and the cold solution deluged with sulphuretted hydrogen. It is then filtered, heated to ebullition, and poured into boiling dilute hydrochloric acid. The solution is filtered while hot and then allowed to cool. The thallium chloride which crystallises out on cooling is washed by decantation until the washings are free from sulphuric acid, and further purified by recrystallising twice from water. The thallium chloride thus obtained is dried, mixed with pure sodium carbonate, and projected by small portions at a time into pure potassium cyanide, kept in a state of fusion in a white unglazed crucible. The chloride is rapidly reduced to the metallic state; the crucible is then allowed to cool, and the contents exhausted with water. The resulting ingot of metal is well boiled in water, dried and fused in an unglazed porcelain crucible with free access of air, stirred with a porcelain rod to facilitate

oxidation, and finally cast in a porcelain mould. It may be preserved under water which has been boiled to expel the air.

(*B*) Ordinary metallic thallium is fused in contact with the air, in an iron crucible, made nearly red-hot, and then poured into water. The granulated metal is then exposed moist to a warm atmosphere to facilitate oxidation, the oxide being continually removed by boiling out with water. When a considerable quantity of oxide (mixed with carbonate) has been obtained, the solution is heated to ebullition and a rapid current of carbonic acid gas passed through until the liquid is quite cold and the excess of thallium carbonate has crystallised out. The resulting salt is recrystallised and divided into three portions. One portion is projected into pure potassium cyanide kept in a state of fusion, in a porcelain crucible at a dull-red heat; carbonic acid escapes with effervescence, and the metal is reduced to the metallic state. The whole is then allowed to cool, the soluble salts boiled out with water, and the lump of thallium fused in a lime crucible and cast in a lime mould as described further on.

(*C*) Thallium carbonate, obtained as in process *B*, is covered with a small quantity of water, and decomposed by the current from six of Grove's cells. Much thallium peroxide is deposited, which is removed [1] and preserved for the preparation of thallium by another method. The reduced thallium is then squeezed into a hard cake, melted in a lime crucible, and cast in a lime mould.

(*D*) A third portion of thallium carbonate, obtained as in process *B*, is crystallised several times from water, carbonic acid being passed through during the cooling of the solution. After six crystallisations the carbonate is perfectly white. It is then placed in a porcelain dish, covered with a little water, and decomposed by four Grove's cells. The spongy metal is washed, boiled in pure water, tied up in a linen cloth, and compressed between steel plates in a vice. The hard lump is broken up, put into a porcelain crucible and melted, no flux being used. It is constantly stirred up with a piece of unglazed porcelain and cast in a warm porcelain mould.

(*E*) The thallium peroxide obtained by the electrolysis of the carbonate (process *C*) is dissolved in rectified sulphuric acid, evaporated to dryness, and heated strongly to decompose any persulphate; it is then dissolved in water and recrystallised twice. The thallium sulphate is then reduced to the metallic state by three Grove's cells, platinum terminals being employed. The metal is then squeezed into a lump and melted under hydrogen, in a porcelain crucible, and cast in a cold polished steel mould.

(*F*) Thallium chloride, as obtained by method *A*, is boiled in nitric acid till most of it is converted into sesquichloride. This is washed

[1] The operation requires this thallium peroxide to be constantly removed from the positive pole, or the passage of the current will be retarded and ultimately stopped.

by decantation, until it begins to decompose with separation of thallium peroxide, and purified by twice recrystallising.[1] The purified thallium sesquichloride is dissolved in boiling water poured into dilute ammonia. The precipitated thallium peroxide is washed by decantation till chlorine is no longer detected in the washings, and then boiled in a little water with pure sublimed oxalic acid till the whole is converted into thallium oxalate. This is dried and heated in a crucible until the whole is decomposed into a mixture of metallic thallium and thallium oxide; the reduced metal is then cast in a mould of polished steel.

(*G*) Ordinary thallium is dissolved in nitric acid, the excess of acid driven off by heat, the residue dissolved in water, and the solution is saturated with sulphuretted hydrogen. A slight black precipitate is generally formed, the solution is filtered cold, and is then freed from sulphuretted hydrogen by boiling. Ammonia is then added, which produces a faint precipitate of iron sesquioxide and thallium peroxide; it is then filtered, and the solution is mixed with ammonium oxalate, and concentrated till the thallium oxalate crystallises out. This is freed from ammonium nitrate by recrystallising, and the thallium oxalate decomposed by heat, as in process *F*. The thallium thus obtained is again fused in a lime crucible, a blowpipe flame being directed downwards on to the surface of the fused metal for about five minutes till the slag unites with the lime, forming a semi-fluid pasty mass. The metal is then cast in a lime mould, washed when cold, and kept under boiled distilled water or very dilute acetic acid.

Purification of Thallium by Fusion in Lime

A piece of well-burnt, very dense quicklime, prepared from black marble, is cut out so as just to fit a porcelain crucible; a hole is then bored in the centre of the lime, and a lump of lime cut to form a stopper. This arrangement is then raised to a temperature above the melting-point of thallium over a gas-burner, and the cavity in the lime is gradually filled with the metal introduced in lumps. The stopper is then put on, and the heat raised to dull redness and kept so for half an hour; after which the melted metal is poured into a lime mould and preserved in a well-stoppered bottle under boiled water or very dilute acetic acid.

Detection of Thallium by the Blowpipe

In a closed tube thallium melts easily, and a brownish-red vitreous slag, which becomes pale yellow on cooling, forms round the fused globule.

[1] A little thallium peroxide is separated each time the sesquichloride is dissolved.

In the open tube fusion also takes place on the first application of the flame, while the glass becomes strongly attacked by the formation of a vitreous slag, as in the closed tube. Only a small amount of sublimate is produced; this is of a greyish-white colour, but under the magnifying-glass it shows in places a faint iridescence.

On charcoal, *per se*, thallium melts very easily, and volatilises in dense fumes of a white colour, streaked with brown, while it imparts at the same time a vivid emerald-green colouration to the point and edge of the flame. If the heat be discontinued the fused globule continues to give off copious fumes, but this action ceases at once if the globule be removed from the charcoal. A deposit, partly white and partly dark red, of oxide and peroxide is formed on the support; but, compared with the copious fumes evolved from the metal, this deposit is by no means abundant, as it volatilises at once where it comes in contact with the glowing charcoal. If touched by either flame it is dissipated immediately, imparting a brilliant green colour to the flame border. The brown deposit is not readily seen on charcoal; but if the metal be fused on a cupel, or on a piece of thin porcelain or other non-reducing body, the evolved fumes are of a brownish colour, and the deposit is in great part brownish black. It would appear, therefore, to consist of thallium peroxide rather than of a mixture of metal and oxide. On the cupel, thallium is readily oxidised and absorbed. It might be employed, consequently, in place of lead in cupellation; but to effect the absorption of copper or nickel a comparatively large quantity is required. When fused on porcelain the surface of the support is strongly attacked by the formation of a silicate, which is deep red while hot and pale yellow on cooling.

The peroxide evolves oxygen when heated, and becomes converted into thallium oxide. The latter compound is at once reduced on charcoal, and the reduced metal is rapidly volatilised with brilliant green colouration of the flame. The chloride produces the same reaction, by which the green flame of the thallium may easily be distinguished from the green copper flame, the latter, in the case of cupreous chlorides, becoming changed to azure blue. With borax and phosphorus salt thallium oxides form colourless glasses, which become grey and opaque when exposed for a short time to a reducing flame. With sodium carbonate they dissolve to some extent, but on charcoal a malleable metallic globule is obtained. The presence of sodium, unless in great excess, does not destroy the green colouration of the flame.

Thallium alloys more or less readily with most other metals before the blowpipe. With platinum, gold, bismuth, and antimony respectively, it forms a dark-grey brittle globule. With silver, copper, or lead, the button is malleable. With tin, thallium unites readily, but the fused mass immediately begins to oxidise, throwing out excrescences of a dark colour, and continuing in a state of ignition until

the oxidation is complete. In this, as in other reactions, therefore, the metal much resembles lead.

Electrolytic Separation of Thallium [1]

(*A*) According to Classen, this metal may be separated as such quantitatively from the solution mixed with ammonium oxalate. The properties of thallium, however, agree with those of lead, so that the direct determination is not possible.

(*B*) G. Neumann, while engaged with a research on the composition of certain double salts of thallium, has occupied himself with the quantitative determination of the metal. As the method is important for the examination of thallium compounds, it is here inserted.

The process is founded on the precipitation of thallium in the metallic state and ascertaining the quantity of hydrogen which it evolves when dissolved in hydrochloric acid. For carrying out the determination G. Neumann uses a flask holding about 100 c.c., containing two platinum plates of 9 square centimetres, which, for connection with the external source of the current, are in contact with platinum loops or wires. In this flask the thallium salt is dissolved with about 5 grammes ammonium oxalate, and electrolysed, after dilution with water, with a current 0·1 ampère. The end of the precipitation is ascertained with ammonium sulphide. As ammonium oxalate is converted by the current into ammonium carbonate, and as the measuring tube cannot hold the volume of carbonic acid liberated, the solution present in the flask is first removed after the decomposition. This can be effected in a well-known manner by means of two syphons. As this process is tedious when a great number of determinations have to be executed, Neumann has arranged a self-acting washing apparatus in which the washing is effected without interrupting the current. In order to remove the gas-bubbles adhering to the electrodes the flask must be heated for a short time after the washing is completed. The flask is then connected with the measuring tube, the thallium is dissolved, and the hydrogen gas evolved is measured in the ordinary manner.

Estimation of Thallium as Platino-Chloride

Thallium forms an insoluble platino-chloride, which may be used for its estimation. The salt has the disadvantage, however, of being difficult to collect on a filter, as it has a great tendency to run through. This salt is precipitated in the form of a very pale yellow crystalline powder when platinum bichloride is added to an aqueous solution of a salt of the thallium protoxide. When heated to redness, it leaves an alloy of thallium and platinum, the latter metal continually volatilising until, after being kept for some time at nearly a white heat, the

[1] For details of operation see chapter on Electrolytic Analysis.

platinum is almost free from thallium. This is the most insoluble thallium salt yet met with, one part requiring no less than 15,585 parts of water at 60° F., or 1948 parts of boiling water, to dissolve it. It may be useful to compare the solubilities of this compound with those of the corresponding potassium, ammonium, rubidium, and cæsium salts :

One part of Chloroplatinate of—	Water at 60° F.	Boiling Water
Potassium dissolves in	108 parts	19 parts
Ammonium ,,	150 ,,	80 ,,
Rubidium ,,	740 ,,	157 ,,
Cæsium ,,	1308 ,,	261 ,,
Thallium ,,	15,585 ,,	1948 ,,

Estimation of Thallium as Iodide

The thallium is precipitated in heat by an excess of potassium iodide in a neutral solution, so that the liquid after precipitation may still contain 1 per cent. of the potassium iodide, which is easily effected by operating with a solution of iodide of known strength. It is filtered by decantation, and repeatedly washed with a solution of potassium iodide at 1 per cent., in order to remove foreign salts, and the washing is completed with alcohol at 80° to 82°.

The precipitate is decanted upon the filter and dried. The collected filtrates and washings, when reduced to a small volume, never show thallium sulphide when tested with an alkaline sulphide. It is, of course, necessary to ascertain previously that all the metal is in the thallous state, otherwise it must be reduced to that state by a little sulphurous acid.

When the product is dried the bulk of the thallous iodide is removed from the filter, and upon the small quantity which remains attached to the filter there are let fall a few drops of hot dilute nitric acid (2 vols. of water to 1 vol. of strong acid). The iodide is decomposed ; it is washed in a little hot water, and all the thallium is carried away as nitrate. The liquid collected in a small tared porcelain capsule is gently evaporated to dryness with a few drops of hydrochloric acid. The chloride formed is decomposed by a drop of a concentrated solution of potassium iodide, which converts the thallous chloride into iodide mixed with iodine from the reduction of a little thallic salt, formed in presence of nitric acid. Thallous iodide is decidedly fixed, even at 170° ; at least its weight does not vary appreciably, even after heating for several hours. The small excess of iodine is, therefore, expelled by heating for some hours to 170°. The thallous iodide which has been previously collected is put into the crucible, and the whole is weighed.

Estimation of Thallium as the Acid and Neutral Sulphates

Sir William Crookes [2] has shown that the salt obtained by heating thallous chloride with sulphuric acid until the excess of the latter is expelled, and then raising the heat to redness, has the constitution of a neutral sulphate.

He also found that continued heating did not result in any essential loss of weight, and suggested the possibility of applying this method of treatment to the estimation of thallium.

Castanjen [3] discusses thoroughly the compounds of thallium, and confirms the statements in regard to the neutral sulphate. He also mentions the acid sulphate, and states that on heating, it first melts, and on continued heating gives off sulphuric acid, leaving the neutral sulphate.

Mr. P. E. Browning has determined under what conditions the formation of these salts may be applied to the estimation of thallium. For the work a solution was made by dissolving a given amount of the nitrate in water, and making up to a litre. Measured amounts of this solution were drawn from a burette into weighed platinum crucibles, and the weight taken as a check on the burette reading. To the solution in the crucible a few drops of sulphuric acid were added, and the water driven off by evaporation over a steam-bath. The crucible was then removed to a radiator, consisting in this work of a conical iron cup, and heated to a temperature ranging from 220° C. to 240° C., until fuming ceased and the weight, after half-hour periods of heating, remained constant. The crucibles were placed in a radiator upon a pipe-stem triangle, so that they were about 5 cubic centimetres from the bottom, which was heated to dull redness. A thermometer, hung so that the bulb occupied the same position as the crucible, gave the reading mentioned above.

The results obtained by this treatment agree closely with the calculated amounts of acid sulphate which should be formed. In several experiments this salt was dissolved in water, and the sulphuric acid present in combination precipitated by barium nitrate. The results obtained agreed closely with the formula of the acid sulphate of thallium. Having obtained by the method described the acid sulphate, the crucibles were removed and heated carefully over a free flame to dull redness, when, after a considerable evolution of sulphuric acid fumes, the weight again became constant, and the results showed a condition closely approximating to that of the neutral sulphate. In several of these experiments the sulphuric acid present in combination was determined and showed amounts closely agreeing with the constitution of the neutral sulphate.

The results would seem to show that thallium may be estimated

[1] *Chemical News*, May 4, 1900.

[2] *Ibid.* vol. viii. p. 243.

[3] *Amer. Journ. of Science*, vol. viii. p. 460.

either as the acid sulphate or as the neutral sulphate by careful attention to the proper conditions of temperature.

Estimation of Thallium in the Thallous State

V. Thomas's method[1] consists in transforming the salts of the protoxide into salts of the sesquioxide. It has the advantage of great simplicity over the older methods which have been in use up to the present, besides being much more accurate.

The oxidising agent used is bromide of gold, or, to speak more accurately, bromo-auric acid. By reduction, the bromide of gold loses three atoms of bromine, and gives a deposit of metallic gold which can be weighed, so that when the reduction is terminated, two atoms of gold correspond to three atoms of thallium, according to the reaction $3TlCl + 2AuBr_3 = 3TlClBr_2 + 2Au$.

It follows that, taking 197 as the atomic weight of gold and 204 as that of thallium, we can immediately find the amount of thallous thallium existing in combination, by multiplying the weight of the reduced gold by

$$\frac{3 \times 204}{2 \times 197} = 1{\cdot}5533$$

The thallium protochloride is dissolved in cold water. The solution is heated on the water-bath, and the solution of bromide of gold added. The reduction takes place immediately, or at the end of a few moments. The gold is precipitated in the form of a brown powder, which sometimes, but rarely, has a metallic lustre. After making certain that the amount of bromide of gold added is sufficient, which can be seen immediately by the colour of the solution, the whole is left in a warm place for eight or ten hours ; the gold is then collected on a filter, dried and weighed.

In this manner the author found the proportion of thallium in the protochloride to be—

	I	II	III	IV	V	Theory
Tl =	85·02	85·29	85·16	85·30	85·18	85·21

When the estimation has to be carried out on very small quantities, the figures come out a little too high.

The bromo-auric acid used is prepared very easily by dissolving gold in bromised bromhydric acid. After solution it is evaporated on the water-bath.

The bromo-auric acid is then deposited on cooling in long dark-coloured needles, which are easily redissolved in water. The filtered solution is kept ready for use. When we use solutions which have been prepared for some time, it is necessary to make certain that they are perfectly clear.

[1] *Chemical News*, July 4, 1902.

It often happens that after a long time solutions of bromide of gold deposit a yellowish-brown powder, on account of a slight reduction which takes place. This powder, if we are not careful, may remain in suspension for a considerable time and be unnoticed; it is therefore advisable to use solutions which have been recently filtered.

Volumetric Estimation of Thallium

The ease with which thallium passes from one degree of oxidation to another gives us a means of estimating the metal volumetrically by potassium permanganate. When a solution of this salt is added to a hot solution of thallium protochloride, it is instantly decolourised. The termination of this reaction is much more easily seen in the case of thallium than with iron. To be sure of success, the thallium must be present in the solution in the state of chloride, or, at all events, with an excess of hydrochloric acid. It is necessary besides to bring back the thallium always to the state of protochloride, which is very quickly done by adding some sulphurous acid. The solution must be boiled to get rid of the excess of the latter, and then the estimation may be proceeded with. In consequence of the slight solubility of the protochloride, it is necessary to have about half a litre of water to one gramme of the salt. The solution of potassium permanganate must be more dilute than that used for estimating iron.

The solution of the permanganate may be titrated by means of pure iron, or by a crystallised stable compound of thallium, such as the sulphate.

0·884 gramme of pure thallium is dissolved in sulphuric acid, the solution diluted with half a litre of water, a few cubic centimetres of hydrochloric acid added, and some drops of sulphurous acid, to make certain of the degree of oxidation of the thallium. After boiling for half an hour to drive off the sulphurous acid, allow it to cool a little, and then add the permanganate; it is necessary to employ 27·3 c.c. To ascertain the degree of oxidation to which the thallium passes in this reaction, dissolve 0·371 gramme of pure iron, and add the permanganate with the usual precautions. Suppose 21·5 c.c. are required; by bringing up these figures to the equivalents of thallium (203) and of iron, we find that—

2·03 of thallium require 63 c.c. of permanganate
0·28 of iron requires 16 „ „

One of thallium therefore requires four times more oxygen than one of iron, and as one of iron requires half an equivalent of oxygen to pass from the protoxide into the sesquioxide, so one of thallium takes two of oxygen, and passes consequently from the state of protoxide into the peroxide, or rather perchloride.

Separation of Thallium from Zinc

Thallium is present in many specimens of blende and calamine, especially from Nouvelle Montagne and the neighbourhood of Spa, in Belgium. In such cases it accompanies the zinc in most of its preparations, and may therefore be frequently detected in the commercial metal. By proceeding in the following manner, the black residue which is left behind when zinc is dissolved in sulphuric acid will generally be found to contain thallium. Dissolve the residue in nitric acid; evaporate the solution with excess of sulphuric acid; dissolve the residue in a small quantity of water; filter the liquid from lead sulphate and add sodium sulphite. Upon adding potassium iodide to the solution the thallium will be precipitated.

When thallium is present in larger quantities, precipitate the zinc with sodium carbonate, which has no action on thallium.

Separation of Thallium from Cadmium

These two metals frequently occur together. The thallium may be detected by adding potassium bichromate and then excess of ammonia to the acid solution of these metals; the insoluble thallium chromate will then be precipitated.

Sulphuretted hydrogen passed into an acid solution of these two metals only precipitates the cadmium.

Potassium iodide added to a neutral solution only precipitates the thallium.

Commercial cadmium sulphide, as sold for artists' use, varies considerably in tint, some specimens being of a much deeper orange than others. Thallium is frequently present in the dark-coloured varieties, and it is therefore not improbable that the variations of colour in cadmium sulphide are due to traces of thallium. As an instance of a highly thalliferous cadmium sulphide, we may especially mention a beautiful specimen from Nouvelle Montagne, which formed a prominent object in the Belgian Department of the Exhibition of 1862.

Separation of Thallium from Gallium

This separation is not effected satisfactorily by precipitating the alcoholic solution with potassium iodide, as thallium remains in the filtrate and sensible traces of gallium are in the deposit. It is not more advantageous to reduce the thallium to the metallic state by means of a sheet of zinc. There are thus introduced into the analysis the impurities so frequently contained in zinc, and the thallium carries down gallium, unless the liquid is kept sufficiently acid, and then the

precipitation of the thallium is incomplete. The following processes may be recommended, though in different degrees :—

(*A*) Boiling after supersaturation with ammonia gives good results with thallium sulphate, chloride, or nitrate, if slightly acid. The salts must previously be reduced to the lowest stage of oxidation by the addition of a few drops of a solution of sulphurous acid. If slight traces of thallium remain in the precipitate they are entirely eliminated by repeating the boiling with ammonia ; the gallium oxide obtained then gives no spectroscopic indication of thallium.

(*B*) Calcium and barium carbonates precipitate gallium in the cold without rendering the thallium insoluble beyond slight traces, which disappear entirely during the operations for removing the lime or baryta. Before adding the carbonates the liquid is reduced by means of sulphurous acid.

(*C*) Calcium carbonate may be used in heat after reduction by means of sulphurous acid. There are sensible traces of thallium in the precipitate, but they are subsequently eliminated along with the lime.

(*D*) Cupric hydrate, as also metallic copper and cuprous oxide, are the best reagents, for the gallium is totally precipitated without carrying down a trace of thallium. If cupric hydrate is employed, the thallium salts must previously be reduced to the lowest stage of oxidation by means of sulphurous acid.

(*E*) If the quantity of thallium is not too considerable, so that its chloride remains dissolved, gallium may be precipitated by potassium ferrocyanide in a very acid solution and at a temperature of 70°. Traces of thallium contaminate the deposit, which is redissolved in a small excess of potash ; there are added to the liquid a few drops of ammonium sulphide recently prepared, and the whole is filtered to separate thallium sulphide. The clear solution is evaporated to a small bulk, supersaturated with a large excess of hydrochloric acid, and mixed with a little ferrocyanide. The slight traces of gallium carried down by the small quantity of thallium sulphide may generally be neglected. If needful, they may be separated by known methods.

(*F*) Thallium may be thrown down by platinum chloride from an alcoholic solution, acidified with hydrochloric acid. A prolonged current of sulphuretted hydrogen removes the platinum contained in the liquid, from which is afterwards obtained gallium containing merely traces of thallium. The chloro-platinate, suspended in water acidified with hydrochloric acid, is treated with hydrogen sulphide, which renders the platinum insoluble. The thallium salt obtained does not contain sensible traces of gallium.

CHAPTER V

URANIUM, VANADIUM, MOLYBDENUM, TUNGSTEN

URANIUM

Estimation of Uranium

(*A*) H. Rose[1] recommends the employment of ammonium sulphide as a precipitant for uranium, as it completely separates this metal from its solutions, provided they are previously saturated with ammonia. No inconvenience attends the presence of a quantity of ammoniacal salts in the solution, excepting, of course, ammonium carbonate and alkaline carbonates in general. The precipitate is black, but with a large excess of sulphide it may be reddish brown. It is to be washed with water containing a little ammonium sulphide. The precipitate contains no uranium sulphide, but consists essentially of uranium protoxide.

After desiccation it is roasted, to expel any sulphur which may adhere to it ; it is then calcined at a high temperature in a current of hydrogen, and left to cool.

Pure uranium protoxide is thus obtained. Should the solution contain much potassium salts, or other strong non-volatile base, the precipitate may retain a little of them.

(*B*) If a rapid process is required for the estimation of the commercial value of uranium, the following process of Patera's will give sufficiently accurate results, although it is not so trustworthy as the one just described.

A weighed quantity of the mineral is dissolved in nitric acid, taking care not to employ a large excess of acid. The solution is diluted with water, and, without filtering, supersaturated with sodium carbonate. It is now boiled to complete the solution of the uranium, and to promote the separation of the iron, lime, &c., carbonates. The filtered solution of uranium oxide in sodium carbonate now contains only traces of foreign substances, and the uranium will be precipitated in the form of sodium uranate with an excess of acid, on the addition of caustic soda. The orange-yellow precipitate is collected on a filter, washed for a short time, and then dried. It is then removed from the

[1] *Pogg. Ann.* vol. cxvi. p. 352.

filter and heated to redness in a platinum crucible, the ashes of the filter, burnt apart, being added to the precipitate. The mixed residues are now placed on another filter and again washed, dried, and ignited, as before. The residuum of this second calcination is acid sodium uranate, from the weight of which the amount of uranoso-uranic oxide in the mineral may be calculated. 100 parts of the sodium uranate represent 83 parts of uranoso-uranic oxide.

Volumetric Estimation of Uranium

The author prefers Guyard's process for this estimation, which depends on the precipitation of an insoluble triple ammonium, uranium, and manganese phosphate, when an acid solution of manganese phosphate is added to an acid solution of uranium and ammonium acetate.

The test solution of manganese phosphate is prepared as follows :— Phosphoric acid solution of a syrupy consistency is heated in a platinum dish, and manganese sesquioxide in fine powder is added by degrees, stirring frequently. The mixture is then heated for some time, and when the fused mass assumes a blue tint, and the phosphoric acid begins to volatilise, it is allowed to cool. It then becomes purple, and if dissolved in water it forms a purple solution resembling that of a permanganate. This solution is diluted, so that 30 c.c. shall represent 1 gramme of metal. The tinctorial power of manganese phosphate is very weak.

To titrate this solution use a known quantity of pure uranium sesquioxide in the form of acetate. The precipitate appears white with a yellowish shade. As soon as the precipitation is complete the precipitate has a rose colour. It must be remembered that the presence of ammonium oxalate interferes with the reaction.

To apply this process to ores, &c., dissolve a gramme or more of the substance in nitric or hydrochloric acid, or a mixture of the two. The solution is then supersaturated with ammonium carbonate, which separates uranium sesquioxide from the metallic oxides which so often accompany it. In many cases this operation suffices ; but if the ore contains phosphorus or arsenic, or an oxide soluble in ammonium carbonate, the uranium must be precipitated by ammonia and ammonium sulphide in the state of protoxide, as already described, and filtered off. The precipitate is dissolved in ammonium carbonate, and then transformed into the acetate of the sesquioxide. In any case the uranium must be brought into this state before estimation ; but oxalic acid must be absent.

The solution is now diluted with about a litre of cold water, and then the standard solution of manganese phosphate is gradually added from a burette until the whitish precipitate of uranium, manganese, and ammonium phosphates appears rose-coloured. This process is very rapid, and with a little practice is accurate.

In testing for uranium with potassium ferrocyanide, it must be borne in mind that the presence of ammonium oxalate prevents the formation of the red precipitate.

Estimation of Uranium

Patera's method for the estimation of uranium in its ores is as follows :—The mineral is dissolved in nitric acid, the solution is diluted, saturated with carbonate of soda, heated to boiling, and filtered. The uranium is precipitated in the clear liquid by means of caustic soda ; the precipitate of uranate of soda is collected and weighed as such. This method, although sufficiently exact in the case of pure minerals, gives results which are much too high, in the case of samples rich in silica, as the precipitate will then contain a considerable proportion of silicic acid. The precipitate must in such a case be treated with hydrochloric acid, evaporated to dryness, taken up with dilute hydrochloric acid, filtered, and the uranium in the clear liquid reprecipitated by means of caustic soda or ammonia.

H. McCoy [1] gives the following process for the analysis of uranium ores :—The determination of uranium is perhaps performed most quickly by reduction with zinc in dilute sulphuric acid and subsequent titration with potassium permanganate. The method is quick and fairly accurate. For the determination of uranium in pitchblende or gummite, which contain iron, lead, calcium, and perhaps thorium as well as uranium, the ore is dissolved in warm dilute nitric acid and treated with a large excess of a saturated solution of sodium carbonate. After boiling for two minutes, the precipitate, which contains all the iron, together with calcium, thorium, and the greater part of the lead, is filtered off. The filtrate, which contains all the uranium, is neutralised with sulphuric acid and heated to drive off the carbon dioxide. The uranium is then precipitated as sodium uranate with sodium hydroxide, and the precipitate filtered off. This is then dissolved in dilute sulphuric acid, reduced with zinc, and titrated with permanganate.

Separation of Uranium from the Cerium Metals

Wolcott Gibbs's method of precipitating the cerium metals with sodium sulphate in the form of double sodium sulphates with cerium, lanthanum, and didymium will effect this separation perfectly. These double sulphates are insoluble in a saturated solution of sodium sulphate, while the double sulphate of sodium and uranium sesquioxide is readily soluble, and may be easily washed out from the highly crystalline insoluble double sulphates of the cerium group.

[1] *Chemical News*, Oct. 21, 1904.

Separation of Zinc from Uranium

To a nearly neutral and somewhat dilute solution of the two metals add sodium acetate in excess, boil, and pass sulphuretted hydrogen through the boiling solution till all the zinc is precipitated as sulphide. Filter quickly, wash, and finish as described at page 145.

Separation of Aluminium from Uranium

The separation of these two metals may be effected in the same manner as that of aluminium and zinc above described.

Separation of Gallium from Uranium (Yellow Uranic Salts)

The four following methods are suitable for exact analyses :—

(*A*) The hydrochloric solution, slightly acid, is treated at a boil with an excess of cupric hydrate. The deposit contains all the gallium as well as a very sensible portion of uranium. It is redissolved in hydrochloric acid, diluted with water, and boiled in presence of a large excess of cupric hydrate. With from 10 to 15 parts of uranium to 1 of gallium four successive precipitations are required. The uranium is then entirely contained in the liquids, which are acidified, and are then traversed by a current of sulphuretted hydrogen. Copper sulphide is deposited, and the uranium salt is obtained on evaporating the filtrate.

(*B*) If there is iron to remove along with uranium, it is first reduced by heat with metallic copper, and then boiled with an excess of cuprous oxide. Four successive operations suffice to separate completely 1 part gallium from 10 to 15 parts uranium. The presence of very considerable quantities of alkaline salts does not interfere with the execution of the two methods just described, which may serve for the analysis of a mixture of gallium and of an alkaline uranate.

(*C*) The hydrochloric solution, slightly acid, is mixed with an excess of ammonium acetate, as also a certain quantity of zinc free from gallium, and is then treated with a current of sulphuretted hydrogen. The zinc sulphide carries down the gallium, while the uranium remains in solution. Only the zinc sulphide, being very difficult to wash, ought to be redissolved in hydrochloric acid and reprecipitated in an acetic solution. The gallium is separated from the zinc, as described below. The uranium is separated by evaporating the liquids with an excess of hydrochloric acid to expel acetic acid, and then destroying the ammoniacal salts with aqua regia. It is essential to add to the liquid so much zinc chloride that the zinc sulphide may carry down all the gallium. Some drops of zinc chloride should be added to the filtered sulphuretted liquids to ascertain the absence of gallium in this last zinc sulphide. Alkaline salts do not interfere with the separation

of uranium and gallium by means of zinc sulphide. The present process is suitable for the detection of small traces of gallium in large masses of uranic compounds, especially in presence of metals such as aluminium. But in ordinary cases it is better to make use of the reactions of copper hydrate, or of metallic copper and cuprous oxide.

(*D*) Uranium may be precipitated by a slight excess of caustic potash as an alkaline uranate, scarcely retaining a slight trace of gallium, which may be entirely removed by redissolving in hydrochloric acid and reprecipitating with potash. The alkaline liquids collected contain all the gallium and traces of uranium. These liquids are slightly supersaturated with hydrochloric acid, mixed with an excess of cupric hydrate and raised to a boil, when the gallium is completely precipitated. In the filtrate, copper, uranium, and potassium are separated by known methods. When the potash employed contains a little carbonate (a frequent case), the proportion of uranium not precipitated is sensibly increased. This is without inconvenience, since the separation of the gallium and of the dissolved uranium is effected afterwards by the action of cupric hydrate.

Separation of Uranium from most Heavy Metals

(*A*) Uranium may be easily separated by H. Rose's method from metals which are precipitated from their solutions by ammonium sulphide, in the following manner :—Add to the solution an excess of ammonium carbonate mixed with sulphide. All the oxides which the sulphide transforms into sulphides are precipitated, while the uranium protoxide is dissolved in the ammonium carbonate. Leave it to deposit in a closed vessel, wash the precipitate by decantation in water containing ammonium carbonate and sulphide, and filter. Gently heat the filtered liquid to expel most of the carbonate, decompose the sulphide by hydrochloric acid, oxidise the uranium protoxide with nitric acid, and precipitate the uranium oxide by ammonia. If the operation is quantitative, it should, before weighing, be calcined in a current of hydrogen.

(*B*) A. Remelé recommends ammonium sulphide as the best reagent for the separation of uranium from alkaline earths and alkalies, except in case of barium. Foullon and Alibegoff find that uranium and calcium cannot be separated in this manner. Foullon recommends in this case the use of ammonium oxalate in a solution previously rendered alkaline by ammonium carbonate. He first mixes the hydrochloric solution with a little ammonium oxalate, and then adds ammonium carbonate until all the uranium oxide is redissolved ; ammonium oxalate is then added in excess, and the precipitate allowed to deposit in the absence of strong light.

(*C*) Alibegoff, working in this manner, obtained better results than with ammonium sulphide, but the calcium oxalate was always more

or less contaminated with uranium. He therefore adds to a solution of uranium chloride some elutriated mercury oxide, when the uranium is completely deposited on boiling, and the supernatant liquid has quite lost the colour of the uranium salts. In case of uranium solutions in the oxygen acids, a solution of ammonium or sodium chloride is added. A very dilute solution of ammonium chloride is used for washing, as the precipitate, a mixture of uranyl hydroxide and basic mercury uranate, is slightly soluble in water.

In carrying out this method the author adds to the solution of uran-oxychloride a few drops of ammonium chloride solution, and heats to a boil. He then adds the pure elutriated mercuric oxide, carefully avoiding excess. After again boiling and shaking round (in preference to stirring) allow it to cool, when the precipitate settles quickly, and the liquid becomes colourless. Decant a few times, pour it upon the filter, and wash in cold water containing ammonium chloride. The precipitate along with the filter is heated in a platinum crucible, carefully at first, then in the uncovered crucible with a gradually increasing heat, and lastly over a blast. The product is weighed as the olive-green uranous-uranic oxide.

In presence of calcium the process is the same. If the alkaline earths are in large proportion, their partial precipitation may be avoided by boiling up once more after decantation with water containing ammonium chloride. In the filtrate the strontium and calcium are determined in the usual manner after removing the mercury with ammonium sulphide.

Uranium may be separated from magnesium by boiling with a sufficiency of ammonium chloride and then precipitating with mercuric oxide as above.

Separation of Uranium from Phosphoric Acid

(*A*) In laboratories where the estimation of phosphoric acid by the uranium process is frequently practised, it occasionally becomes advisable to effect the separation of uranium from the acid. M. Reichardt describes the following plan, which has proved very successful in the author's laboratory :—Dissolve the uranium phosphate in hydrochloric or nitric acid, apply heat, add excess of iron perchloride, and next, excess of solution of sodium carbonate, wherein, aided especially by the large quantity of carbonic acid which is thus set free, the uranium oxide is readily dissolved, while the phosphoric acid is combined in an insoluble form with the iron oxide. The solution of uranium oxide in sodium carbonate is acidified with hydrochloric acid, boiled to expel carbonic acid, and the uranium oxide finally precipitated with ammonia.

(*B*) He has since proposed the following modification :—He dissolves the uranium phosphate in sodium carbonate, and precipitates

with a magnesium salt. If the precipitate of uranium phosphate is old, it is necessary to dissolve it first in hot concentrated hydrochloric acid, adding nitric acid to peroxidise any iron present. The solution is then heated and soda added in excess. After filtration the phosphoric acid is thrown down by adding ammonia and magnesium chloride. After twenty-four hours the liquid is separated from the ammonio-magnesium phosphate. It is acidified with hydrochloric acid, heated, and the uranium oxide precipitated by ammonia, avoiding excess.

VANADIUM

Detection of Vanadium

(*A*) Mr. Richard Apjohn uses the following process:—8 grammes of the finely powdered mineral are fluxed with four times their weight of sodium carbonate. The fused mass is allowed to cool, and a small quantity of nitre added. It is now heated over a Bunsen lamp, taking care that the crucible does not attain more than a dull-red heat. The mass is lixiviated with water, and the aqueous solution boiled with ammonium carbonate and filtered to remove silicic acid. The filtrate is evaporated with hydrochloric acid, and sulphuretted hydrogen passed through to precipitate any metals of the lead group which might be present. The filtered solution is then heated with an equal volume of a very concentrated solution of ammonia, and sulphuretted hydrogen is passed through till all the free ammonia is saturated.

The solution assumes a beautiful intense cherry-red colour, a sure indication of vanadium. This coloured liquid is filtered off and saturated with hydrochloric acid; the precipitate, containing sulphur and vanadium sulphide, is dried and ignited, and the residue melted with nitre. From the potassium vanadate thus formed the characteristic blowpipe reactions are obtained.

(*B*) For the analysis of vanadium sulphates Dr. B. W. Gerland proceeds as follows:—To estimate the sulphuric acid, vanadium and alkalies, the weighed sample is dissolved in water, according to circumstances, with the aid of nitric acid or ammonia, or both. After cooling, the clear solution is acidulated with nitric acid, mixed with lead acetate and alcohol until all sulphuric acid is precipitated. After a few hours' rest, when the lead sulphate has settled, it is filtered and washed with dilute alcohol. No difficulty is experienced if the vanadium is present as tetroxide, but with the pentoxide it often happens that lead vanadate is mixed with the sulphate, recognisable by the intense yellow colour of the latter. In that case only the clear liquor is poured off and passed through a small filter, the precipitate treated with a little nitric acid, if necessary heated on a water-bath, then mixed with water and afterwards with alcohol, and allowed to stand for a few hours. The vanadate is generally dissolved by this

treatment, and the lead sulphate appears perfectly white it is now thrown on the same filter and treated as before. But it may happen, particularly when the precipitation has taken place at a higher temperature, that the sulphate still retains a small amount of vanadate. Ammonium carbonate is the most efficient means for separating this small residuum. The solution of this reagent scarcely acts upon the pure lead vanadate ; but if the latter is mixed with lead sulphate the former is left intact, while the sulphate is rapidly converted into lead carbonate. The solution, therefore, contains all the sulphuric acid, and only inappreciable traces of vanadium ; it is treated with barium chloride in the usual way, and the barium sulphate weighed. The insoluble part, after washing, is heated with acetic acid to dissolve the lead carbonate, and the remaining vanadate is thrown upon the filter already used, washed, and united to the main vanadium precipitate.

The solution from the lead sulphate is neutralised with ammonia, acidulated with acetic acid, and precipitated with lead acetate in small excess. If vanadium tetroxide is present, as shown by the dark colour of the precipitate, it is necessary to oxidise it, and this is readily effected by the addition of bromine water. The precipitate will now be of a bright orange or yellow colour, and very bulky ; but heating, assisted by agitation, causes it to contract to a heavy curdy mass. In this condition it can be easily filtered and washed on a Bunsen filter under a low pressure. It is of advantage to add a small amount of lead acetate to the wash-water. The precipitate is dissolved in nitric acid, the solution treated with sulphuric acid and alcohol, and after a few hours' rest separated from the lead sulphate, which after washing is free from vanadium, as Roscoe has already pointed out. The filtrate containing the vanadium is evaporated in a porcelain basin, at a very low temperature (the water-bath at boiling-heat would cause a very lively evolution of gas, and loss, particularly when sulphuric acid is added in great excess), the residuum transferred to a platinum dish, is again evaporated, and the sulphuric acid driven off by carefully raising the temperature. All the vanadium sulphates (those of the trioxide, tetroxide, and pentoxide) leave vanadium pentoxide at red heat. But this is readily reduced at that temperature by dust, and even by the gases from the lamp ; it is therefore necessary to cover the capsule well, and prevent the access of fire gases, which is best accomplished by the use of a Rose's tube. The heat is then increased to a bright red, which again causes an evolution of gas, and leaves a pure pentoxide, whose weight is taken. (If the vanadium sulphates are decomposed at a dark-red heat, until gas-bubbles cease to appear, the pentoxide gives off gas again, when the heat is raised and loses weight amounting to about 0·5 per cent.) The platinum vessel suffers in shape by this operation. A dish which was used very often had originally a flat bottom, but now the latter is pressed out by the vanadium pentoxide, so that the form is hemispherical, and at least 3 millimetres deeper.

The filtrate from the lead vanadate contains, besides the alkalies, a small amount of vanadium. Vanadium solutions behave, as I have ascertained, similarly to those of cobalt under the influence of sulphuretted hydrogen; a dilute acetic solution with small excess of free acid, particularly in presence of an alkaline acetate, is slowly acted upon by that gas, and the vanadium precipitated as vanadyl sulphide. If the filtrate, therefore, is treated with sulphuretted hydrogen, according to Roscoe's direction, the vanadium which it contains will be separated with the lead sulphide; it is on that account preferable to use sulphuric acid and alcohol for the elimination of the lead. The filtrate from this lead sulphate is evaporated, and the residuum heated until the ammonium salts are driven off. The remaining alkalies are dissolved, treated with acetic acid, and once more submitted to the described process for the separation of the small quantity of vanadium with lead acetate. The filtrate from this lead vanadate precipitate is most expeditiously treated with ammonia and ammonium sulphide at boiling-heat, and the solution separated from the lead sulphide is worked up for the estimation of the alkalies.

The Estimation of Vanadium by Titration with Permanganate

The first condition is the conversion of vanadium to a certain stage of oxidation. Aqueous sulphurous acid converts vanadium pentoxide in solution to tetroxide, which is perfectly unchangeable in acid liquors, so that these can be boiled for the expulsion of the excess of sulphur dioxide. The tetroxide solutions undergo a further reduction, which, if not guarded against, might make the test fallacious. The tetroxide in solution, containing an excess of sulphuric acid, is converted into vanadium trioxide by carbonaceous matter (which is introduced by alcohol or with dust), and by sulphur at a temperature of 120°, and that at higher temperatures (about 150°) the acid vanadium sulphate separates in the form of insoluble needles, and at about 200° the yellow vanadium sulphate appears as a heavy amorphous sediment mixed with the former. If such conditions are apprehended, it is necessary to add permanganate until the test-solution remains pink after boiling, as proof that all vanadium is oxidised to the pentoxide, then to treat with sulphurous acid, and after expelling the excess, titrate again with permanganate.

The colouration obtained by the permanganate generally disappears after a short time, and is reproduced by the first drop of this solution, to bleach again, and so on, until, after a large quantity (up to 20 per cent. of what was used to produce the first pink) has been added, the solution becomes opaque by the separation of manganic peroxide. In every case the first appearance of the pink colour is the

indication that all vanadium is converted into the pentoxide, and the quantity of permanganate used corresponds exactly with that required by an equivalent quantity of oxalic acid. In hot solutions the first appearance of pink is permanent. The reaction of the permanganate solution takes place instantaneously; the colour changes from blue, through green, to yellow and pink, indicating at every stage the quantity of the standard solution required. The titration of vanadium with a standard solution of permanganate is in fact one of the most elegant, expeditious, and accurate methods of volumetric analysis.

Detection of Vanadium in Iron Ores

R. Böttger heats the finely powdered ore to redness for a long time with nitre and sodium carbonate. He lixiviates with boiling water and almost neutralises with nitric acid, free from the lower oxides of nitrogen, leaving the solution slightly alkaline. The bulk of the alumina and silica falls down. The filtrate is treated with barium nitrate, when barium vanadate is thrown down, from which vanadic acid is easily separated.

Preparation of Vanadic Acid from Lead Vanadate

(*A*) For the following method the author is indebted to the late Professor Wöhler:—Finely pulverise the mineral and attack it with a mixture of concentrated hydrochloric acid and alcohol; wash the precipitated lead chloride with alcohol, and drive off the hydrochloric acid by means of heat from the blue solution of vanadium chloride. This solution, treated with excess of caustic soda, deposits vanadium oxide, which may be converted into vanadic acid by a current of chlorine.

(*B*) For the following method of preparing vanadic acid on the large scale from the cobalt red sandstone at Mottram, we are indebted to Sir Henry Roscoe, whose researches on the chemistry of this metal [1] have afforded so great an insight into the properties of this remarkable element.

The sandstone possesses a light colour, and contains from 0·1 to 0·3 per cent. of the cobalt, nickel, and copper oxides. These metals are extracted commercially by the Alderley Edge Copper Mining Company; the ore is crushed and digested with hydrochloric acid; bleaching liquor and milk of lime are then added to alkaline reaction; a portion of the copper, together with the whole of the nickel and cobalt, remains in solution, while the small portion of vanadium which the ore contains falls down in the precipitate. It was from this precipitate that Sir H. Roscoe was fortunate enough to secure a plentiful supply of this rare metal. A rough analysis of the crude lime precipitate

[1] *Phil. Trans.* 1868, p. 1, and 1869, p. 679.

showed that it contained about 2 per cent. of vanadium, together with lead, arsenic, iron, lime, and sulphuric and phosphoric acids.

In order to prepare pure vanadium compounds in quantity from this material, 3 cwt. were dried and then finely ground with four times its weight of coal, and the mixture well furnaced with closed doors for several days until the greater part of the arsenic had been driven off. The coal having been thus burnt off, the mass was then ground up with one quarter of its weight of soda-ash, and well roasted in a reverberatory furnace with open doors for two days to oxidise the vanadium to a soluble vanadate ; the mass was then lixiviated, and the solution drawn off from insoluble matters ; the liquid was acidified with hydrochloric acid, and sulphurous acid was then passed into the solution to reduce the arseniates, when the remaining arsenic was precipitated by sulphuretted hydrogen. The deep-blue solution thus obtained was carefully neutralised by ammonia (an excess causes much of the vanadium to pass into solution), the precipitated vanadium oxide washed on cloth filters, oxidised by nitric acid, and evaporated to dryness. The well-dried crude vanadic acid was then boiled out with a saturated solution of ammonium carbonate, which left iron oxide, calcium sulphate, and aluminium sulphate insoluble, and the filtrate evaporated until the insoluble ammonium vanadate separated out. This crude vanadate was then washed with sal-ammoniac solution to free it from sodium salts, and recrystallised.

In order to prepare pure vanadic acid from this salt, it was roasted in the air, and the powdery acid obtained was suspended in water into which ammonia gas was passed ; the dissolved ammonium vanadate was separated by filtration from a residue containing silica, phosphates, &c., and was crystallised by evaporation in platinum.

(*C*) Another method of preparing pure vanadic acid is to obtain the pure oxychloride, and decompose this by water, when vanadic acid is yielded as a fine orange-coloured powder. The oxychloride is prepared by intimately mixing sugar charcoal with crude vanadic acid, and heating the mixture to redness in a current of hydrogen. After cooling in hydrogen, the mixture of trioxide and carbon is removed to a hard glass retort heated by a large Bunsen lamp, and a current of dry chlorine gas passed in. The crude oxychloride comes off as a reddish-yellow liquid, which is purified by distillation in a current of carbonic acid, and afterwards rectified several times over clean sodium. It is a lemon-yellow liquid, boiling at 126·7° C.

Purification of Vanadic Acid from Phosphorus

Sir H. Roscoe has found that phosphorus is very difficult to separate from vanadium. The action of even traces of phosphoric acid on vanadic acid is most remarkable ; if present in quantities exceeding 1 per cent. of the weight of the vanadium, it altogether prevents the

crystallisation of the vanadic acid, and the fused mass possesses a glassy fracture and a black vitreous lustre. If much phosphorus is contained with the vanadium, the method which has proved most effectual for its removal is to deflagrate the finely divided impure acid with its own weight of sodium in a well-covered wrought-iron crucible, and wash the resulting mixture of vanadium oxides by decantation until the wash-water ceases to give an alkaline reaction ; frequently this operation has to be repeated three times before the molybdenum test ceases to indicate phosphorus.

Detection and Estimation of Vanadium and Titanium in Basalts

Mr. G. Roussel proposes the following process :—The samples, in fine powder, are fused with thrice their weight of sodium carbonate ; the mass, when cold, is powdered, and treated with water acidulated with hydrochloric acid ; it is evaporated to dryness, heated for twenty-four hours on the water-bath, treated again with acidulated water, and then filtered. The silica eliminated is, after calcination, set to digest for twelve to eighteen hours in hot concentrated sulphuric acid, treated after cooling with an excess of cold water, and filtered. This operation is repeated, and the total liquid is mixed with ammonia, which throws down titanic acid. It is filtered, washed, and ignited. The liquid separated from the silica also contains titanic acid. To separate it, it is treated with sodium sulphite, sulphurous acid, and sodium thio-sulphate, boiled for twenty minutes, and there is left the mixed precipitate of sulphur, alumina, and titanic acid. The sulphur is driven off by gentle heating, and the residue is mixed with the former precipitate, and digested in a sealed tube with pure hot concentrated hydrochloric acid, in order to eliminate the alumina. After this series of operations, the titanic acid is pure, and may be dried and weighed. The same basalts contain vanadium, but in a far smaller proportion. To obtain a ponderable quantity, it is necessary to operate upon a sample twenty times larger than is required for the detection of titanium. The basalt is fused with sodium carbonate and the mass oxidised with a little saltpetre. After cooling, the pulverised mass is treated with a large quantity of boiling water, filtered, and washed perfectly. The liquid is evaporated, boiled with ammonium carbonate and filtered, treated with ammonium sulphide, and left to settle for two or three days. If the solution contains vanadium, at this moment the fine red colour of vanadium sulphide, when dissolved in an alkaline sulphide, appears in the liquid. It is filtered, and hydrochloric acid is poured into the liquid, which throws down vanadium sulphide mixed with sulphur. The latter disappears on careful heating, when the vanadium sulphide, VS_2, is weighed. The largest percentage of titanium was 2·378, and that of vanadium 0·023.

Separation of Uranium and Vanadium

Carnotite is perhaps the uranium ore which occurs most abundantly in America. It is chiefly a potassium-uranium vanadate of unknown composition. Different methods for the separation of the uranium from the vanadium have been suggested, but none of them seems to be quite satisfactory. The methods of Friedel and Cumenge and of Ohly have been examined, but the separation was not complete in either case. A modification of the method of Langmuir [1] gave satisfactory results. Langmuir's method consists in precipitating vanadium as mercurous vanadate from a nitric acid solution neutralised by addition of mercuric oxide. An excess of oxide, however, may easily give rise to the precipitation of some of the uranium. Hence the method was altered to avoid this difficulty. It was found that no uranium separated from a feebly acid solution of uranium nitrate if a large excess of sodium acetate was added and the solution then boiled, but that by addition of sodium acetate and mercurous nitrate to a feebly acid solution of a vanadium salt, the vanadium was completely precipitated.

The method of analysis of carnotite finally employed is as follows:— A gramme of the mineral is dissolved in a small quantity of warm dilute nitric acid, and filtered from the insoluble residue after being diluted with water. The filtrate is almost, but not quite, neutralised with sodium hydroxide, and heated to boiling. A solution of about 1·5 grammes of mercurous nitrate is then added, and a solution of 3 grammes of sodium acetate. After boiling for a short time, the precipitate of mercurous vanadate separates out, and is at once filtered. The excess of mercury in the filtrate is removed by means of sulphuretted hydrogen, and the uranium is determined in the usual way in the solution obtained, which is always found to be free from vanadium.

Oliver P. Pritchle [2] gives the following process for the analysis of carnotite. Both uranium and vanadium can be reduced to their lower oxides in a sulphuric acid solution, with metallic aluminium, and then again oxidised to their higher oxides with a solution of potassium permanganate.

Weigh into a 6-oz. flask ½ gramme of the finely powdered ore, moisten with a few drops of water, add 10 cubic centimetres of nitric acid, and digest at a slow boiling temperature for about one hour. Remove from the source of heat, dilute with 10 cubic centimetres of water, add gradually to neutralisation a saturated solution of sodium carbonate and then 5 cubic centimetres excess; then add 20 cubic centimetres of a 20 per cent. solution of caustic soda. Boil slowly for

[1] *Journ. Am. Chem. Soc.* 1901, vol. xxiii. p. 688.
[2] *Chemical News*, Nov. 30, 1900.

about half an hour, and then allow the precipitate to settle until the supernatant liquid is quite clear.

The uranium, vanadium, and iron are all precipitated by the sodium carbonate, but on adding a moderate excess of sodium carbonate, and a large excess of caustic soda, the vanadium is dissolved, while the uranium and iron remain insoluble. Uranium is easily precipitated by sodium carbonate and sodium hydrate in the presence of an iron salt.

Filter off the precipitates of iron and uranium, and wash a few times with a solution of caustic soda. Do not wash with water, as it washes the uranium precipitate through the filter. The filtrate should show no uranium on testing a nitric acid solution with potassium ferrocyanide. The filtrate contains all the vanadium, and it could be determined from this solution were it not for the fact that so large a volume of salt solution is difficult to evaporate and displace with sulphuric acid, without violent bumping and considerable loss by spattering. Furthermore, vanadic acid is not easily soluble in nitric acid, and only by long digestion is all the vanadium obtained in solution. Therefore, it is more expedient to determine the vanadium in a separate sample as given below.

Dissolve the precipitates on the filter with 20 cubic centimetres of hot dilute nitric acid (1 : 1), letting the solution run into the original flask. Dilute the solution with about 40 cubic centimetres of water, add ammonia until a slight permanent precipitate forms ; then add 40 cubic centimetres of a saturated solution of ammonium carbonate, freshly prepared and heated slightly to remove any excess of carbonic acid. Uranium is easily soluble in an excess of ammonium carbonate, and the iron is insoluble.

Heat to boiling for a few minutes, but do not boil, as the ammonium carbonate will be decomposed, and the uranium precipitated by the ammonia. Filter off the iron precipitate, and wash well with a 2 per cent. solution of ammonium carbonate. The filtrate contains all the uranium, and should not show a trace of vanadium by testing with hydrogen peroxide in a nitric acid solution. A red colouration shows the presence of vanadium. Add slowly 20 cubic centimetres of dilute sulphuric acid (1 : 1), and boil until dense white fumes are given off. Cool, dilute to about 100 cubic centimetres, add about 4 square inches of sheet aluminium, cut into half a dozen strips, and boil for half an hour or until the yellow solution is reduced to a sea-green colour. Fill the flask with water, decant into a No. 4 beaker, and titrate the uranous solution, hot, with a standard solution of potassium permanganate. The iron equivalent of the permanganate, multiplied by 120/56, will give the amount of uranium in the $\frac{1}{2}$-gramme sample.

Dissolve the iron precipitate with hot dilute HCl, add 10 cubic centimetres sulphuric acid, boil to white fumes, cool, dilute, reduce with metallic aluminium, decant into a beaker, and titrate with the standard solution of potassium permanganate.

The vanadium is determined in a separate sample, as follows :— Weigh into a 6-oz. flask ½ gramme of the ore, add a few drops of water, 10 cubic centimetres nitric acid, and 10 cubic centimetres sulphuric acid. Boil until the nitric acid is all expelled, and dense white fumes of sulphuric acid are evolved. Cool, dilute, add aluminium, and reduce the uranium, vanadium, and iron by boiling for half an hour. Fill the flask with water, decant into a beaker, and titrate, hot, with the standard solution of potassium permanganate. The number of cubic centimetres of permanganate, less the number of cubic centimetres required for the uranium and iron, is the permanganate required to oxidise the vanadium, which, multiplied by 51·1/112, gives the amount of vanadium in the ½-gramme sample.

The end reaction of vanadium is slow, and permanganate must be added slowly until a permanent pink is obtained. The use of aluminium is preferable to either zinc or sulphurous acid as a reductor. In the case of vanadium, if sulphurous acid is used, the vanadium is not reduced as low as when aluminium is used, but only to the blue colour, and requiring, approximately, half the amount of potassium permanganate.

The volumetric estimation of vanadium by potassium permanganate is a beautiful titration, changing from purple, through blue, green, and yellow, to pink.

MOLYBDENUM

Detection of Molybdic Acid

M. O. Maschke has improved the process of Schoenn. According to the latter, traces of molybdic acid and its compounds may be discovered by the blue colouration produced on heating it with concentrated sulphuric acid in a porcelain capsule. This test is rendered exceedingly convenient and much more certain by the following modification :—A little concentrated sulphuric acid is applied to a piece of platinum foil, bent so as to form a slight depression ; upon the acid is placed a little of the substance in powder, and the foil is heated till vapours escape in abundance ; it is then allowed to cool, and repeatedly moistened with the breath. When, after cooling, only minute spots are visible, the sulphuric acid, after being breathed upon, takes an intense blue colouration. On heating the platinum foil, the blue colour vanishes, but reappears on cooling. It is completely decolourised if a considerable quantity of water is added.

Estimation of Molybdic Acid

T. M. Chatard proceeds as follows :—Add to the boiling solution of the molybdate, lead acetate in slight excess. Boil for a few minutes ; the precipitate, at first milky, will become granular and will subside

easily, leaving a perfectly clear supernatant liquid. Care must be taken in boiling, as the thick milky fluid is very apt to boil over. A ribbed filter is to be used, and the precipitate is to be washed with hot water. The washing proceeds with great ease and thoroughness, and not the slightest milkiness should be apparent in the filtrate. The precipitate is dried at 100°, separated from the filter, and ignited in a porcelain crucible.

The process gives very good quantitative results and is both easy and expeditious. The precipitated molybdate separates easily from the filter, and can be heated to low redness without decomposition.

Separation of Molybdic Acid from Phosphoric Acid

E. Reichardt dissolves the phospho-molybdic compound in sodium carbonate, and precipitates by means of magnesia mixture; the solution is treated with aqua regia, and evaporated to dryness to expel excess of acid. The residue is then treated with water, which leaves the molybdic acid undissolved.

Estimation of the Available Molybdenum in Molybdenite

H. Borntrager[1] recommends the following method:—1 gramme of the mineral is digested for two hours with 25 cubic centimetres of concentrated nitric acid in an Erlenmeyer flask. The molybdic acid formed is redissolved in ammonia, the solution is filtered, and the residue again treated with nitric acid and ammonia. The filtrates are added together, acidulated with nitric acid, and evaporated to dryness. The dry residue is digested with alcohol at 50 per cent., which dissolves the nitrate of ammonia and leaves the molybdic acid intact. The latter is collected on a tared filter, and weighed. It may also be dissolved in normal ammonia and estimated by titration.

TUNGSTEN

Preparation of Tungstic Acid from Wolfram

The following process, due to Professor Wöhler, has been found to answer very well:—Reduce the wolfram (an iron and manganese tungstate) to fine powder, and digest at a gentle heat in a mixture of four parts strong hydrochloric and one part nitric acid, till yellow pulverulent tungstic acid is left behind. Wash this by decantation, dissolve in ammonia, and evaporate the solution to the crystallising point. The resulting ammonium tungstate calcined in the air leaves pure yellow tungstic acid.

[1] *Chemical News*, Feb. 2, 1900.

When the impure tungstic acid is dissolved in ammonia, a residue will be left which contains, besides undecomposed wolfram, small white grains composed of silica and niobic acid, and constituting about 2 per cent. of the wolfram.

Separation of Tungsten and Molybdenum

Of the few methods one can find for effecting the separation of tungsten and molybdenum, volatilisation of the molybdenum in a stream of hydrochloric acid gas is best known, and appears to be most commonly used. As a rule, tube volatilisations are made use of in metallurgical laboratories only as a last resource, or for research purposes. On this account a separation which can be made in every-day apparatus and with common reagents has been investigated by Fred Ibbotson and Harry Brearley.[1]

A number of circumstances can be arranged under which molybdenum and tungsten behave in diverse ways, but very few in which the behaviour (when the two elements are together) of the one is so sharply different from that of the other as to provide an accurate means of separating them. These methods chiefly depend on the solubility of the one and the insolubility of the other metallic compounds (generally oxides) in certain acids, and they are deficient because the WO_3 is never perfectly insoluble nor the MoO_3 perfectly soluble, except when alone.

The following experiments were made with the object of determining with what degree of accuracy one or two theoretically sound principles could be applied.

(*A*) Precipitate the Mo and W together by means of lead acetate, wash slightly with very hot dilute acetic acid, and ignite. Transfer to a beaker, and dissolve in concentrated HCl, using about as many cubic centimetres of acid as centigrammes of the lead salts.

The precipitates are most conveniently dissolved by heating just short of the boiling-point of the acid; in this way very few irritating fumes are evolved, and the acid is not weakened to any considerable extent before complete solution has been effected. To the clear or possibly faintly opalescent solution, add two or three times its bulk of boiling water; boil, allow to settle, decant the clear liquid through a small pulp filter, redissolve in about half the quantity of acid previously used, reprecipitate with water, and filter through the same pulp. The Mo is determined in the filtrate, either with or without removing the HCl, by precipitation as $PbMoO_4$.[2]

A number of experiments show that the complete decomposition of $PbWO_4$ can be relied on only by dissolving in strong HCl, and precipitating by dilution; diluted HCl does not completely decompose $PbWO_4$ after ignition.

[1] *Chemical News*, Jan. 12, 1900. [2] *Ibid.* vol. lxxviii. p. 203.

If twice as many cubic centimetres of acid are used as there are centigrammes of the lead salts, the tungsten is completely precipitated by diluting to three times the volume of the solution. Generally, larger amounts of acid used to dissolve the ignited precipitates require proportionately larger amounts of water for complete precipitation of the WO_3. The estimation is not then so satisfactory, as the greater the dilution the greater the liability to contamination with MoO_3.

(*B*) If the amount of W is small compared with the Mo, it is not by any means totally precipitated on diluting to the usual volume. The following method, which gives as good results under any circumstances as the preceding, should then be adopted :—

The HCl solution of the ignited lead salts, to which a few drops of HNO_3 have been added, is evaporated, preferably over the water-bath, until nearly pasty, when the WO_3 will have almost entirely separated. The mass is then diluted with 100 to 200 cubic centimetres dilute HCl (3 water to 1 acid), the solution boiled, and the WO_3 filtered off. The weak acid precipitates any WO_3 still unseparated by the evaporation, and is yet strong enough to hold the molybdenum in solution.

Whether the evaporation be performed slowly over the water-bath, or more rapidly, some of the WO_3 always adheres to the vessel, and cannot be cleared off. A good plan for estimating this consists in dissolving it in two or three drops of dilute ammonia. The solution is then absorbed by a piece of ashless paper which is ignited along with the main portion of the precipitate.

Separation of Tungsten Trioxide from Molybdenum Trioxide

Max J. Ruegenberg and Edgar F. Smith [1] effect the separation of tungsten from molybdenum as follows :—Their process is based on a statement that tungstic acid is insoluble in concentrated or dilute sulphuric acid, hot or cold, whereas molybdenum trioxide is very easily and rapidly dissolved. Upon trial it was found that sulphuric acid of specific gravity 1·378 dissolved molybdenum trioxide very readily, and apparently did not affect the tungsten trioxide. Acid of this concentration was therefore used with the following mixture of the two oxides :—

0·7355 gramme of tungsten trioxide and 0·0185 gramme of molybdenum trioxide were digested for a few minutes with 25 cubic centimetres of warm sulphuric acid. The insoluble portion was filtered out, and washed with water containing sulphuric acid. After drying, it was ignited and weighed. It equalled 0·7350 gramme.

[1] *Chemical News*, Jan. 4, 1901.

The other trials, conducted in precisely the same manner, were as follows :—

	II	III	IV	V	VI
	Grammes	Grammes	Grammes	Grammes	Grammes
Tungsten trioxide taken . . .	1·0638	0·0871	0·3588	0·8868	0·5996
Molybdenum trioxide taken . . .	2·2712	0·6871	1·1836	1·1986	1·0770
Tungsten trioxide found . . .	1·0630	0·0870	0·3587	0·8866	0·5996

The filtrate containing the dissolved molybdic acid showed no tungstic acid upon examination.

These results indicate that where the two oxides are present together, this mode of separation is of value and merits consideration.

CHAPTER VI

CHROMIUM, IRON, MANGANESE, NICKEL, COBALT

CHROMIUM

Estimation of Chromium

(*A*) Professor Storer has shown that chromic oxide is quickly changed to chromic acid when boiled with a mixture of concentrated nitric acid and potassium chlorate. All the chromium in ½ gramme of chromium oxide, or of any of the ordinary chromium salts, can in this way be converted into chromic acid in a few moments ; and even compounds as refractory as chrome-iron ore, or chromium oxide, which has been strongly ignited, can be oxidised in less time than would be required to complete their oxidation by the process of fusion ordinarily employed.

(*B*) Mr. A. H. Pearson, experimenting on this process, finds that the chromic acid thus formed in the wet way can be readily and accurately estimated in the form of barium chromate, if care be taken to wash the precipitated chromium with ammonium acetate, or some other saline solution in which barium chromate is insoluble. Anhydrous chromic oxide is placed in an evaporating dish, together with a quantity of nitric acid and some potassium chlorate, and covered with an inverted funnel with a bent stem. The acid is heated, and fragments of potassium chlorate are added to it from time to time, until the chromic oxide has completely disappeared. This result is attained in the course of half an hour. The acid solution is diluted with water, then neutralised with ammonia, and the ammoniacal solution in its turn treated with enough acetic acid to make it slightly acid. After the acidulated solution has become cold a solution of barium chloride is added to it in slight excess, and the mixture is left at rest for ten or twelve hours. The precipitated barium chromate is washed by decantation with a cold solution of ammonium acetate, then collected on a filter, rinsed with water, dried, heated in a crucible to expel the last traces of water and of the ammonium-salt, and weighed.

The precipitate of barium chromate must be allowed to stand for some time before filtering, lest it pass through the pores of the filter

and render the filtrate cloudy. The ammonium acetate employed for washing serves to dissolve any barium nitrate or barium chloride which may have been precipitated with the chromate; it has the further advantage of dissolving less of the barium chromate than pure water would.

Experiments on various compounds of chromium show that this process is tolerably exact. Estimations of chromium in different specimens of sesquioxide gave 68·31, 68·65, 68·60, 68·31 per cent. Theory requires 68·62 per cent.

(*C*) Rose strongly recommends the method of Berzelius, which consists in precipitating the chromic acid by mercurous nitrate, and washing with a dilute solution of the same salt. The precipitated chromate is voluminous, and has a brown-red colour when the precipitation takes place in the cold. A better result is obtained by precipitating at a boiling heat, when the mercurous chromate almost immediately becomes highly crystalline, its colour changing to a bright scarlet. It may then be washed with the greatest ease, and ignited in the usual manner. It is absolutely necessary, in applying this method, that the mercurous nitrate used should be perfectly free from nitrous acid. Hot solutions must not be employed, on account of the reduction of chromic acid by mercurous nitrate. This reduction is not due to the temperature, but to the presence of a small quantity of nitrous acid in the mercurous nitrate employed. It is easy to avoid this source of error by dissolving the mercury in nitric acid in an open vessel, and crystallising the nitrate two or three times, using for solution dilute nitric acid which has been perfectly freed from nitrous acid by a current of air or carbonic acid. We arrive more quickly at our object when we precipitate at once at the boiling-point, and then wash with a hot dilute solution of the nitrate.

(*D*) Very accurate results may be obtained by precipitation with barium acetate at a boiling heat, adding a small quantity of strong alcohol to the liquid, washing with water containing alcohol, and igniting. The wash-water need not contain more than $\frac{1}{12}$ of its volume of alcohol. The precipitated chromate must, before filtering, be allowed to settle completely, leaving the supernatant liquid perfectly clear. The filtrate never becomes turbid, even after all the soluble salts are washed out. Finally, it is not necessary to weigh the barium chromate upon a weighed filter. A very small quantity of the chromic acid is always reduced by the carbon of the filter in igniting, but the loss of weight is inappreciable. This method is much shorter than that which is usually employed, as the filtration and washing may be executed almost immediately after precipitation.

Detection of Bichromate and Free Chromic Acid

To detect a monochromate along with a bichromate, add to a few c.c. of the boiling solution a drop of a moderately concentrated solution of

manganese sulphate. In the presence of monochromate a blackish-brown precipitate is formed. Bichromate in monochromate is detected by adding to a boiling solution of sodium thiosulphate an equal volume of a hot solution of the chromate in question. A brown precipitate or a distinct turbidity proves the presence of bichromate. The precipitate is chromic oxide. Free chromic acid in a solution of bichromate is detected by adding a solution of potassium iodide and shaking with carbon disulphide, which is coloured a deep purple by the liberated iodine.

Estimation of Chromium as Phosphate

Chromium may be determined exactly as phosphate, and this method is often convenient. On boiling a solution of a chromium salt slightly acidified, to which has been added an alkaline phosphate and sodium acetate, the whole of the chromium is precipitated as phosphate. This method succeeds both with the green and the violet salts, chlorides and sulphates, and with the acetates, but not with the oxalates. It is also suitable for alkaline chromates, but in this case the action of the phosphoric acid must be combined with that of sodium thiosulphate, which acts as a reducing agent. The solution of chromate, to which is added a sufficient quantity of phosphoric acid, or of a phosphate, then of acetate, and lastly of thiosulphate, and which has been slightly acidified, is boiled for about an hour: it deposits all the chromium as phosphate, with a little sulphur derived from the thiosulphate. The phosphate precipitated is a green hydrate. It may be washed with boiling water, or preferably with hot solutions, first, of ammonium acetate, followed by ammonium nitrate. On calcination it turns grey, and contains chromic oxide in the proportion of 51·86 per cent.

Volumetric Estimation of Chromium in the Presence of Ferric Oxide and Alumina

If a solution of permanganate is made strongly alkaline with sodium carbonate and a little caustic soda, heated to a boil, and a neutral solution of chromic oxide is run in, the chromic oxide is at once converted into chromic acid, while manganese peroxide is separated out. The process is completed when the supernatant fluid has the pure yellow tint of alkaline chromates without the slightest reddish tinge, which may be recognised with sufficient distinctness.

The presence even of considerable quantities of ferric oxide and alumina in the solution containing chromium does not prevent the completion of the reaction from being distinguished, since these oxides, if precipitated in a hot solution, are rapidly deposited along with the manganese peroxide. If the approximate relation of the alkaline permanganate to the chromium solution in question has been determined by a preliminary experiment, on further titration the end of the reaction

can be observed with sufficient accuracy. In fact the volumetric determination of chromium is in this manner rendered possible without the previous separation of iron and alumina.

Volumetric Estimation of Chromic Acid

The following method, devised by Mr. W. J. Sell, yields rapid and accurate results. The solution, containing chromium acidified with sulphuric acid, is boiled and a dilute solution of permanganate added to the boiling liquid until a purplish tint remains after boiling for three minutes. The solution is then rendered slightly alkaline with sodium carbonate, alcohol is added, and the manganese filtered off. The chromic acid in the filtrate is estimated by titration with iodine and sodium thiosulphate.

For the valuation of chrome-iron ores, see Iron.

Separation of Chromium from Uranium

The author's analyses show that mercurous nitrate gives very accurate results. The employment of this salt in separating chromium from uranium is indicated only in those cases where the chromium exists as chromic acid, where relatively small quantities of chlorine or sulphuric acid are present, and when no other acid is present which, like phosphoric acid, gives an insoluble mercurous salt not completely volatilised by ignition. In the presence of chlorine, sulphuric acid, &c., the following process may be very advantageously employed. The solution is to be boiled for a few minutes with a small excess of sodium hydrate, the precipitate of sodium uranate filtered off and washed with hot water containing a little sodium hydrate, until the washings no longer give any turbidity with a solution of mercurous nitrate. The sodium uranate in the filter is then to be dissolved in hydrochloric acid and the uranium determined in the usual manner. The filtrate contains all the chromium. After adding hydrochloric acid in excess, the chromic acid may be most conveniently reduced to chromic oxide by adding a solution of potassium or sodium nitrite and boiling for a few minutes, after which the oxide may be precipitated by ammonia in the usual manner. An alkaline nitrite is a better reducing agent than alcohol, as the chromic oxide may be precipitated immediately after the reduction.

It remains to consider the case in which chromic and uranic oxides occur together in solution. A solution of sodium hydrate in small excess is to be added, and the whole heated to boiling. To the hot liquid, bromine water is to be added. Chromium oxide is almost instantly oxidised to chromic acid, which remains in solution, while sodium uranate, with a small percentage of uranic chromate, remains undissolved. After washing with hot water containing a little sodium hydrate, the precipitate, which has a deep orange colour, is to be

dissolved in hot nitrous acid, the solution boiled for a few minutes to expel any traces of nitric acid, mercurous nitrate added, and the whole allowed to stand until the small quantity of mercurous chromate has settled. This, after washing, may be ignited in the same crucible with the chromic oxide obtained as above from the sodium chromate in the filtrate. The filtrate is free from uranium.

Separation of Chromium from Zinc

Obtain the zinc and chromium sesquioxide in the form of a nearly neutral solution, by the addition, if necessary, of sodium carbonate, then add excess of sodium acetate, and oxidise the chromium to the state of chromic acid by a current of chlorine, or (if it be present in small quantity only) by addition of chlorine water, or bromine. The solution should be kept hot and as neutral as possible by the cautious addition of sodium carbonate. When the oxidation is complete, expel the excess of chlorine or bromine by heat, and add barium acetate, which will precipitate the whole of the chromium present in the form of barium chromate, taking the precautions already described at page 198.

The oxidation of the chromium to the state of chromic acid may also be effected by Professor Storer's method, with nitric acid and potassium chlorate, as described at page 198.

Separate the excess of barium from the solution by addition of sulphuric acid, and then precipitate the zinc with sodium carbonate; or the acid solution may be supersaturated with ammonia so as to redissolve the zinc oxide, filtered if necessary, to remove iron, &c., and the zinc precipitated by sulphuretted hydrogen. When barium sulphate and chromate are thrown down together, the chromic acid may be reduced to sesquioxide by boiling with concentrated hydrochloric acid and alcohol, after which the barium may be precipitated by sulphuric acid, and the chromium sesquioxide thrown down in the filtrate by boiling with ammonia in the usual manner. As the reduction of barium chromate by means of hydrochloric acid and alcohol does not take place very readily, it is better to boil the chromate with an excess of potassium or sodium carbonate, to filter off the barium carbonate, and determine the chromic acid by means of mercurous nitrate, as explained at page 199, or by reduction to chromium oxide and precipitation with ammonia in the usual manner.

Separation of Chromium from Aluminium

(*A*) To a strong solution containing these two metals add potassium chlorate and concentrated nitric acid; the chromium is quickly oxidised to chromic acid. Or, the same thing may be effected by means of chlorine or bromine, as described at page 201. The chromic acid is then precipitated with barium chloride, taking the precautions described at page 198. With care, this process gives very accurate results.

(*B*) Another, and, under some circumstances, a better plan, is the following, for which the author is indebted to Professor Wöhler. Pass chlorine through the solution of the chromium and aluminium sesquioxides in caustic potash, until all the chromium is oxidised to chromate. The aluminium will then be in the form of precipitated hydrate, with the exception of a small quantity, which is readily precipitated by digestion with ammonium carbonate. Filter the solution of potassium chromate from the alumina, and to the filtrate add alcohol and excess of hydrochloric acid, and heat till the reduction to chromium sesquioxide is complete. Add ammonia to the warm solution, when the whole of the chromium will be precipitated as sesquioxide.

(*C*) For the quantitative separation of uranium and chromium, in a first series of experiments, weighed quantities of potassium bichromate were mixed with much larger, but undetermined, quantities of uranium nitrate. The chromic acid was then precipitated by mercurous nitrate from the boiling solutions.

The mean of the analyses was 51·73 per cent., which is precisely the percentage required by the formula.

Separation of Chromium from Thallium

The thallium chromates are insoluble in water, but readily soluble in hydrochloric acid, chlorine being evolved and a soluble perchloride being produced. When boiled with hydrochloric acid and alcohol, these chromates are quickly decomposed, thallium protochloride being precipitated, while chromium sesquichloride remains in solution. Filter off and wash with alcohol, in which thallium protochloride is insoluble.

Separation of Chromium from Vanadium

A method of separating chromium from vanadium, based on the solubility of chlorochromic acid, has been devised by Paul Nicolardot.[1]

The compound containing the chromium and the vanadium is melted with a mixture of a chlorate and carbonate, or with a large excess of a chlorate alone. The small quantities of iron and manganese, if present, are separated by the ordinary methods. The alkaline salts are then concentrated, dried, and melted. The molten mass is completely washed until there is an absence of colour in the wash-water. If there is no iron present, the mixture can be directly melted in the little bulb which was used for the first reaction. Attached to the bulb, a small wash-bottle is placed, containing a little concentrated sulphuric acid, then a flask containing a dilute solution of soda, through which the gases evolved during the reaction can bubble. The apparatus is attached to a pump.

A current of dry air traverses the apparatus, and a few drops of

[1] *Chemical News*, April 15, 1904.

strong sulphuric acid containing a little anhydride are introduced through a dropping funnel. The reaction at once starts. When it becomes less brisk the pump is brought into play, and a few more drops of acid added, and the air or dry HCl is allowed to enter bubble by bubble. Then the bulb is slightly heated until it no longer evolves red vapours. In a very few minutes the whole reaction ceases. The bulb must not be overheated, a temperature of 60° being usually sufficient. We prove that all the chromium has been extracted by treating the contents of the bulb on a water-bath, first with SO_3Na_2, then with excess of ammonia. The precipitate of Cr_2O_3, if it is abundant, still retains some vanadium, and the process must be repeated. The vanadium can be separated at first if the operation has worked satisfactorily. To estimate it, a little alcohol is added to the liquor. This is heated on a water-bath until all the alcohol is driven off, and then titrated with permanganate. The presence of molybdenum does not interfere with this volumetric estimation.

IRON

Preparation of Pure Iron

(*A*) The preparation of metallic iron in a pure state is a problem of enormous difficulty. The British Association appointed a committee, consisting of Sir F. A. Abel, Dr. Forbes, and Dr. Matthiessen, to investigate the subject. The plan finally adopted by the committee was as follows:—Pure dried iron protosulphate and pure dried sodium sulphate are mixed in nearly equal proportions, and introduced gradually into a red-hot platinum crucible. The mass is kept in fusion until the evolution of sulphurous acid gas ceases. The crucible is then allowed to cool, and the fused mass is extracted with water. If the heat be properly regulated, the whole of the iron is left as a very fine crystalline oxide. This oxide is thoroughly washed by decantation, to remove every trace of the sodium sulphate, and, after being dried, is reduced by hydrogen in a platinum crucible; the spongy iron thus obtained is pressed into solid buttons by means of a strong coining-press and a diamond mortar, and then melted in lime crucibles, the lime having been previously burnt, slaked, and reburnt, thus forming a fine impalpable powder, which is compressed in the crucible mould. The best method of fusion has been found to be as follows:—The lime crucible is placed in a slanting position on a piece of lime. A large oxyhydrogen blowpipe plays on the outside of the crucible, while the flame of another is directed inside. When white-hot a cylinder of the compressed iron is thrown into it. It quickly melts, but at the expense of a large quantity of the iron which is oxidised, the amount so lost varying between 25 and 50 per cent. In order to obtain a good solid button of melted iron, it is necessary to cool it in an atmosphere of hydrogen, which is easily obtained by turning off the

oxygen from the blowpipe playing inside the crucible. On analysis it was found that buttons so prepared, weighing about 15 grammes each, were free from phosphorus, silicon, and calcium, and only contained sulphur to the extent of from 0·00025 to 0·0007 per cent.

(*B*) Metallic magnesium put into a solution of a proto- or sesqui-salt of iron, causes an evolution of hydrogen, and a precipitation of metallic iron in the pulverulent state. When freed from the saline solution by washing, then dried and compressed, this metallic sponge possesses great brilliancy, and dissolves in acids without leaving any residue, and without communicating any odour to the hydrogen. As the distilled magnesium of commerce is almost chemically pure, and as ferrous salts of iron can readily be freed from impurities by crystallisation or other means, this affords a good method for obtaining pure iron. The compressed metallic sponge is consolidated, as above described, by heating in lime crucibles before the oxyhydrogen blowpipe.

Electrolytic Determination of Iron [1]

(*A*) Professor Classen finds that if we mix the solution of a ferrous salt with potassium or ammonium oxalate, there appears a precipitate of ferrous oxalate of an intense yellowish-red colour, soluble in an excess of the reagent with the formation of a yellowish-red double salt. For this operation sulphates are most suitable, chlorides less convenient, while nitrates are quite excluded.

Ferric salts are not precipitated by the above-named oxalates, but if they are present in sufficient quantity there is formed a solution of a ferric double salt of a more or less distinct green colour. If its solution is submitted to electrolysis, there is first formed a ferrous double salt which is further decomposed with deposition of metallic iron, the green solution becoming first red and then colourless. Hence the determination of iron can be effected more rapidly in ferrous than in ferric solutions. The potassium-iron double salt is not adapted for electrolysis because the potassium carbonate formed on the decomposition of the oxalate occasions a precipitate of iron carbonate, in consequence of which a complete reduction is impossible. The electrolysis of the ammonium-iron double salt takes place quite smoothly in presence of a sufficient excess of ammonium oxalate without any separation of an iron compound. If the iron solution contains free hydrochloric acid, it is advisable to expel it by evaporation on the water-bath.

Free sulphuric acid can be neutralised with ammonia, as the ammonium sulphate formed increases the conductivity of the liquid. Nitrates are converted into sulphates or chlorides by evaporation with sulphuric acid or repeated evaporation with hydrochloric acid.

For the determination, supposing that 1 gramme of iron may be

[1] For details of the manipulation see subsequent chapter.

present in the liquid to be heated, dissolve about 6 grammes of ammonium oxalate in a minimum of water in a platinum capsule with the aid of heat, and add the iron solution gradually while stirring. It is not advisable to add the ammonium oxalate to a ferrous solution, as a sparingly soluble ferrous oxalate is deposited which must be converted into the soluble double salt by prolonged heating. If there is a ferric salt in solution, it is indifferent whether the ammonium oxalate is dissolved in it, as no precipitate is formed. Dilute with water to 150–175 c.c. and submit the warm solution to electrolysis. The decomposition is effected with a current of 8 to 10 c.c. detonating gas per minute, increasing it towards the end of the process to 12 or 15 c.c. to promote the separation of the last traces. If a red flocculent ferric precipitate is formed during the electrolysis, we add oxalic acid drop by drop until it is redissolved.

For detecting the end of the reaction take out of the capsule a minute quantity of the decolourised liquid by means of a capillary tube, supersaturate it with hydrochloric acid, and test with potassium sulphocyanide.

After the completion of the reaction the positive electrode is taken out of the liquid, which is at once poured off, rinsing the capsule three times with 5 c.c. cold water and three times with pure absolute alcohol. The capsule is dried for a few minutes in the air-bath at from 70° to 90° and weighed when cold.

The deposit of iron has a shining steel-grey colour, adheres very firmly to the capsule, and may be exposed to the air for days without the occurrence of oxidation.

(*B*) F. Rüdorff has laid down the conditions under which the precipitation of iron is effected from the double ammonium oxalate with Meidinger elements. The solution must not contain more than 0·3 gramme of iron. In presence of free acid we add, after previous neutralisation with ammonia, 60 c.c. of ammonium oxalate saturated at the ordinary temperature, dilute with water to 120 c.c., and electrolyse with a battery consisting of from 6 to 8 elements.

As electrodes Rüdorff uses a crucible-shaped platinum capsule 60 mm. in height, 75 mm. in diameter at the top, about 40 grammes in weight, and capable of containing 170 c.c. of water. As the positive electrode he uses a thick platinum wire coiled partly in a spiral. The quantitative deposition takes about fourteen hours as compared with four hours by the former process.

To Dissolve Ignited Ferric Oxide

Instead of fusing insoluble ferric oxide with sodium bisulphate, A. Classen prefers to boil it with dilute caustic potash. As soon as the previously pulverulent mass becomes flocculent, the alkaline liquid is decanted off and the oxide dissolved in concentrated hydrochloric acid.

Estimation of Iron Protoxide in the Presence of Peroxide

Messrs. Wilbur and Whittlesey have carried out a suggestion of Avery,[1] and applied it very successfully to the estimation of ferrous and ferric oxides in silicates. Avery found that silica and many silicates can be readily and completely dissolved by a mixture of some normal fluoride with almost any of the stronger acids, whether concentrated or dilute.

These chemists have applied this observation to the estimation of the two iron oxides, and have obtained such satisfactory results that their process deserves to be generally adopted for the estimation of iron in silicates. The method is as follows:—A quantity of the finely powdered silicate to be examined is weighed in a platinum crucible; as much, or rather more than as much, powdered fluor spar (or powdered cryolite), free from iron, is poured into the crucible; the powders are thoroughly mixed by stirring with a glass rod; the rod is wiped clean upon a fresh portion of the powdered fluoride; and the latter is thrown upon the mixture in the crucible. Strong hydrochloric acid is then poured into the crucible, until the powder is thoroughly drenched and the crucible about two-thirds filled with the liquid. The crucible is set upon a water-bath, and heated until the iron has all dissolved; the proportion of iron is finally determined by titrating with a standard solution of potassium permanganate. To protect the mineral from the air during the process of solution, the crucible must be kept full of some non-oxidising gas, which can be either carbonic acid or coal gas as may suit the convenience of the operator.

If carbonic acid be used, it is sufficient to cover the crucible with a bit of sheet-lead, perforated with two holes, through one of which is thrust a glass tube communicating with a gas-bottle in which the carbonic acid is generated, while the other serves as an outlet for the escape of carbonic acid and acid vapours. The crucible is, in this case, simply set upon an ordinary water-bath.

When coal-gas is used (and this agent is to be preferred on the whole), the apparatus may be arranged as follows:—Set the charged platinum crucible upon a glass or leaden tripod, inside a wide beaker, in the bottom of which there is about an inch of water. Invert a narrower beaker within the first, so that its mouth shall be sealed by the water and the crucible be enclosed in a transparent chamber. Coal-gas is led into the chamber through a bent glass tube, which passes down between the side of the upright and that of the inverted beaker, and delivers the gas near the top of the chamber. The surplus gas escapes through another tube similarly bent, which starts from a point below the crucible, and is burned in the outer air. To facilitate the passage of the glass tubes, the mouth of the inverted beaker may be made to rest upon three or four bits of stone or metal, or an

[1] *Chemical News*, vol. xix. p. 270.

orifice large enough to admit the tubes may be made upon the rim of the beaker. During the process of solution, the upright beaker is kept immersed in water, at or near the boiling temperature. In case the coal-gas should contain any sulphuretted hydrogen, it would be well to purify it by means of a potash-tube. An hour and a half is ample for the solution of the iron in 0·5–1 gramme of finely powdered trap rock. Fifteen minutes, on the other hand, will suffice for the solution of 0·2 gramme of iron wire. Instead of hydrochloric acid, sulphuric acid may be used to act upon the mixture of fluor spar and mineral. The calcium sulphate frequently formed is objectionable, from its liability to envelop portions of the mineral and so protect the iron from being dissolved, rather than from any tendency to interfere with the actual titration.

Experiments have shown that the presence of iron sesquioxide does not interfere in any way with the estimation of the protoxide. Commercial iron-alum, which of itself has no decolourising action on potassium permanganate, has none after it has been heated with cryolite and hydrochloric acid. It is found, also, by acting upon weighed quantities of iron wire mixed with cryolite and iron-alum, that the iron can be estimated as well in the presence of the alum as in its absence, provided only that the metallic iron be dissolved in hydrochloric acid, with the necessary precautions to prevent oxidation, before adding the other ingredients of the mixture. If the iron wire, cryolite, and ferric alum were treated all at once with acid, some of the hydrogen generated by the solution of the metallic iron would reduce a part of the ferric salt ; so that, in the final titration, more iron would be found than was introduced into the mixture in the form of wire.

If time enough be allowed, finely powdered iron sesquioxide can be dissolved in this way, even after intense ignition.

To estimate iron sesquioxide in a silicate, a separate portion of the mineral may be treated with fluor spar and acid, the solution reduced by zinc in a small flask in the usual way, and the total amount of iron determined with permanganate. Or, if the mineral contains only a small proportion of ferric oxide, it will be sufficient to put a bit of zinc into the crucible with the mixture of mineral, fluor spar, and acid. The difference between the total iron and that determined as protoxide is calculated as peroxide.

Reduction of Sesqui-Salts of Iron to Proto-Salts

Sulphurous acid or metallic zinc is the reducing agent usually employed, but a much more effectual and rapid agent has been proposed, in sulphuretted hydrogen, by Mr. Reynolds. This answers much better than either zinc or sulphurous acid. The reduction, even in a strongly acid solution, takes place immediately, and on boiling until the sulphuretted hydrogen is expelled, the sulphur separated coagulates

completely ; so that, after allowing the solution to cool in the flask in which it has been boiled, a cork being placed in the neck during the cooling, filtration may be effected so rapidly that no oxidation need be feared, and the determination may then be effected with permanganate, as usual. It is better to add a considerable quantity of water to the solution before reduction, to avoid the oxidation which would afterwards ensue in the filtration of a concentrated solution of iron protoxide.

Volumetric Estimation of Iron by Sodium Thiosulphate

M. Mohr has shown that the direct estimation of iron perchloride, by means of a solution of sodium thiosulphate, does not give satisfactory results. The cause of error lies chiefly in the decomposing action exercised by free hydrochloric on thiosulphuric acid.

By using sufficiently diluted acetic instead of hydrochloric acid, or by treating the weak hydrochloric solution with sodium acetate, it will be found that the thiosulphuric acid is not decomposed, even after some length of time. Consequently, a solution of iron perchloride may be estimated by means of a thiosulphate solution, taking care to add previously sufficient sodium acetate to make apparent the red colour of the ferric acetate, and then sufficient weak hydrochloric acid to make this colour again disappear. Then pour into the solution a known quantity of thiosulphate, and estimate the excess of this reagent, which colours the liquid a deep violet, by means of starch paste and iodine solution.

Very exact results are obtained in this way ; but care must be taken to use liquids not too much diluted ; 0·00012 gramme is the minimum amount of iron which should be contained in 1 c.c.

One equivalent of iron perchloride decomposes exactly two equivalents of sodium thiosulphate.

Volumetric Estimation of Iron with Copper Subchloride

Copper subchloride has been found by Dr. Winkler to be a very powerful reducing agent for iron sesquioxide, analogous to tin protochloride in its effects. But while tin protochloride causes but a partial reduction in a cold solution, copper subchloride acts directly with theoretical accuracy at the lowest temperature, and at any dilution. It is, therefore, particularly adapted for the volumetric determination of iron. The completion of the reduction may be ascertained with certainty by the addition of a few drops of potassium sulphocyanide to the solution to be tested, when the well-known deep-red colour appears. When the subchloride solution is dropped into one of iron so coloured, the red colour becomes lighter and lighter, and finally disappears entirely. After the solution is bleached, the reduction of the iron is complete, and the next drop of copper solution causes a precipitation of copper subsulphocyanide. This gives a double indication

of the end of the reduction: namely, the bleaching of the red colour of the iron sulphocyanide, and the cloudiness produced by the insoluble copper salt. The rapidity and simplicity of the process, as well as the few accessories required, especially recommend this method to technical laboratories, where the want of a short and accurate process has long been felt.

The solution of copper subchloride is made by dissolving sheet-copper in nitric acid; evaporate to drive off the excess of nitric acid, and dissolve the residue in water containing hydrochloric acid. This solution is put into a flask, and a quantity of common salt equal in weight to the residue of dry copper-salt is added, in order to prevent the separation of a precipitate of copper subchloride during the subsequent reduction. Several pieces of sheet-copper are put in the flask, and the liquid is then heated to boiling. This is continued until the solution is nearly colourless, and all the copper chloride has been changed to subchloride. The flask is then corked, and allowed to cool; the solution is then diluted with water containing hydrochloric acid, until 1 c.c. corresponds to 6 milligrammes of iron. In order to keep this solution without change for further use, it should be poured into a bottle, to which is fitted an air-tight stopper, and containing a spiral of thick copper wire reaching from the bottom to nearly the neck. This completely protects the copper subchloride from oxidation, so that the strength of the solution remains nearly always the same. It is, however, best to determine the strength of the standard from time to time, since this requires but a few minutes. For this purpose, there is needed a solution of iron sesquichloride of known strength. This may be made, according to Fresenius, by dissolving in hydrochloric acid and potassium chlorate 10·03 grammes of piano-wire, corresponding to 10·0 grammes of pure iron, and diluting to 1 litre. For each test of the standard, 10 c.c. of this solution are taken, containing 100 milligrammes of iron.

In performing this volumetric determination of iron, there are but few rules to be observed. It is advisable that the solution to be treated be decidedly acid, and very dilute, before it is brought under the burette. A solution that contains from 100 to 200 milligrammes of iron should be diluted to 500 c.c. or more.

In noting the end of the reduction, though it is not necessary that the solution of potassium sulphocyanide should contain a known amount of this salt, yet it will be found better to use about the same strength at all times, since the presence of too much sulphocyanide makes the reaction less marked.

In adding the sulphocyanide, care must also be taken; for, if too much is added to the iron solution, although a deeper blood-red will be obtained, yet a difficultly soluble copper subsulphocyanide may separate, clouding the solution and redissolving with trouble. Four or five drops of solution are quite sufficient to be added. Then, by dropping

in the copper solution, the bleaching takes place with extraordinary sharpness, and only when all the iron has become a protoxide does the next drop cause a permanent cloudiness.

The presence of coloured metallic compounds (such as cobalt, nickel, and copper salts) does not in the least hinder the recognition of the reactions, if the solution is properly dilute. Neither does the presence of arsenic acid affect the process, since this is not reduced by copper subchloride. This process, therefore, is important to the metallurgist, who is often compelled to determine quickly and correctly the amount of iron contained in a matt, or speiss, or other product. By the above process this is possible in an hour.

Volumetric Estimation of Iron with Potassium Permanganate

(*A*) To estimate iron very rapidly, with a reasonable degree of accuracy, no process has given better results than that by the reduction of the hydrochloric solution of the ore by stannous chloride. The ore is dissolved in hydrochloric acid in a beaker, and evaporated nearly to dryness. The solution is then diluted with a little water, and an excess of stannous chloride run in from a burette. After the fluid has lost colour a little starch solution is added, and iodine solution run in from another burette until the blue iodide of starch remains permanent. It is found best to have the iron solution rather concentrated and warm. One c.c. of the stannous chloride solution is equivalent to about 0·012 grm. metallic iron and 3 c.c. of iodine solution. The stannous chloride works best when freshly prepared.

Four samples have been weighed, dissolved, reduced, and titrated in an hour and twenty minutes. In a second trial, with four more samples, the same time was taken. In both cases the solutions were standardised while the ore was dissolving. This gives an average of twenty minutes required for one determination, which is all that could be desired. It is best to standardise the stannous chloride solution by means of metallic iron. This is dissolved in hydrochloric acid and a few pieces of potassium chlorate added ; after which the solution is evaporated nearly to dryness. By this means every trace of free chlorine seems to be expelled. A solution of ferric chloride, when freshly prepared, is reduced almost immediately upon the addition of the stannous chloride. After standing some time, however, it is more slowly reduced, and seems to require less tin solution.

(*B*) Messrs. W. F. Stock and W. E. Jack make the following remarks on the working of the stannous chloride process. They find certain objections presenting themselves—viz. the liability to add excess of stannous salt, and the want of suitable means to prevent such excessive addition; but by the method given below, these objections no longer hold good.

In this process 1 gramme of ore is dissolved in 30 c.c. of strong

hydrochloric acid, and, if not decomposed by hydrochloric acid, it is first fused with an alkaline carbonate, and brought into hydrochloric acid solution; in either case, the solution is made up to 500 c.c. with distilled water and caused to boil. The stannous chloride may now be added in small portions at a time, but it *must* be in *dilute clear acid* solution, a convenient strength containing 10 grammes of tin per litre. The colour of the ferric solution is a fair guide to the addition of the tin-salt within certain limits; but when the colour becomes faint some other indicator must be used, and this we find in a dilute, recently prepared solution of potassium sulphocyanide, which is disposed in drops over the surface of a white tile. Special care must be taken to add the trial drops of iron solution quickly to those on the tile, and to have the beaker containing the solution in pretty close proximity to the tile, so as to guard against oxidation of solution on the glass rod with which the test drops are added. The reduction is carried so far that only a faint tinge of pink is produced when the last addition of tin-salt has been made and allowed to boil for a few moments. The next step is the titration with potassium bichromate; and, as a vital part of the process, make the preliminary addition of three drops of bichromate (standard solution 1 c.c.=0·01 gramme iron), then test with potassium sulphocyanate. A distinct access of colour in this test, as compared with the last test made in reducing, is accepted as proof of the absence of stannous salt, and it only remains to complete the assay in the usual manner.

Decomposing Pyrites with Sodium Peroxide

Mr. C. Glaser has examined more closely the proposal of M. Hoehnel, as it offered a possibility of avoiding the tedious and repeated evaporation with hydrochloric acid to expel nitric acid from melts with carbonate and nitrate. But it was found that the matter was less simple than it appeared at first sight. A series of experiments was instituted, the results of which, in so far as they are conclusive, were as follows:—

Pyrites with 41·12 per cent. total sulphur gave, according to Hoehnel's process, only 38·37 per cent. On acidulating the filtrate from the melt, some sulphur was separated out, and a distinct odour of the decomposition products of hyposulphurous acid was recognised. More sodium peroxide was therefore used for the following experiments, at least 5·0 grammes sodium peroxide to 0·5 gramme pyrites. In order to avoid any loss before acidulation with hydrochloric acid, some cubic centimetres of hydrobromic acid were added, and the liquid was then boiled until nearly all the bromine was expelled. Precipitation with barium chloride then followed in the usual manner. The result was 41·13 per cent. To avoid the destruction of the nickel crucible, it is advisable to heat at first for ten minutes with so small a flame that the mixture in the crucible merely softens and sinters together. It is then heated for fifteen to twenty minutes with a powerful 'roaring' burner.

If these precautions are observed, the determinations can be effected without notable injury to the crucible. Towards the end it is necessary to heat the melt so strongly that it enters into wavy ebullition. When the attempt is made to avoid this, the brown metallic oxides become black on lixiviation by the re-formation of iron sulphide. The examination of the residue on the filter after separate treatment with hydrobromic acid gave each time a notable quantity of barium sulphate; while when the mixture is heated to wavy ebullition, the filtrate passes off colourless, and without the use of hydrobromic acid there appeared on acidulation merely a slight separation of sulphur, the residue insoluble in water being quite free from sulphur. It is therefore necessary to attend to the following points:—(1) Gentle heat at the commencement of the fusion; (2) towards the end, ignition to full ebullition; (3) oxidation by means of hydrobromic acid. A determination can be effected in from two to two and a half hours.

Sodium peroxide may be used conveniently for determining the sulphur in burnt ore. We take for 1 gramme burnt ore, 0·5 sodium peroxide and 2·0 grammes sodium carbonate, and heat the mass in a nickel crucible with a moderate flame for fifteen minutes. The melt is easily lixiviated, but before acidifying with hydrochloric acid it is recommended to add a few drops of hydrobromic acid. We then precipitate with barium chloride. Watson's method, which Lunge strongly recommends, is not applicable to American ores, but it gives satisfactory results with Spanish pyrites.

Immediate Analysis of Meteoric Iron

The numerous researches hitherto made with regard to the composition of meteoric irons have demonstrated the existence of the following compounds in these extra-terrestrial bodies:—

I. The *general mass*, which is formed by the union of several alloys in which iron and nickel are predominant, and which we will designate under the name of *nickeliferous iron*. Among the substances comprised in this mass, *kamacite*, *tænite*, and *plessite* are specially noticeable.

II. The *carburetted iron*, comprising *campbellite* and *chalybite*, recognisable by the carboniferous deposit which they give under the action of acids.

III. *Sulphuretted iron*, or *troilite*, which appears in nodules and in veins.

IV. *Iron and nickel phosphide*, or *schreibersite*.

V. *Graphite*.

VI. *External crust*.

VII. *Stony grains*, or *crystals*.

VIII. *Gases* retained by occlusion.

IX. Several compounds which are only met with exceptionally, as *chromite* and *iron protochloride*.

(The last may indeed have a terrestrial origin, according to the opinion of Mr. Shepard.)

M. Stanislas Meunier, Aide-Naturaliste at the Museum of Paris, has tried to separate these different substances, and has submitted each of them to a special examination. His experiments, which have resulted in fixing their chemical formulæ, were communicated to the *Chemical News*, and are given in abstract in the following pages.

I. **Nickeliferous Iron.**—The first problem to be solved is the separation of the different alloys which are mixed in the general mass of meteoric irons; but it is necessary first of all to prepare that general mass free from other substances already named. For this end, the iron being reduced to powder by means of a hard file, the metal is thrown into pure potash, in a state of fusion, in a silver crucible. Instantaneously the alkali, hitherto limpid, becomes turbid, owing to the presence of little grey flakes, which consist of iron oxide, and are the result of decomposition of troilite, schreibersite, stony matters, &c.

When this decomposition of foreign substances is complete, the alkaline mass is cooled and treated with water. All the potash is washed away with the greater part of the iron oxide. The remainder of this oxide is easily dissolved by strong nitric acid, in which the metallic iron becomes passive. The metallic powder is then well washed and dried; it is formed exclusively of nickeliferous iron, containing, however, in certain cases, a small proportion of carburetted iron.

Chemical methods have not yet completely succeeded in separating the alloys mixed in the nickeliferous iron, and, after several attempts, M. Meunier was obliged to have recourse to physical processes. His experiments have been made with the meteoric irons of Caille (France), and of Charcas (Mexico).

It was necessary, first of all, to estimate with accuracy the number of constituent compounds contained in the nickeliferous iron of these masses. For this purpose a small polished plate of the iron of Caille was carefully and uniformly heated. This operation, of which the first idea is due to Widmanstätten, drew, by the unequal oxidation of the different immediate principles, a yellow net upon a blue ground. There were also several portions of an intermediate colour, clearly limited like the others, and occupying the spaces bounded by the crossing of the yellow lines. An attentive examination showed that the three metallic compounds were reducible to two; the third being formed by the mixture of the others, reduced to alternate thin sheets. The blue colouration is formed by kamacite, and the yellow by tænite.

Their separation was very difficult, on account of the analogy of the chemical properties of the two minerals. Although it is true that kamacite is more soluble than tænite (and this is proved by the experiments of Widmanstätten), this difference is too small to permit of a separation. When all the kamacite is dissolved, only a very small proportion of tænite remains, the greatest part being dissolved also.

To effect the separation, some metallic powder was heated upon a glass plate. The particles formed by kamacite became blue, while the particles of tænite were yellow. The two sorts of grains were then separated with pincers. After about fifteen operations, 2 grammes of kamacite and 0·5 gramme of tænite were collected fit for chemical examination. The Charcas iron gave the same results.

The specific gravity of tænite is 7·38. Its analysis yielded the following numbers :—

Iron	85·0
Nickel	14·0
	99·0

which agree with the formula Fe_6Ni.

Kamacite has a specific gravity of 7·652, and its composition was found to be—

Iron	91·9
Nickel	7·0
	98·9

agreeing with the formula $Fe_{14}Ni$.

On this subject it will be remarked that, admitting, according to the numbers given above, that the Caille iron contains 80 per cent. of kamacite, and 20 per cent. of tænite, its elementary formula will be expressed by

$$Fe_6Ni+4(Fe_{14}Ni)=Fe_{62}Ni_5,$$

which gives numbers very near those which M. Rivot obtained in the elementary analysis of that mass.

The above formula gives—

Iron	91·4
Nickel	8·6
	100·0

while M. Rivot found, in two analyses—

Iron	92·3	92·7
Nickel	6·3	5·6
	98·6	98·3

All meteoric irons are not so simple as those of Caille and of Charcas. There are some which contain, with kamacite and tænite, a certain quantity of other metallic alloys. One of the most important of these is plessite, which abounds, for example, in irons of Jewell Hill (North Carolina) and of Oldham (Kentucky). This has been isolated by the same method which served for the preceding substances. Plessite has a density of 7·85, and its composition appears to be satisfactorily represented by the formula $Fe_{10}Ni$.

Among the other alloys of iron and nickel may be mentioned *octibbehite*, whose composition is exceedingly remarkable, owing to the large proportion of nickel (59·6 per cent.) it contains. Its density is only equal to 6·854. The meteoric iron of Octibbeha (Mississippi)

seems to be entirely formed of that alloy, according to the researches of Mr. Taylor.

II. **Carburetted Iron.**—Several meteoric irons give, by the action of acid, a black deposit, more or less abundant, consisting of carbon. This carbon comes from a compound whose position is analogous to that of steel. In this point of view, the meteoric iron of Campbell (Tennessee) may be specially mentioned. It gives, on analysis, a metallic substance, formed by the union of 1·5 per cent. of carbon with 97·54 per cent. of iron. For it the name of *campbellite* may be proposed; its density is 7·05. Mr. Shepard gives the name of *chalybite* to an iron carbide which Forchammer has detected in the meteoric iron of Niakornak (Greenland), and of which the formula is CFe_2.

III. **Sulphuretted Iron.**—To obtain the sulphuretted iron, or *troilite*, in a complete state of purity, we may have recourse to the metallic powder. This powder is placed for a quarter of an hour in a boiling concentrated solution of copper sulphate. All the nickeliferous iron is dissolved, and, by decanting and washing, a mixture of metallic copper, troilite, schreibersite, graphite, and stony matter may be obtained.

A small quantity of concentrated nitric acid dissolves the copper. The magnet, acting under water, is the best means to separate troilite and schreibersite (which are magnetic) from graphite and stony matter. Finally, lixiviation can be employed to separate troilite from schreibersite.

When the iron under experiment contains only a small quantity of troilite, it is preferable not to use nitric acid, which always dissolves a little of the desired substance. In such cases the nickeliferous iron may be dissolved by means of mercury bichloride. The mercury protochloride is carried off by a solution of chlorine, and it is easy to separate the metallic mercury.

It is, however, always better, when possible, not to extract troilite from the iron, but from the cylindroid nodules in which the substance has concentrated. In these, sulphuretted iron contains only some graphite and stony matter, which can be got rid of by the action of the magnet. There is no doubt that this troilite is one of the most characteristic principles of meteoric iron. Notwithstanding this, its crystalline form has not yet been recognised, and there is some doubt about its chemical composition. The first chemists who examined it considered it as a variety of Breithaupt's pyrrhotine, and gave to it the formula Fe_7S_8. But Professor Lawrence Smith concluded from his estimations of the sulphur in the iron of Tazewell, that it had the composition of a protosulphide, FeS. Notwithstanding this, he continued to give it the name of pyrrhotine, and thus a great confusion was introduced into science. Moreover, Professor Smith rested both upon the results of his own experiments and upon those obtained by several chemists in the examination of other samples of troilite; his conclusion

was not admitted, and the existence of true crystalline magnetic pyrites in meteorites will increase the difficulties. The distinction between the troilite (or Professor Smith's pyrrhotine) and Breithaupt's pyrrhotine, is not so clear as would appear at first sight. The difference of composition is very slight, and the physical properties are very similar.

M. Meunier has lately had occasion to analyse several specimens of troilite taken from the meteoric irons of Charcas and of Toluca (Mexico), and the figures which he has obtained have given him reason to think that the mineral in question is nearer to magnetic pyrites than to iron protosulphide.

Before giving the results of these analyses, we may call attention to a reaction which seems calculated to permit in all cases of the distinguishing of the iron protosulphide from magnetic pyrites, and, *a fortiori*, from compounds which are still richer in sulphur. When iron protosulphide is placed in a solution of copper, it precipitates this metal almost like iron itself; pyrrhotine, on the contrary, produces no such precipitation. The protosulphide obtained by the action of ammonium sulphide upon iron salts produces the same effect as the sulphide of exactly the same composition prepared by igneous means. This being well established, several examples of troilite were put into a solution of copper, and no precipitation could be observed; troilite, therefore, is very like magnetic pyrites in this respect, and we may draw the same conclusion as to its chemical composition. In fact, Professor Smith has based the formula FeS upon his analysis of Tazewell's troilite, which gave him—

Iron	62·38
Nickel	0·62
Copper	trace
Lime	0·08
Silica	0·56
Sulphur	35·67
	99·31

But these numbers show that the substance employed in his experiments was very impure.

Troilite purified by the process described above yielded a substance of which the specific gravity was 4·799. Its colour was bronze, and its analysis gave—

Iron	59·01
Nickel	0·14
Copper	trace
Sulphur	40·03
	99·18

The formula Fe_7S_8 requires—

Iron	60·4
Sulphur	39·6
	100·0

The Charcas troilite, previously purified, yielded—

Iron	56·29
Nickel	3·10
Sulphur	39·21
	98·60

Its density is 4·78. The normal presence of nickel makes troilite a species distinct from pyrrhotine, and its true formula becomes $(FeNi)_7S_8$.

IV. **Schreibersite.**—Schreibersite, or iron and nickel phosphide, may be prepared by the same method as troilite. It is, besides, always preferable to select the schreibersite in the places where it is naturally concentrated. It is a yellowish, or almost white, metallic-looking substance. Its specific gravity is 7·103, and it contains—

Iron	57·11
Nickel	28·35
Cobalt	trace
Magnesium	trace
Phosphorus	15·01
	100·47

numbers which lead to the formula Fe_4Ni_2P. Schreibersite is magnetic, and takes permanent polarity by contact with a magnet. It is brittle. Hydrochloric acid has no action upon it. Its crystalline form has not yet been observed.

V. **Graphite.**—Graphite may be isolated by the following method: A few grammes of metallic powder are projected into fused potash, and thus a mixture of nickeliferous iron and graphite is obtained. This mixture may be treated in several ways.

1st. The iron is dissolved in hydrochloric acid, which leaves the almost pure graphite as residue.

2nd. The graphite is separated by lixiviation. This process presents the advantage of giving both graphite and nickeliferous iron; but the separation is never complete.

3rd. When the graphite is abundant the magnet may be employed; in other cases it is drawn up with the metal.

In all cases the residue is washed with hydrochloric acid to dissolve foreign matters, such as troilite and schreibersite, or what is left after attacking with fused alkali.

The graphite extracted from the Caille iron has a specific gravity of 1·715. Its analysis gave—

Carbon	97·3
Iron	2·4
Nickel	trace
	99·7

The graphite of the Charcas iron has a density of 1·309, and yielded on analysis—

Carbon	98·0
Iron	0·9
	98·9

The graphite is remarkable on account of its great unalterability.

VI. **External Crust.**—Those portions of meteoric iron upon which is a crust, being separated by means of a saw, are placed in a concentrated solution of mercury bichloride. After a sufficient time all metallic particles are dissolved, and the oxides, among which is the crust, remain alone.

The crust is, however, still mixed with foreign matters. It usually contains with it the products of its alteration by atmospheric agents, and particularly limonite. Some schreibersite, troilite, and stony grains may also be mixed with the principal substance, and their separation is very difficult. Weak hydrochloric acid carries away limonite and troilite; earthy particles remain as residue after the action of the magnet; lixiviation permits of the purification of the crust from schreibersite. These operations may, however, be simplified by choosing those portions of the crust that seem almost pure. They frequently detach themselves from the subjacent metallic matter.

Very few chemists have analysed the external crust of meteoric irons. The analyses given by Pugh, as showing the composition of the crust of the Toluca iron, were evidently executed on an impure portion. These are Pugh's results :—

Metallic iron	18·717
Iron protoxide	19·309
Iron sesquioxide	32·750
Nickel and cobalt protoxides	5·751
Lime	trace
Silicates	10·203
Water	13·270
Chlorine	trace
	100·00

The metallic iron, silicates, and water are evidently not essential elements of the crust, and must be considered as impurities.

Having purified as much as possible by the method above described the crust of the Toluca meteoric iron, M. Meunier found it possessed a density of 4·89, and the following composition :—

Iron sesquioxide	68·93
Iron protoxide	28·12
Nickel protoxide	2·00
Cobalt protoxide	trace
	99·05

These numbers agree with the formula Fe_2O_3,(FeNi)O, which does not differ from that of magnetite, except by the substitution of a

small portion of nickel for a corresponding quantity of the iron of the protoxide. If in Pugh's analysis we only consider iron sesquioxide, iron protoxide, and nickel and cobalt protoxide, we arrive at numbers very near to those required by the above formula.

VII. **Stony Grains.**—Several of the operations described above evidently yield the stony grains in a state of purity. But when it is especially intended to obtain these grains, they should be separated in the following way:—

The meteoric iron in the form of lumps is left protected from the contact of the air in a concentrated solution of mercury bichloride, and frequently stirred. After a sufficient time the metal disappears, and the liquid contains the stony particles mixed with mercury protochloride, and generally with a small quantity of metallic mercury, besides troilite, schreibersite, and graphite. A solution of chlorine carries off the calomel, and the magnet removes the schreibersite and the troilite; lixiviation may be employed to get rid of the graphite.

These grains are of different composition, and it appears that there exists a certain relation between their composition and their situation. Some are localised in the iron; others are situated in the troilite, or, perhaps, in the graphite which surrounds this sulphide.

The grains of the first category may be found in meteoric irons of Tazewell and of Tuczon. They consist of peridot, and this is confirmed by the analyses published by Mr. Lawrence Smith. Their density is equal to 3·35.

The grains of the second category are yielded by the troilite of the Caille iron. Submitted to blowpipe assay, they only exhibit the reaction of silica.

The troilite of Charcas iron gave analogous results.

VIII. **Gases.**—Gases have been recognised in the meteoric iron of Lenarto, by Mr. Graham and by M. Boussingault.

M. Meunier has sought for the same bodies in another iron of the same origin by effecting the solution of those masses in concentrated mercury bichloride. As, however, he was not aware that the occluded hydrogen would be all absorbed by the solution of mercury bichloride, reducing it to the state of calomel or metal, he erroneously considered that the absence of visible gas proved that there was no gas occluded. The mass of Krasnojarsk (Siberia) gave a small bubble of gas, having the composition of atmospheric air; but it must be remarked that this iron was cracked.

IX. **Rare Substances.**—In concluding this enumeration, chromite and iron protochloride must be mentioned as having been found in certain irons. Their separation is evidently easy, and their composition is identical with that of analogous terrestrial compounds.

After having described the methods which have permitted him to separate in a state of complete purity the *immediate principles* of meteoric irons, M. Meunier remarks that these methods can be

employed to estimate the relative quantity of the substances in question.

He has, for instance, submitted to a *quantitative immediate analysis* the meteoric iron discovered in 1784, at Xiquipilco, in the valley of Toluca (Mexico), and has found in it—

Nickeliferous iron	96·301
Graphite	1·176
Troilite	1·482
Schreibersite	1·232
	100·191

Preservation of Iron Proto-Salts

Iron protosulphate may be preserved from oxidation by placing with it a piece of camphor wrapped in clean dry paper.

Iron protochloride may be obtained pure by evaporating the fresh solution almost to dryness, and adding powdered iron and strong hydrochloric acid in the proportion of one part of the former to five of the latter; the mixture is then evaporated to dryness with continual stirring by an iron spatula. The nascent hydrogen evolved effectually reduces all the sesqui- to the proto-chloride, and the dry salt will keep for a considerable time.

Separation of Iron from Aluminium

(*A*) M. Vignon adds to the dilute solution an excess of trimethylamine, and filters after twenty-four hours. All the ferric oxide remains on the filter, while the alumina passes into solution. Chromium oxide may be separated from iron in the same manner.

(*B*) Add to the cold, strong and slightly acid solution an excess of sodium hydrocarbonate in such quantity that after stirring, a little remains undissolved, and the iron and alumina both appear to be thrown down. Add potassium cyanide until the precipitate dissolves, and heat gently until the pale yellow colour of the ferrocyanide is produced. Now add a few drops of potassium hydrate to the somewhat turbid yellow solution until it becomes perfectly clear; then boil with the addition of ammonium chloride, when the alumina will be precipitated free from iron. The potassium hydrate and cyanide, as well as the sodium hydrocarbonate for this separation, should be tested for alumina and silica, impurities almost invariably present.

(*C*) Neither the thiosulphate nor the caustic alkali process succeeds when only traces of aluminium are present with the iron. In this case Robert T. Thomson proceeds as follows:—The iron, if in the ferric state, is first reduced to the ferrous condition by passing a current of sulphurous acid through the solution. The excess of sulphurous acid is boiled off, the mixture cooled, and at least as much phosphoric acid,

or ammonium or sodium phosphate, added as will be equivalent to the aluminium present. It is advisable to use a large excess of phosphoric acid, as the aluminium may not be completely precipitated if it has not at least its own equivalent of the former. One drawback to the unlimited use of phosphoric acid is that if manganese is present it will be thrown down, but if the quantity of the former is limited the latter will remain in solution. Ammonia is now added until a faint permanent cloudiness is formed; then excess of ammonium acetate, which throws down the aluminium as phosphate. The precipitate always contains some ferric phosphate, which forms from any traces of ferric-iron salt which may have escaped reduction, and from the oxidising action of the air during filtration. The great bulk of the iron, however, remains in solution in the ferrous condition. The precipitate is now collected on a filter, washed two or three times with water, and dissolved by passing dilute warm hydrochloric acid through the filter. If it does not seem sufficiently free from iron, the solution thus obtained should be put through the same process as has just been described, beginning at reduction with sulphurous acid. It is well to reduce the iron as much as possible.

After obtaining a satisfactory precipitate it is dissolved in hydrochloric acid, boiled with a little nitric acid to oxidise any proto-salt of iron, nearly neutralised with pure caustic soda, and added to a considerable excess of the latter in a nickel basin. The mixture is boiled for a short time, filtered, the filtrate acidified with hydrochloric acid, and a large excess of phosphoric acid or phosphate of ammonia or soda added. The presence of at least two equivalents of phosphoric acid to one of alumina is necessary to give rise to the normal aluminium phosphate. The latter is now precipitated by adding ammonia till a slight cloudiness is produced, and then excess of ammonium acetate. The aluminium phosphate is now collected in a filter, washed thoroughly with a hot 1-per-cent. solution of ammonium nitrate containing about 0·1 gramme of the di-acid ammonium phosphate per litre, dried, ignited, and weighed. If the aluminium phosphate is washed with water, it partially loses its gelatinous form, and becomes tedious to filter. But, besides this, the precipitate is decomposed to a considerable extent, and a portion of the phosphoric acid passes into solution. For these reasons the precipitate must be washed in the manner described, when pure aluminium phosphate is weighed, and may be calculated to alumina or aluminium as required.

The presence of titanium is not injurious in the above process, as only slight traces of titanic acid are dissolved by strong caustic soda.

(*D*) A. Leclère [1] separates aluminium and iron very exactly by the precipitation of the aluminium in the form of basic formate. For example, using a dilute solution containing a slight excess of sulphuric acid, first the iron is reduced to a protoxide salt. For this purpose it

[1] *Chemical News*, Feb. 19, 1904.

is best to use ammonium hyposulphite, as no residue is left in the precipitates. Ammonium formate is then added, and the whole kept boiling. The iron is kept in the form of protoxide, while the aluminium is precipitated gradually, not in the state of sulphite, but of basic formate mixed with a little sulphur. When drying the precipitate, nitric acid should be added to drive off the formic acid and to prevent the presence of a residue of carbon in the calcined alumina. The iron can be precipitated by the addition of sulphuretted hydrogen to the liquid filtrate. The sulphide is produced.

(*E*) Several years ago, Campbell and Hess [1] described a method for precipitating aluminium in the presence of iron after the latter had been reduced to the ferrous state by sulphurous acid. The reagent used was phenylhydrazine. The results appeared satisfactory; and, as a good method for the direct determination of aluminium in the presence of iron was needed, Mr. E. T. Allen [2] has studied this separation more closely, especially in regard to its application to rock analysis, where titanium is nearly always present, and sometimes zirconium.

The results indicate that it is practically impossible to separate the iron completely in one precipitation. With a double precipitation the results are good. When the quantity of precipitated alumina is large, there is apt to be a loss, which is ascribed to the long contact with the faintly acid wash-solution which is necessary to remove the iron. The method is excellently adapted to the separation of very small quantities of aluminium, such as a milligramme, or even less, from a large excess of iron, a point of considerable practical importance.

To the conditions laid down by Campbell and Hess a few additions might be made. The volume of the solution may vary, according to the quantity of alumina to be precipitated, from 100 to 200 cubic centimetres. It should be heated, and reduced by adding saturated ammonium bisulphite. From 5 to 20 drops, according to the quantity of the iron, may be used. If the solution turns deep red (ferric sulphite) it is not acid enough, and a few drops of hydrochloric acid should be added, for the sulphide itself does not reduce ferric salts—at least, not with rapidity. Now quickly bring to neutrality with ammonia, and then add several drops of dilute hydrochloric acid. If this last operation is done too slowly, the oxygen of the air helps to form a little ferric hydroxide which does not always readily dissolve in the dilute acid. Finally, add from 1 to 3 cubic centimetres phenylhydrazine, according to the weight of the alumina to be precipitated. If too little has been used, a few drops added to the filtrate will disclose the mistake. Stir until the precipitate has become sufficiently flaky, and allow to settle. The supernatant liquid will now be plainly acid to litmus. One need not be disturbed if the precipitate has a brownish colour, for it is not due to ferric hydroxide, but to the colouring matter

[1] *Journ. Am. Chem. Soc.* vol. xxi. p. 776.
[2] *Chemical News*, Jan. 22, 1904.

contained by all phenylhydrazine which has not been freshly distilled. When the determinations are allowed to stand too long, the air increases this oxidation product, and a brown insoluble scum forms on the surface of the liquid and on the sides of the vessel, which is rather troublesome to the analyst. Fortunately, equilibrium appears to be established in a short time. The vessels need not stand more than an hour, at any rate.

(*F*) Add sodium hydrocarbonate and then potassium cyanide as recommended for the separation of iron from aluminium. To the clear pale yellow solution of the cyanides add excess of colourless ammonic sulphide and boil, until the steam is neutral to test-paper. The zinc is wholly precipitated as sulphide quite free from iron (or nickel and cobalt if present), and in a granular condition, and it may be filtered and washed with the utmost ease.

Electrolytic Separation of Iron from Zinc [1]

M. Classen finds that when double iron and zinc oxalates are submitted to electrolysis there is not deposited at the negative pole an alloy of both metals, but, in the first place, zinc with a little iron. The electrolysis proceeds quite smoothly, and the sum of both metals may be easily ascertained if the proportion of zinc is less than one-third of the iron. If the proportion of zinc is higher as the electrolysis proceeds the zinc is redissolved with a considerable evolution of gas, while at the same time ferric oxide is deposited.

For larger proportions of zinc it is merely needful to dissolve a weighed quantity of a pure salt of iron (*e.g.* iron-ammonium sulphate which contains one-seventh of its weight of iron) in the liquid to be electrolysed in order to effect the determination of both metals in all cases.

Separation of Iron from Uranium

When, as is generally the case, ammonium carbonate is employed for this separation, it is well known that some of the iron is always dissolved with the uranium. The following is, however, a method for rendering the separation complete :—As uranium oxide in solution in ammonium carbonate is not precipitated by ammonium sulphide, add to the liquid, separated by filtration from the bulk of the iron oxide, a few drops of ammonium sulphide to eliminate from it, in the state of sulphide, the small quantity of iron which has been dissolved. After filtering again, a solution is obtained containing all the uranium without any trace of iron.

Separation of Iron from Chromium

(*A*) When the iron is in very large excess, the following is a good method for separating the chromium :—Treat the metal or ore by the

[1] For details of operation see chapter on Electrolytic Analysis.

ordinary processes, to separate the silica, and obtain a liquid containing all the metals in solution, the iron being at its maximum of oxidation; then precipitate the liquid by an excess of a strong solution of potash, and pour, drop by drop, into the solution containing the precipitate (and heated to 80° or 90°) a dilute solution of potassium permanganate until the permanganate loses its colour; the reaction is terminated when the liquid takes a greenish tinge, owing to the presence of potassium manganate. Then filter, and saturate the filtered liquid with acetic acid, which immediately reduces the small quantity of potassium manganate that gave to the solution its green colour. Into the liquid, which frequently has a yellow tinge, pour lead acetate, which produces a yellow precipitate of lead chromate, if the least trace of chromium be present.

(*B*) Another method is to nearly neutralise the solution, containing chromium and iron peroxide, with sodium carbonate, and add sodium acetate in excess. A current of chlorine gas or addition of chlorine water then readily converts the whole of the chromium present into chromic acid. Upon now boiling the solution, the excess of chlorine is expelled, while, at the same time, the iron is precipitated as basic acetate. The chromic acid in the filtrate may either be reduced with alcohol and hydrochloric acid and the chromium sesquioxide precipitated with ammonia, or lead acetate may be added and the lead chromate collected.

If it is not desired to precipitate the iron as basic acetate, it may be precipitated with ammonia; all the chromium will remain in solution as chromic acid.

R. B. Riggs[1] separates iron from chromium and aluminium by making use of the efficiency of hydrogen peroxide as an oxidising agent.

The following is an outline of the method of treatment:—Given a mixture of the hydroxide or basic acetate precipitates equivalent to 0·1 gramme of each of the three elements. Digest this precipitate in 100 cubic centimetres of water, to which 10 cubic centimetres of hydrogen peroxide and 1 gramme of sodium (or potassium) hydroxide have been added, until effervescence ceases. Separate the iron by filtration. Acidify the filtrate slightly with acetic acid, and precipitate the alumina by means of ammonia. (Where small quantities are present, long-continued boiling and a concentration of the solution may be necessary.) Filter off the alumina, and test the filtrate for chromium. The yellow colour of either the iron or alumina filtrates is characteristic. A confirmatory and more delicate test may be made by acidifying the filtrate from alumina slightly and adding a few cubic centimetres of hydrogen peroxide, obtaining the blue colour so characteristic of chromium compounds thus treated.

[1] *Chemical News*, Dec. 28, 1894.

Separation of Iron from Manganese, Nickel, Zinc, and Aluminium

According to G. Von Knorre, in neutral and faintly acid solutions of ferric salts, iron is precipitated by nitroso-naphthol quantitatively as ferri-nitroso-naphthol. In this manner iron can be separated from manganese, nickel, zinc, and aluminium. To about 0·1 gramme of iron present at least 1 gramme of nitroso-naphthol should be used. If considerable quantities of free acid are present, ammonia is added until a precipitate begins to appear, which is then redissolved in a few drops of hydrochloric acid. The weight taken for analysis must be so small that not more than 0·3 gramme iron is present, as otherwise the bulk of the ferri-nitroso-naphthol is too considerable.

The separation of iron from manganese gives very good results. In order to determine the manganese in the filtrate the liquid is concentrated by evaporation, rinsed into a capacious Erlenmeyer flask, and mixed with ammonium chloride and ammonia in large excess. The manganese is then precipitated by means of a current of air charged with bromine. It falls as hydrated peroxide. The washings retain to the end a slight yellowish colour, but the results are not affected.

The separation of iron from zinc and from nickel presents no difficulty. In the filtrates zinc is precipitated with sodium carbonate, nickel with bromine water, and pure potash-lye, as nickel sesquihydroxide.

In precipitating iron by means of nitroso-naphthol it is accompanied not only by copper and cobalt, if present, but also by phosphoric acid.

Separation of Iron from Chromium and Uranium

According to M. A. Ditte, the separation of these oxides may be effected with great accuracy by operating in the manner proposed by M. Sainte-Claire Deville for the separation of iron and alumina. The metals are brought to the state of sesqui-salts; all metals whose sulphides are insoluble in dilute acids are removed by known methods, and the ferric, chromic, and uranic oxides are then precipitated together by an excess of ammonia. Care must be taken to drive off by ebullition any free ammonia which might dissolve a little uranium. The oxides are well washed, calcined, placed in a porcelain tube, and heated to redness in a current of pure hydrogen. The ferric oxide becomes metallic iron, the uranic oxide is reduced to uranous oxide, while the chromic oxide remains unaltered. This mixture of iron, and uranium and chromium oxides is weighed, returned to the tube, and submitted to the action of a current of gaseous hydrochloric acid at a red heat. The uranium and chromium oxides remain entirely unattacked by the acid, and their weight suffers no variation. As for

the iron, it is entirely volatilised as ferrous chloride, and deposited in white crystals in a cooler part of the tube. After an hour or an hour and a half the tube is allowed to cool in a current of hydrogen, to drive out the hydrochloric acid, and the mixture of chromic oxide and uranous oxide is weighed and treated with pure nitric acid. The uranium protoxide, which remains in the form of a brown amorphous powder, is at once attacked, even in the cold, with evolution of nitrous fumes and formation of uranium nitrate. It is well, however, to heat for a few moments, in order to be certain that the chromic oxide retains no traces of uranium; the solution is then filtered off, and the residue calcined and weighed.

Separation of Iron and Alumina from Zirconium

Charles Baskerville [1] adds sulphurous acid to a solution of zirconium chloride, in a cold acid solution, when a dense white precipitate immediately forms. On boiling with an excess of sulphurous acid in a neutralised solution—*i.e.* the hydrochloric acid solution neutralised by ammonium hydroxide until the slight precipitate formed is no longer dissolved on boiling—this precipitate is taken up with two or three drops of dilute hydrochloric acid; the zirconium is completely precipitated.

This method affords an excellent means of separating zirconium from iron. Several experiments were carried out upon solutions containing known amounts of the chlorides of these two metals. The zirconia was precipitated by sulphurous acid, boiled five minutes, and washed four or five times with hot water.

The same method may be applied for the separation of zirconium from alumina.

Mr. F. S. Havens and R. F. Way [2] have shown that iron oxide may be completely volatilised as chloride by a strong current of hydrochloric acid gas acting at a temperature of 450°–500°; and the addition of a little free chlorine to the gaseous hydrochloric acid renders this action complete at lower temperatures (180°–200°) without the danger of error arising from the liability of ferric chloride to dissociation, or from deficiency of oxidation in the oxide treated, or mechanical loss due to too rapid volatilisation. It has been shown that this reaction can be employed for the separation of iron and aluminium, taken as the oxides, and its application to the separation of iron from other metallic oxides has been suggested.

The oxides of chromium, zirconium, and beryllium, like aluminium oxide, are not acted upon by a current of dry hydrochloric acid gas at the temperatures before mentioned, and these oxides also can be entirely freed from iron by this reaction, as the experiments to be described will show. The procedure was the same in each case and

[1] *Chemical News*, Aug. 3, 1899. [2] *Ibid.* Dec. 15, 1899.

analogous to that employed for the separation of iron from aluminium. A mixture of a weighed portion of one of these oxides with a weighed portion of ferric oxide, contained in a porcelain boat and placed within a roomy glass tube supported in a small combustion furnace, was submitted to the action of a dry current of hydrochloric acid gas and chlorine generated by dropping sulphuric acid upon a mixture of strong hydrochloric acid, common salt, and a small amount of manganese dioxide. The gas was admitted at one end of the combustion tube and passed out at the other through a water trap, while the required temperature (from 200°–300°) was maintained by regulating the various burners of the furnace. The time of action varies somewhat with the condition of the oxide to be volatilised, and the temperature, generally an hour's heating at 200°, proves sufficient for the complete removal of 0·1 gramme of iron. At higher temperatures the action is more rapid; but the lighter oxide, the beryllium especially, is liable to mechanical loss through the too rapid volatilisation of the iron.

The separation of iron from chromium, zirconium, and beryllium by this method is obviously complete within very satisfactory limits of error.

Separation of Iron from Zirconium

Render the solution nearly neutral with sodium carbonate, and add excess of sodium thiosulphate. Boil the liquid for a short time, and all the zirconia will be precipitated, with a little sulphur, but perfectly free from iron, which will all be in solution.

The solution containing zirconium and iron may also be boiled with nitric acid to peroxidise the iron, and then precipitated with excess of ammonia. The precipitate is then digested with excess of oxalic acid, which dissolves the whole of the iron, together with a trace of zirconia, but leaves the greater part of the zirconia in the form of an insoluble oxalate.

Or, the mixed precipitate of iron sesquioxide and zirconia may be digested in ammonium sulphide until the whole of the iron is in the state of sulphide. Decant the supernatant liquid and digest the black precipitate in a dilute solution of sulphurous acid. This dissolves the iron sulphide and leaves the zirconia quite colourless.

The process given on page 138 for the preparation of pure zirconia, &c., may also be used to separate iron and zirconium.

Mr. J. Merritt Matthews [1] gives the following details for the separation of iron from zirconium:—

On introducing a small quantity of water into an ethereal solution of zirconium tetrachloride, it was noticed that a white precipitate was formed, insoluble in excess of ether. This precipitate was no doubt an oxychloride of zirconium.

[1] *Chemical News*, March 3, 1899.

On testing the precipitate with a solution of potassium thiocyanate, not a trace of iron was indicated, although the zirconium tetrachloride used in the solution showed a decided contamination by iron under the same conditions.

Weighed quantities of the chlorides of zirconium and iron were mixed together. The mixed salts were dissolved in water and carefully evaporated to dryness on a water-bath; after cooling they were treated with absolute ether, and dry hydrochloric acid gas was passed through the liquid. Experience proved that this latter treatment was necessary to effect a rapid and complete solution of the iron-salt by the ether, as the ferric chloride on evaporation to dryness evidently forms basic compounds of indefinite composition which are with difficulty soluble in ether. The solution was rapidly filtered, and the residue washed with absolute ether several times to ensure the removal of the last traces of the iron-salt. The residue was then dissolved in water, and the zirconium determined by precipitation as hydroxide by means of ammonium hydroxide; drying the precipitate, igniting, and weighing as zirconium dioxide. The ether was evaporated or distilled from the filtrate, and the residue dissolved in water, with the addition of a few drops of hydrochloric acid if necessary; and the iron was determined by precipitation with ammonium hydroxide, drying the precipitate, igniting, and weighing as ferric oxide.

On testing the aqueous solution of the residue containing the zirconium with potassium thiocyanate solution, not a trace of iron was discovered, showing that the separation had been a complete and successful one.

In making a practical use of this separation it is only necessary to obtain the two metals in solution in the form of chlorides, and then the details as already given may be applied.

The fact that zirconium oxychloride is perfectly white in colour should not be taken as a final indication that it is absolutely free from traces of iron; and this should be borne in mind in the preparation of salts for atomic weight determinations.

This method is especially recommended for the separation of iron from zirconium. A point, however, which may prove of practical importance, and which it is most desirable to emphasise, is that by carefully following out the procedure herein described, zirconium oxychloride and dioxide may be easily and quickly prepared perfectly free from iron. This fact may be of considerable importance and utility in the preparation of zirconium compounds for use in atomic weight determinations, where a high degree of purity is absolutely necessary in order to obtain authentic results.

The details of the separation of iron from zirconium are the same as those for the separation of titanium. The results show that a single precipitation is not always sufficient to remove all the iron.

Separation of Iron from Thallium

Certain kinds of iron pyrites constitute the richest natural source of thallium. At page 165 the methods of separating thallium from thalliferous pyrites on the large scale are fully described. Thallium may be readily detected in thalliferous pyrites in the following manner :—Dissolve the finely powdered mineral in nitro-hydrochloric acid ; evaporate with excess of sulphuric acid until the nitric acid is evolved ; dissolve in water, and add sodium sulphite to reduce the iron and thallium to the state of proto-salts. On adding potassium iodide, and allowing the liquid to stand for some time, a bright yellow precipitate of thallium iodide will separate. This test is sufficiently delicate to show thallium in a few grains of a pyrites which does not contain more than 1 part in 10,000.

If the iron only is in the state of peroxide (as in the case of thallium-iron alum) the separation may be effected by ammonia, which precipitates the iron sesquioxide and leaves the thallium in solution.

Separation of Iron from Titanium

(*A*) Phenylhydrazine gives a practically complete separation of titanium from iron in two precipitations. Mr. E. T. Allen has never found more than traces of titanium remaining with the iron. It was sought for as follows :—The iron, with any titanium it might contain after the precipitation with phenylhydrazine, was removed from the solution by ammonium sulphide, washed a few times, and dissolved in nitric acid, from which solution it was subsequently precipitated by ammonia, and weighed. The weighed oxide was now tested for titanium by the method described in Bulletin 176, U.S. Geol. Survey, p. 67.

The same details apply to this separation as were laid down for the separation of iron from aluminium (see page 223), except that here the solution may be considerably more acid before adding the phenylhydrazine. If much titanium is present, a considerable precipitate will form before the solution is completely neutralised by ammonia. When the neutral-point is reached, half a dozen drops of 1 : 1 hydrochloric acid may be added. This quantity is frequently insufficient to redissolve all the titanium precipitate, but that is a matter of no consequence.

(*B*) When iron sesquioxide and titanic acid are together in dilute solution, they can be separated by ebullition with sodium thiosulphate, as in the case of iron and zirconium. The titanic acid precipitates while the iron remains in solution. Or, add ammonia in excess to the solution, digest the mixed precipitate of titanic acid and iron sesquioxide with ammonium sulphide, and then dissolve out the iron with sulphurous acid.

(*C*) Other methods of separating iron and titanium may be found under the heading Titanium (page 137).

Separation of Iron from Cerium

The metals must be in solution in the form of sulphates. Reduce the iron completely to the form of protosulphate by means of a current of sulphuretted hydrogen passed into the hot solution. To the solution, which should be concentrated, add a saturated solution of sodium sulphate, together with a sufficient quantity of the dry sulphate in powder to saturate the water of solution. It is most advantageous to use hot solutions. The insoluble double sodium sulphates and the cerium metals separate immediately as a white, highly crystalline powder, which is to be thrown upon a filter and thoroughly washed with a saturated solution of sodium sulphate. After washing, the double sulphates upon the filter are to be dissolved in hot dilute hydrochloric acid, the solution largely diluted with water, and the cerium metals precipitated by ammonium oxalate in the manner already pointed out (page 55). From the filtrate the iron may be precipitated at once as sesquioxide by ammonia, after peroxidising it by means of chlorine water, and rendering the solution slightly acid with hydrochloric or sulphuric acid.

Separation of Iron from Magnesium

(*A*) When iron sesquioxide is precipitated by means of ammonia from a solution containing magnesium, some magnesium is always carried down with it in spite of the presence of an excess of ammoniacal salts. They may, however, be perfectly separated in this manner:— Dilute the solution considerably, neutralise with sodium carbonate, then add acetic acid and sodium acetate to the cold solution. Boil for a short time, when the whole of the iron will be precipitated as basic acetate. Filter hot, and wash quickly with hot water. All the magnesium will be in the solution.

(*B*) Dr. Calvert dissolves the oxides in hydrochloric and a little nitric acid, nearly neutralises with ammonia, and precipitates the iron with ammonium succinate. The succinate of iron sesquioxide is rapidly filtered off and washed with cold water. The filtrate will contain the whole of the magnesium.

Separation of Iron from Calcium

When iron sesquioxide is precipitated in the ordinary manner with ammonia, in the presence of excess of ammoniacal salts, it always carries down a considerable quantity of calcium if present, and the larger the proportion of iron as compared with that of calcium, the

greater is the proportion of calcium carried down by the iron. This error can be avoided by precipitating the iron as succinate, or by throwing the iron down as basic acetate as just described (Separation of Iron from Magnesium). In either case the whole of the calcium will remain in the solution.

Iron sesquioxide may be safely precipitated by ammonia if the precaution is taken to boil until all smell of ammonia has gone off, before filtering; the iron does not now retain any calcium. If much calcium be present, a little ammonium chloride may be added to make sure of getting all into solution. As the solution no longer contains free ammonia, it can be filtered without there being danger of the calcium coming down as carbonate by absorption of carbonic acid from the atmosphere. The filtrate may be concentrated by evaporation, and the calcium precipitated as oxalate.

MANGANESE

Chromium and manganese, according to Professor E. J. Chapman, may be distinguished before the blowpipe as follows :—When a mineral is expected to contain manganese, it is commonly tested by fusion with sodium carbonate. But chromium compounds form with that reagent a green enamel, much resembling that formed by manganese compounds. The sodium chromate enamel is yellowish green after exposure to the oxidising flame, and never exhibits any tinge of blue. The sodium manganate enamel is greenish blue when quite cold. To prevent mistakes, the bead may be saturated with vitrified boracic acid until all the carbonic acid is expelled and a clear glass is obtained. The chrome glass will retain its green colour, while the manganese glass will become amethystine or violet. In place of boracic acid, silica may be used if more convenient. In this case the reaction is assisted by the addition of a very small amount of borax.

Electrolytic Separation of Manganese [1]

(*A*) Classen finds that manganese ranks among those metals which are oxidised by the current to peroxide and separated out as such at the positive electrode. The quantitative separation as peroxide can be effected from the solution of the potassium manganese oxalate (the precipitation from the double ammonium oxalate is not complete) or from the solution of any manganese salt containing free nitric or sulphuric acid. For the execution of the former method the solution of the manganese salt is mixed with the potassium oxalate in slight excess, diluted with water, and electrolysed with a current of 9 to 12 c.c. detonating gas per minute. Small quantities of peroxide adhere

[1] For details of operation see chapter on Electrolytic Analysis.

sufficiently fast to the positive electrode, so that after previous washing with water they may be converted into mangano-manganic oxide by igniting the electrode, which must have been previously weighed. For larger quantities it is admissible to use the platinum capsule as a positive electrode, and to try after the completion of the precipitation[1] to convert (without filtration) the deposit of peroxide into mangano-manganic oxide by ignition. If this is not practicable the precipitate is filtered off, washed with hot water, and the manganese is converted either into mangano-manganic oxide or sulphate.

The above-described method, as will be further explained, admits of the separation of manganese from a considerable number of metals and their simultaneous determination.

The deposition of manganese in an acid solution is practicable in presence of free nitric or sulphuric acid.

For the execution of the former method the solution of manganese nitrate (containing at most 0·05 gramme manganese) is acidified with nitric acid, the platinum capsule is taken as the positive electrode, and a platinum spiral is immersed as a negative electrode; the liquid is continuously heated to about 30° in the water-bath and electrolysed with a current of about 0·03 c.c. detonating gas per minute. As the nitric acid is transformed into ammonia, we ascertain from time to time if the liquid has still an acid reaction. If not, nitric acid is added until an acid reaction is obtained. The coating of manganese peroxide is carefully washed off with water, and the capsule is dried until the weight is constant, either in the air-bath at 60° or over sulphuric acid in the air-bath. The deposit has the composition $MnO_2 + H_2O$. On ignition MnO_2 is converted into Mn_3O_4, the weight of which may be determined.

(*B*) If the manganese exists in solution as sulphate, F. Rüdorff acidifies the solution with 3 drops of dilute sulphuric acid, dilutes with water to 100 c.c., and electrolyses with a battery of two Meidinger elements.

The maximum quantity of manganese which may be present in solution is 0·04 gramme. The deposition is complete in from twelve to fourteen hours, and the end is ascertained by testing with ammonium sulphide.

For removing the manganese peroxide from the capsule we use strongly diluted sulphuric acid with the addition of hydrogen.

(*C*) For depositing the manganese as peroxide from a solution of the double pyrophosphate, A. Brand mixes the solution with as much sodium pyrophosphate as is amply sufficient for forming the double salt and adds ammonia until the precipitate has been redissolved. If

[1] To ascertain the end of the reaction ammonium sulphide is quite unsuitable, as oxalic acid greatly retards the precipitation of the manganese as sulphide. It is best to evaporate a small portion upon the platinum cover, and fuse it with potassium carbonate.

the quantity of manganese is not more than about 0·02 in 100 c.c., he electrolyses with a current of 0·1 c.c. per minute. If the quantity of manganese is greater, the decomposition is begun with a current of only 0·01 c.c. of detonating gas, which, towards the end of the operation, is increased to about 0·4 c.c. Brand washes the peroxide only with water, as on the addition of alcohol the coating easily shells off; or he converts the MnO_2 into Mn_3O_4 by ignition over the blast. If we use the platinum capsule as a positive electrode, we can, according to Brand, obtain from 150 c.c. of liquid 0·2 gramme manganese as firmly adhering peroxide.

Estimation of Manganese

(*A*) Under many circumstances manganese can be estimated with great accuracy by precipitation as ammonio-phosphate, and weighing as pyrophosphate, like magnesium. This salt, from its highly crystalline structure, the facility with which it is formed, and its insolubility, appears well adapted to the quantitative estimation of manganese.

Dr. Wolcott Gibbs, who has worked out this method, recommends that to the solution of manganese, which may contain salts of ammonium or of the alkaline metals, di-sodic ortho-phosphate be added in large excess above the quantity required to precipitate the manganese as ortho-phosphate. The white precipitate is then to be redissolved in excess of sulphuric or hydrochloric acid, heated to the boiling-point, and ammonia added in excess. A white or semi-gelatinous precipitate is produced, which, on boiling or standing for some time, even in the cold, gradually becomes crystalline, and finally is completely converted into beautiful talcose scales which have a pearly lustre and a pale rose colour. It is best to precipitate each time in a platinum vessel, in which the ammonio-phosphate may be boiled for ten or fifteen minutes, and to allow the salt to remain at a temperature near the boiling-point of the liquid for an hour after it has become crystalline. The ammonio-phosphate may then be filtered off and washed with hot water. The washing takes place with extraordinary facility on account of the crystalline character of the salt. The ortho-phosphate, after drying and ignition, yields manganese pyrophosphate as a nearly white powder.

The advantage of this method over that commonly employed for the estimation of manganese is that the process admits of the metal being weighed in the form of a perfectly definite compound, and not as an oxide which cannot be safely assumed to be manganoso-manganic oxide. When manganese is associated with the alkaline earths, it is, of course, first to be separated as sulphide, or as a hydrate of the sesquioxide. The ammonio-phosphate is almost absolutely insoluble in boiling water, in ammonia, and in solutions of ammonium salts. The salt is nearly white, but sometimes becomes a little red upon the filter. If it assumes a rather deep dull-red colour, the whole of the manganese

phosphate has not been converted into ammonio-phosphate. The precipitate is then to be redissolved in dilute hydrochloric acid, more sodium phosphate added, and then ammonia in excess, after which the boiling is to be repeated. This repetition is very rarely necessary, a little practice enabling the analyst to judge when the conversion from the flocky gelatinous to the crystalline condition is complete. The filtrate from the crystalline salt is perfectly free from manganese. This process will not give accurate results in the presence of copper, or of metals which form precipitates with phosphates. Phosphoric acid cannot be estimated in this way by precipitation as manganese ammonio-phosphate, because the crystalline character of the salt upon which the success of the process depends is only produced by digestion with an excess of phosphate.

(*B*) Manganese may be estimated by precipitation as oxalate, and subsequent titration with potassium permanganate (see page 145, Leison's process for the estimation of zinc). To a soluble manganese salt add oxalic acid, and then a large excess of strong alcohol; manganese oxalate is completely precipitated. The subsequent filtration and titration with potassium permanganate is conducted as described at page 145. From the amount of oxalic acid thus found the quantity of manganese may be calculated.

(*C*) A. Guyard estimates manganese by precipitation with potassium permanganate, which forms, with salts of manganese protoxide, a precipitate of permanganate of manganese protoxide, insoluble in water and dilute inorganic acids. All the other metals whose protoxides react on potassium permanganate are found in the state of peroxide in the same liquor in which the manganese exists as protoxide; consequently, these foreign metals, whatever they may be, do not interfere with the results. As long as there is manganese in the liquor it is precipitated, and the potassium permanganate is decolourised; but as soon as the reaction is ended a drop of the permanganate communicates a persistent rose tint to the solution.

The operation is best performed in the following manner:—1 or 2 grammes of the manganese salt to be assayed are dissolved in aqua regia. The solution is boiled for some time to transform all the manganese into a protoxide salt; the solution is then very nearly neutralised by an alkali; that done, it is diluted with a large quantity of boiling water, and the whole is kept at a temperature of about 80° C. The standard solution of potassium permanganate is now gradually added from a burette. The manganese is immediately precipitated in the form of violet-brown flocculi of manganese permanganate. The operation is arrested occasionally to allow the precipitate to collect, which it does very quickly, and is entirely stopped when a persistent rose colour is obtained.

To estimate the strength of the solution of potassium permanganate use pure sulphate of the manganese protoxide dried at rather a

high temperature. This salt has then a fixed composition and keeps well in a tightly stoppered bottle. A normal solution may also be prepared for each operation.

For every equivalent of potassium permanganate added, three equivalents of manganese protoxide will be precipitated. In any case the solution must be so prepared that 30 c.c. correspond to about 1 gramme of manganese.

The permanganates of the manganese protoxide are three in number:—

1. The oxide Mn_7O_{12}, the formula of which should be written $5MnO,Mn_2O_7$.
2. „ Mn_6O_{11} „ „ „ „ $4MnO,Mn_2O_7$.
3. „ Mn_5O_{10} „ „ „ „ $3MnO,Mn_2O_7$.

Each of these bodies is formed according as we mix 1 equivalent of potassium permanganate with 5, 4, or 3 equivalents of a salt of the manganese protoxide. The first is formed in the cold when there is more manganese salt than potassium permanganate; the second is also formed in the cold when more permanganate than manganese salt is present in the solution. The binoxide is only formed in a hot solution.

(*D*) Mr. John Pattinson finds that the whole of the manganese in a solution of manganous chloride can invariably be precipitated in the condition of dioxide, if a certain amount of *ferric chloride* be present, by a sufficient excess of a solution of calcium hypochlorite or bromine-water, adding, after heating the solution to from 140° to 160° F., an excess of calcium carbonate, and then well stirring the mixture. Without the ferric salt the precipitation as dioxide is imperfect. Zinc chloride may be substituted for ferric chloride, but neither aluminium nor barium chlorides have the same desirable effect. The author recommends the following solutions, &c.:—The clear liquid obtained by decantation from a 1·5-per-cent. solution of bleaching powder; light granular calcium carbonate obtained by precipitating an excess of calcium chloride by sodium carbonate at 180° F.; a 1-per-cent. solution of ferrous sulphate in dilute (1 in 4) sulphuric acid; standard solution of potassium bichromate equivalent to 1 part of iron in 100 of solution. The application of the process to manganiferous iron ores is as follows:—10 grains of the ore, dried at 212°, are dissolved in a 20-ounce beaker in about 100 fluid grains of hydrochloric acid (sp. gr. 1·18). Calcium carbonate is then added until the free acid is neutralised and the liquid turns slightly reddish. 6 or 7 drops of hydrochloric acid are now added, and 1000 grains of the bleaching-powder solution, or 500 grains of saturated bromine-water, and boiling water run in until the temperature is raised to 140° or 160° F.; 25 grains of calcium carbonate are added, and the whole well stirred. If the supernatant solution has a pink colour, the permanganate is reduced by a few drops of alcohol. The precipitated iron and manganese oxides are filtered off

and washed; 1000 grains of the acidified ferrous sulphate solutions are carefully measured into the 20-ounce beaker already used; the filter with its washed contents added. A certain quantity of the ferrous sulphate is oxidised by the manganese dioxide; this quantity is estimated with the standard bichromate solution, when the quantity of manganese dioxide can easily be calculated. The iron present must be at least equal in weight to the manganese during the precipitation, in order to ensure the absence of lower oxides.

Detection of Manganese in Ashes

Professor E. Campani proceeds thus:—When there are sufficient phosphates in the ash it is treated with an excess of hot aqua regia, the liquid filtered, and evaporated to dryness in a porcelain capsule on the water-bath. If the ash contains manganese the residue presents an amethyst or violet colour, more or less intense, according to the quantity of the manganese phosphate produced. As all ashes do not contain phosphates, the author finds it useful to treat with a mixture of 15 c.c. of syrupy phosphoric acid and 85 c.c. of nitric acid.

Electrolytic Separation of Manganese from Iron[1]

(*A*) According to Classen, a solution of ammonium oxalate is decomposed under the action of the galvanic current chiefly into hydrogen and ammonium hydrocarbonate. The latter is again partially resolved into ammonia which remains principally absorbed in the liquid, and carbonic acid. In the electrolysis of a hot solution of ammonium oxalate the ammonium carbonate produced by the current is partially neutralised. At the positive electrode there ensues a very rapid evolution of carbonic acid.

If the solution of the double iron and manganese oxalates is electrolysed without previously adding a large excess of ammonium oxalate, there at once appears at the positive electrode the characteristic colour of permanganic acid, and by degrees manganese peroxide is separated out at the positive electrode and iron at the negative. It is not practicable to carry out the electrolysis in this manner, since the manganese peroxide as it is being formed carries down with it appreciable quantities of iron hydroxide. A quantitative separation of both metals is possible only when the formation of manganese peroxide is prevented until the chief part of the iron has been deposited.

If we electrolyse a solution of iron-manganese oxalate, containing a large excess of ammonium oxalate, in the cold, there is not a large precipitation of manganese until the ammonium oxalate is for the most part decomposed. On the electrolysis of the above-named double salt the separation of manganese peroxide is only slight until, on the copious

[1] For details of operation see chapter on Electrolytic Analysis.

formation of ammonium carbonate or ammonia, there occurs a more considerable precipitate (a mixture of peroxide and oxide) in consequence of the action of the ammonium carbonate or ammonia upon the manganese double salt.

The strong dissociation of ammonium oxalate when heated supplies a very simple means of avoiding or greatly limiting the formation of a manganese precipitate during electrolysis. If we decompose by heat a solution of iron and manganese mixed with a large excess of ammonium oxalate (proceeding for conversion into double oxalates as given under iron, but with the difference that from 8 to 10 grammes ammonium oxalate are dissolved in the liquid), with a current of from 10 to 12 c.c. detonating gas per minute, a sharp separation of manganese is at once effected, as, even when the proportion of manganese is high, only a small fraction thereof is deposited as a peroxide on the positive electrode, and the electrolysed liquid is scarcely rendered turbid.

After the completion of the reduction the liquid is decanted off, the capsule is cleansed by repeated rinsings with water, and the latter, as well as any traces of the deposit of peroxide, is removed with alcohol, the capsule being, if needful, gently rubbed with the finger.

The execution of the method is so simple that even the least experienced operator readily obtains accurate results. In order to satisfy himself on this point, Classen caused the method to be carried out by a student who had not previously been accustomed to any quantitative work. He obtained figures which differed only by 0·05 per cent. from the substance weighed out.

As stated in the quantitative determination of manganese in the state of peroxide, its precipitation from a solution in ammonium oxalate is not quantitative. For its complete separation the liquid containing the manganic precipitate in suspension is boiled in order to decompose the ammonium hydrocarbonate formed by electrolysis on the addition of pure potash or soda-lye. This is effected in a porcelain capsule until the liquid no longer smells of ammonia. Sodium carbonate is then added, and then *a little* sodium hypochlorite or, preferably, hydrogen peroxide. The manganese peroxide rapidly subsides, and may be filtered immediately. The precipitate should be washed with hot water to which a little ammonium nitrate has been added; and it is converted by ignition into mangano-manganic oxide (Mn_3O_4), or, better still, into manganese sulphate ($MnSO_4$).

For executing the latter method the precipitate in the crucible is moistened with a little pure concentrated sulphuric acid and heated very slightly, so that the bottom of the crucible appears scarcely red-hot.

If it is intended to separate the manganese as sulphide, the liquid is boiled for the decomposition of the ammonium carbonate, the remaining ammonia is neutralised with nitric acid, and precipitated with ammonium sulphide.

The manganese sulphide is determined either as such by ignition in a current of hydrogen, or, what is simpler, it is converted into manganese sulphate by heating with a few drops of sulphuric acid.

(*B*) For separating manganese from iron and cobalt, A. Brand has utilised an observation made by Classen in the year 1881, proceeding as follows:—The solution is mixed with a large excess of sodium pyrophosphate, so as to form a clear solution, in which from 4 to 8 grammes ammonium oxalate are further dissolved. Strongly acid solutions must be neutralised before adding the pyrophosphate. The electrolysis is effected with a current of 5 c.c. detonating gas per minute, which, towards the end of the process, is increased to 15 or 20 c.c.

For the determination of the manganese the liquid is slightly acidified with sulphuric acid, and the red manganic double salt is reduced in heat by means of oxalic acid. About 15 per cent. of concentrated ammonia is then added, and the manganese is then determined according to Brand's method.

Separation of Manganese from Iron

(*A*) Obtain the two metals in the form of chlorides (iron sesquichloride and manganese protochloride), dilute the solution considerably, and neutralise as nearly as possible with sodium carbonate. To the cold solution add sodium acetate in more than sufficient excess to change all the iron and manganese by double decomposition to neutral acetates. Add a few drops of acetic acid. Raise to the boiling-point and keep in brisk ebullition for a short time, and then filter rapidly through a ribbed filter, keeping the liquid as hot as possible during filtration. The whole of the iron will be in the precipitate as basic acetate, while the manganese will be in solution. If an absolutely complete separation is needed, redissolve the precipitate in hydrochloric acid, and repeat the operation. Traces of manganese, which the first precipitate of basic iron acetate may have carried down, are in this manner removed. The two filtrates containing manganese may be added together.

(*B*) Ammonium succinate added to a neutral solution of iron sesquichloride and manganese protochloride entirely precipitates the iron. Filter off and wash with cold water; all the manganese will be in the filtrate.

(*C*) Barium carbonate added gradually, with constant stirring, to a similar solution precipitates all the iron as sesquioxide.

(*D*) Pour the solution of the two metals into an excess of a concentrated aqueous solution of potassium cyanide. After standing from half an hour to an hour the precipitate redissolves, and only a slight turbidity remains. The whole is filtered, the residue is dissolved in a few drops of dilute hydrochloric acid, the solution is mixed with excess of potassium cyanide, and the clear solution is added to the filtrate.

All these operations are performed in the cold. Iodine is then added till the liquid appears brown, when any traces of free iodine are removed by the addition of a few drops of free alkali. The complete separation of the manganese is ascertained by adding iodine to a small portion of the liquid, decanted or filtered, heating very gently and adding soda-lye. The liquid should remain clear. The precipitated manganic oxide is filtered off, washed, dissolved in hydrochloric acid, precipitated with ammonium sulphide at a boil, and weighed as manganese sulphide.

The salts of the two metals are dissolved in concentrated nitric acid (1·35), heated to a boil, and kept at this temperature, while potassium chlorate is gradually added in small portions. The liquid is diluted with water and filtered. The precipitate, when washed, is always found to contain iron. It is therefore redissolved in hydrochloric acid, evaporated to dryness, and the residue taken up in concentrated nitric acid, and treated again with potassium chlorate at a boil. A peroxide is now precipitated containing very small traces of iron.

Separation of Manganese from Iron when Phosphoric Acid is present [1]

Proceed, in the first place, as directed for the electrolytic separation of iron from manganese (page 237), separating the iron as metal and the manganese as peroxide. The filtrate from the latter precipitate contains all the phosphoric acid. For its determination the liquid is acidified with hydrochloric acid, one-third its volume of ammonia is added, and then magnesia mixture. If the acidification is omitted, crystals of potassium-ammonium hydrocarbonate are deposited along with the magnesium-ammonium phosphate, and cannot be subsequently eliminated by washing with dilute ammonia. The precipitate of magnesium-ammonium phosphate is converted into magnesium pyrophosphate in the ordinary manner.

The above procedure must also be followed in case of the determination of phosphoric acid along with iron and manganese. If the liquid freed from iron, but only partially freed from manganese (and therefore not mixed with sodium hypochlorite or hydrogen peroxide), were used directly for the precipitation of phosphoric acid, the residue of the manganese would be thrown down as phosphate along with the ammonium-magnesium phosphate, whence the result would be too high.

Separation of Manganese, Iron, and Aluminium from Phosphoric Acid [2]

Classen finds that if aluminium is simultaneously present, it is not practicable, as directed above, to precipitate the manganese as peroxide;

[1] For details of operation see chapter on Electrolytic Analysis. [2] Ibid.

as aluminium phosphate is also thrown down along with the manganese, even if the peroxide is redissolved and the precipitation repeated. Neither citric acid, tartaric acid, nor glycerin is able to prevent the precipitation of aluminium phosphate. The presence of phosphoric acid along with aluminium demands the separation of the manganese as sulphide. He proceeds in the usual manner, submitting the double oxalates to electrolysis and decanting the liquid freed from iron into a beaker. The manganese peroxide adhering to the positive electrode is dissolved in hydrochloric acid, the solution is mixed with an excess of pure soda-lye, and added to the bulk of the solution. Tartaric acid is then added, followed by ammonia until the reaction is alkaline, and finally by ammonium sulphide. After standing for three or four hours all the manganese is deposited as green sulphide, which is determined in the usual manner.

The application of electrolysis for the determination of phosphoric acid presents in this case little advantage ; it is preferably precipitated in a separate portion by means of the molybdenum solution.

Separation of Manganese, Iron, and Sulphuric Acid

Classen proceeds as for the separation of phosphoric acid : iron and manganese are converted into soluble double salts by means of potassium and ammonium oxalate, and electrolysed. The precipitation of the sulphuric acid may be (if the determination of the manganese is not important) directly undertaken in the filtrate from the manganese peroxide without previously separating the last traces of manganese by means of hydrogen peroxide or sodium hypochlorite. It is only requisite to acidulate with hydrochloric acid and to precipitate the boiling liquid with barium chloride.

Separation of Manganese from Aluminium

(*A*) Manganese and aluminium may be separated by employing a similar process to the one described for the separation of manganese from iron (page 289) with sodium acetate, bearing in mind that the precaution of dissolving the precipitated basic aluminium acetate, and reprecipitating it by treatment with sodium acetate as there advised, should always be adopted, since aluminium has more tendency than iron to carry down manganese.

(*B*) Another process consists in adding ammonium chloride, heating to ebullition, pouring in caustic ammonia, and boiling till the excess of the latter is disengaged. The small quantity of manganese protoxide at first carried down decomposes the ammonium chloride upon ebullition and dissolves as chloride, the ammonia going off. When no more smell of ammonia is perceived, the solution may be filtered without taking special precautions against free access of air.

Separation of Manganese from Zinc

(*A*) Obtain the solutions in the form of protochlorides, nearly neutralise with sodium carbonate, dilute with a large quantity of hot water, and keep the solution at about 80° C. Add solution of potassium permanganate until the supernatant liquid is of a persistent rose colour. All the manganese will be in the precipitate in the form of manganese permanganate or manganese binoxide, while the zinc will be in solution. If the strength of the solution of potassium permanganate has been previously ascertained, the manganese may be determined in this way quantitatively; if not, the precipitate may be filtered off, calcined, and weighed as Mn_3O_4. Three-fifths of the total quantity of manganese found will represent the amount originally in solution.

(*B*) Messrs. Jannasch and Niederhofheim's process is the following: The manganese and zinc in the form of sulphates, say 0·5 gramme of each, are dissolved in 50 c.c. of water in a large platinum dish provided with a lip, and mixed with 10 c.c. of a 10-per-cent. solution of potassium cyanide, after which 10 c.c. of 25-per-cent. potash-lye are added, and the mixture is stirred with a platinum spatula until the precipitate is almost entirely redissolved. The manganese is then precipitated with 50 or 60 c.c. of a pure solution of hydrogen peroxide, and the mixture (covered) is heated for fifteen or twenty minutes upon a boiling-water bath and then filtered into a second capacious platinum capsule and washed out with hot water. When the filtrate is quite cold it is supersaturated with hydrochloric acid (30 c.c. of the concentrated acid), and poured back into a capsule of Berlin porcelain (on account of the potassium nitrate often found in no small proportion in commercial hydrogen peroxide), evaporated to dryness, the residue heated in the air-bath to from 110° to 115° for at least half an hour, redissolved in water with the addition of 15 or 20 drops of dilute hydrochloric acid, and separated by filtration from the deposit of silica, which is rarely absent. Lastly, the filtrate while boiling is precipitated in the prescribed manner with sodium carbonate, and the zinc is subsequently weighed as oxide. The zinc oxide, after ignition, should give a clear solution in dilute acetic acid. An insoluble residue, if present, consists of silica or alumina, or of both these impurities, the latter of which appears almost regularly, often indeed in considerable quantities if the alkaline solution has been heated for a long time on the water-bath, not in a platinum capsule, but in a porcelain vessel. As a matter of course, in this method of separation the use of impure reagents which contain alumina, silica, &c., is excluded. It must further be considered that the precipitate of manganese, after washing with hot water, may easily include some potash which cannot be readily removed by ignition with the blast. It is therefore prudent to redissolve the precipitate in

dilute nitric acid in presence of a small quantity of oxalic acid (not more than 0·3 gramme), and to reprecipitate the manganese with hydrogen peroxide in an ammoniacal solution.

Electrolytic Separation of Manganese, Cadmium, Copper, and Mercury

Classen founds this method upon the precipitability of mercury, copper, and cadmium in presence of free pyrophosphoric acid, or preferably from a solution of the pyrophosphates acidified with sulphuric or nitric acid. The metals are converted into double salts by the addition of an excess of sodium pyrophosphate, acidified with nitric or sulphuric acid. Copper is then precipitated with a current of 3 or 4 c.c. of detonating gases per minute, mercury with one of 0·2, to 0·5 c.c., and cadmium with one of the same strength, which towards the end is increased to from 5 to 10 c.c.

In the liquid remaining after the separation of the above metals the manganese is reduced by means of oxalic acid, and separated as peroxide after the addition of ammonia.

Separation of Manganese from Uranium

This separation may be effected by means of potassium permanganate in the same way as that of manganese from zinc, as above described.

Separation of Manganese from Cerium

This is best effected in the same way as the separation of iron from cerium (page 231).

Separation of Manganese from Magnesium

To separate manganese from magnesium, the best plan consists in adding a solution of sodium acetate, heating, and passing a current of chlorine through the liquid, when permanganate is formed. Supersaturate with ammonia, and boil, when all the manganese is reduced to sesquioxide and precipitated, while the magnesium remains in solution. If there be a large quantity of magnesium present, a certain quantity of sal-ammoniac must be first added.

The same process will serve to separate lime from manganese protoxide.

Separation of Manganese from Barium, Calcium, Magnesium, and Alkalies

According to Classen, the precipitability of manganese by the current in the state of peroxide permits of its easy separation from the other metals. On the precipitation of calcium as oxalate from a

solution containing manganese, a portion of the latter is separated along with the calcium in the state of oxalate.

The quantity of manganese in the ignited and weighed precipitate ($CaO + Mn_2O_3$) can be easily determined by dissolving in nitric acid and electrolysing.

NICKEL

Preparation of Metallic Nickel

Nickel can easily be precipitated as a coherent metallic sponge by placing a solution of a pure nickel salt in contact with metallic magnesium in the form of ribbon. Hydrogen is given off, and if the materials are pure the nickel will likewise be pure. The sponge is to be well washed with hot water, dried, and then compressed in a steel mortar, when it will assume a metallic brilliancy. Nickel precipitated in this manner can be moulded and condensed by pressure into bars, which will be found to possess magnetic properties like iron. This compressed sponge can be melted in a lime crucible before the oxy-hydrogen blowpipe (see Iron, page 204).

Electrolytic Precipitation of Nickel [1]

(*A*) Classen finds that the reduction of nickel can be effected under the same conditions as that of cobalt. The nickel is deposited from the solution of the corresponding double salt mixed with an excess of ammonium oxalate, using the current specified (see Cobalt). The metal is deposited on the negative electrode as a pale, dense coating The end of the reaction is ascertained by means of ammonium sulphide or potassium sulpho-carbonate, proceeding otherwise as above.

(*B*) According to Fresenius and Bergmann, nickel, like cobalt, is deposited quantitatively from a solution mixed with ammonium sulphate and ammonia (see Cobalt).

(*C*) According to Brand, nickel may be deposited quantitatively from the solution of the double pyrophosphate, proceeding as for cobalt. From 0·2 to 0·3 gramme nickel may be deposited in twenty-four hours with a current of from 2 to 3 c.c. of detonating gas per minute. For more rapid deposition the decomposition is effected with a current of about 20 c.c.

Estimation of Nickel

(*A*) In precipitating nickel from its solutions by means of ammonium sulphide, the analyst is frequently troubled by the nickel sulphide dissolving in the excess of precipitant, colouring it brown. This can be completely avoided by employing ammonium sulphide fresh and free from polysulphide. A more satisfactory plan is to saturate the solution

[1] For details of operation see chapter on Electrolytic Analysis.

of nickel with sulphuretted hydrogen, and then to add ammonia to slight alkaline reaction. The precipitate is then filtered off as rapidly as possible, and washed with dilute sulphuretted hydrogen water. If this precipitation is for quantitative purposes, it must be remembered that when the nickel sulphide is ignited, some of the sulphur goes off, while another part oxidises and remains as nickel sulphate, the result being a variable mixture of disulphide, sulphate, and nickel oxide.

(*B*) Forbes has examined this reaction and has based upon it an ingenious plan for estimating nickel. As the equivalents of the sulphur in the nickel sulphide and of the oxygen in the oxide are identical, the sulphide and the oxide will be of the same weight, and this fact enables us at once to calculate the amount of nickel contained in a mixture of the disulphide and oxide, however variable the relative proportions of these compounds may be, and it becomes only necessary to remove the small amounts of sulphuric acid present in the incinerated sulphide in order to determine the amount of nickel present. The addition of a small amount of pulverised ammonium carbonate to the incinerated sulphide as soon as it is cold, and then carefully heating until all ammoniacal salts are expelled, completely effects this object. In estimating the nickel present the calculation may be made as if the calcined mass were either all disulphide or all oxide.

It will be found most convenient to add the ammonium carbonate to the incinerated sulphide in the same crucible in which it has been ignited, or, rather, to cover the ignited sulphide with four or five times its volume of this salt, and then, by means of a small agate pestle or glass rod, to break up all grains and mix well together by trituration; this can easily be effected without any loss whatever, as the superstratum of ammonium carbonate effectually prevents any particles flying over the sides of the crucible. This, with its cover loosely placed upon it, is now very gently heated until nearly all ammoniacal salts are expelled; then the heat is increased for an instant, and the whole, after cooling over sulphuric acid, is weighed and estimated as usual.

(*C*) Nickel may be very accurately determined by Leison's oxalic-acid process, for details of which see page 145. In the case of nickel sulphate it is necessary, after adding the oxalic acid, to concentrate the mixture on a water-bath before adding alcohol, and then further to digest for about half an hour, replacing the alcohol as fast as it evaporates. The oxalate is collected on a paper filter, and, after washing, dissolved in ammonia on the filter. The filtrate is then acidified with sulphuric acid, when it is ready for titration with potassium permanganate. But the solution containing nickel sulphate has a green colour, which would interfere with the delicacy of the permanganate test, and to overcome this difficulty an ingenious artifice may be adopted, first employed, we believe, by Dr. W. Gibbs, and based on an

observation of Maumené. The colours of cobalt and nickel are exactly complementary one to the other, so it is only necessary to add gradually a solution of cobalt sulphate to the green nickel solution, when the colour of the latter is gradually discharged, finally giving place to a neutral tint, which in no way interferes with the delicacy of the permanganate colour test. Although the object is to ascertain the amount of nickel present, this is really effected by estimating the quantity of oxalic acid which was united with it; therefore the addition of cobalt at this stage of the process does not interfere.

(*D*) For the estimation of nickel in ores, A. A. Julien directs digesting from 3 to 5 grammes of finely powdered ore with 20 c.c. sulphuric acid, 10 c.c. nitric acid, and 5 c.c. hydrochloric acid. Evaporate to dryness, expelling the excess of sulphuric acid, cool, moisten with hydrochloric acid, add hot water, filter, and wash. Saturate the diluted filtrate with sulphuretted hydrogen gas, filter out the copper, lead, &c., sulphides, and wash with sulphuretted hydrogen water. Boil the filtrate with a little nitric acid, add sodium carbonate almost to neutralisation, and precipitate the iron and alumina as basic acetates, as in the analysis of iron ore; filter and wash. Dissolve the basic acetates in hydrochloric acid and repeat the precipitation, filtration, and washing, to separate a little nickel at first carried down. Unite and concentrate all the filtrates and washings, and add ammonia in excess. If a little iron separates, filter, wash twice, dissolve in hydrochloric acid, reprecipitate with ammonia, filter, wash, and add the filtrate to the main solution. Boil, add a boiling solution of sodium sulphide in excess, acidulate with acetic acid, allow to settle, filter, wash the nickel sulphide with sulphuretted hydrogen water, remove the moist precipitate as completely as possible to an evaporating-dish, dry, and burn the filter; dry and roast the precipitate in the dish, and add the ashes of the filter. Dissolve the whole in a little aqua regia, evaporate the free acid almost entirely, dissolve in hot water, boil, add pure solution of potash in slight excess, heat for some time nearly to ebullition, decant upon a filter three or four times, boiling up each time, filter, wash thoroughly with hot water, dry, ignite, and weigh as mixed nickel and cobalt oxides. Carefully examine the residue for potash, silica, iron, alumina, and cobalt.

(*E*) In American ores the metal in this residue rarely exceeds 1 per cent. of the original ore, and the cobalt is seldom separated; but, if desired, the following method may be employed :—

Dissolve the residue in a few drops of nitric acid, and neutralise the excess of free acid with a few drops of potash. Then add a concentrated solution of potassium nitrite (previously neutralised with acetic acid and filtered from any flocks of silica and alumina that may have separated) in sufficient quantity, and finally acetic acid, till any flocculent precipitate that may have formed from excess of potash has redissolved, and the liquid is decidedly acid. Allow it to stand at least for twenty-four hours in a warm place, take out a portion of the supernatant

liquid with a pipette, mix it with more potassium nitrite, and observe whether a further precipitation takes place in this after long standing. If so, return it to the principal solution, add more potassium nitrite, and repeat the test after long standing. Filter, wash thoroughly with an aqueous solution of neutral potassic acetate (containing 10 per cent. of the salt), and finally with alcohol of 80 per cent. Dry, ignite, incinerate the filter, moisten the whole with sulphuric acid, and drive off the excess and weigh. Result, $2CoSO_4 + 3K_2SO_4$.

Separation of Nickel from Iron

(*A*) A process proposed in the *Zeitschrift für anal. Chemie* for separating nickel and iron depends on the insolubility of ferric phosphate in acetic acid, in presence of sodium phosphate in excess, while nickel phosphate is soluble. The hot solution of the two metals containing free acetic acid is mixed with sodium phosphate, the ferric precipitate is removed by filtration ; from the filtrate nickel phosphate is thrown down by the addition of potash, the precipitate is dissolved in sulphuric acid, the solution is rendered alkaline, and the nickel precipitated by the galvanic current. The process is only applicable where the nickel does not exceed 3 per cent.

(*B*) Mr. Thomas adopts the following method for separating nickel from ores containing much iron. The ore is dissolved in aqua regia, the silica separated ; to the filtrate ammonia is added in excess, the precipitate of iron oxide well stirred, filtered, and washed with ammoniacal water, the iron redissolved with hydrochloric acid, reprecipitated with excess of ammonia, and treated as before. The two solutions are added together, and boiled to expel excess of ammonia; solution of potassium hydrate is then added, and the solution heated till ammonia is no longer given off, the solution filtered, the precipitate well washed with hot water, redissolved in acid and reprecipitated by potash, washed, dried, ignited, and weighed in the usual manner. Care must be taken that no copper is present during the operation. By this method better results are obtained than by the usual way.

Separation of Nickel from Zinc

(*A*) A dilute solution of the nitrates or sulphates is mixed with ammonia till an alkaline reaction is obtained, and then acidified with pure citric acid. When the solution is perfectly cold, sulphuretted hydrogen is introduced till the liquid has a distinct odour, which is generally effected in five to ten minutes. If much zinc is present, sulphuretted hydrogen is introduced for five minutes at a time, letting the liquid stand after each introduction, and repeating this till the odour of the gas does not disappear on standing. In this manner we avoid a needlessly long treatment with sulphuretted hydrogen, by which

traces of nickel sulphide may be carried down. The precipitate of zinc sulphide is allowed to stand for twenty-four hours in the cold, and is then weighed as such. The filtrate is evaporated to a small volume, and after supersaturation with ammonia the nickel is thrown down electrolytically. In this operation care must be taken that no sal-ammoniac is present, as it hinders the precipitation of nickel. The solution should be a nitrate.

(*B*) For the separation of zinc and nickel by means of hydrogen sulphide in presence of acetic acid alone, there are required at common temperatures quantities of acid, so much the greater as the proportion of nickel in solution is greater, and under the influence of a temperature but slightly elevated (40°), even in an open vessel, there is always a precipitation of sulphide. It is sufficient to raise to 70° in an open vessel an acetic solution of nickel acetate, which has been saturated with hydrogen sulphide, letting the liquid cool out of direct contact with the air, so as to avoid a too great loss of sulphuretted hydrogen and the occurrence of oxidation, in order to have all the nickel separated as sulphide, which is entirely deposited in ten to twelve hours.

The method is at fault only if the liquid contains oxidising agents, such as nitrates, but as under these conditions the nitric acid may be destroyed by boiling with ammonium hydrosulphate, it is sufficient to submit the solution to this treatment repeatedly if needful, in order to effect a complete precipitation of the nickel as sulphide in presence of free acetic acid.

(*C*) H. Alt and J. Schulze find that in a solution of zinc and nickel containing a sufficiency of succinic acid, a current of sulphuretted hydrogen precipitates all the zinc as a perfectly white zinc sulphide, while the nickel remains in solution. The succinic solution must be free from salts, as otherwise nickel sulphide may be simultaneously precipitated. The liquid is heated almost to a boil, and treated with a current of sulphuretted hydrogen until it smells strongly of the gas. It is then allowed to stand for twenty-four hours and filtered, the white zinc sulphide is washed, and determined as such.

The filtrate is mixed with a little hydrochloric acid (to prevent any deposition of nickel sulphide on heating in consequence of the great dilution of the succinic acid), and the hydrosulphuric acid is expelled by evaporation. The liquid is then treated at a boiling heat with potash-lye, when nickelous oxide is precipitated quantitatively, even in presence of much succinic acid.

COBALT

Metallic Cobalt

Metallic cobalt is precipitated from the aqueous solutions of its salts by magnesium, in exactly the same manner as metallic nickel. The subsequent treatment is identical. After fusion in a lime crucible

cobalt is one of the most tenacious of known metals, and when made into wire it supports almost double the weight which would break an iron wire of the same thickness.

Electrolytic Estimation of Cobalt [1]

(*A*) Classen finds that the determination is effected very smoothly in a solution of cobalt-ammonium oxalate containing an excess of ammonium oxalate. The metal is separated very quickly and with its characteristic metallic properties at the negative electrode, to which it adheres very firmly. In about 25 c.c. of liquid from 5 to 6 grammes of ammonium oxalate are dissolved with the aid of heat, the solution is diluted from 150 to 175 c.c., and submitted to electrolysis while warm. He then proceeds as in the electrolytic determination of iron.

(*B*) According to another method the solution of cobalt is mixed with from 15 to 20 c.c. ammonium sulphate (300 grammes $(NH_4)_2SO_4$ per litre), 40 c.c. of ammonia of sp. gr. 0·96 are added (or if more than 0·5 gramme cobalt is supposed to be present in the solution, 50 to 60 c.c. NH_3 are added), the whole is diluted with water to about 150 or 170 c.c., and electrolysed with a current of about 5 c.c. detonating gas (normal density 100=0·7 ampère as a maximum) at the ordinary temperature. (Fresenius and Bergmann.)

The presence of chlorides or nitrates hinders reduction. Fixed organic acids (citric and tartaric acids), as also magnesium compounds, are injurious.

(*C*) For the above method Rüdorff gives the following proportions when Meidinger elements are used. The solution containing from 0·1 to 0·3 gramme cobalt is mixed with 25 c.c. of a saturated solution of ammonium sulphate and an equal volume of ammonia (sp. gr. 0·91), and after dilution to 100 c.c. electrolysed with a battery of from 3 to 6 elements. The end of the reaction (after twelve or fourteen hours) is tested with ammonium sulphide.

(*D*) According to A. Brand, cobalt, like iron, may be deposited from the solution of the double pyrophosphate. Sodium pyrophosphate is added until the cobaltous pyrophosphate is completely redissolved, then ammonium carbonate in slight excess, and it is finally reduced with a current giving about 3 c.c. detonating gas. To deposit the last traces a current of about 15 c.c. of detonating gas is required. The metal must be washed without interrupting the current.

Estimation of Cobalt

(*A*) Leison's process with oxalic acid and permanganate is quite as successful with cobalt as with nickel (page 245). A few modifications are necessary. The solution is precipitated in the usual way by oxalic

[1] For details of operation see chapter on Electrolytic Analysis.

acid and alcohol, but it is then collected on a sand-filter and digested with dilute sulphuric acid. The solution, which will be red, must then be mixed with a solution of nickel sulphate until the red colour disappears and a faint smoky hue takes its place; the subsequent titration is performed in the customary manner.

(*B*) Cobalt cannot be estimated by precipitation as sulphide and calcination, with subsequent addition of ammonium carbonate, in the way described under Nickel. Mr. Forbes, who has experimented on this method, says that the calcined mass, instead of consisting of a mixture of cobalt oxide and disulphide, is quite pink from the presence of cobalt sulphate, which appears most strongly to resist decomposition.

Tests for Cobalt

(*A*) If to a solution of a cobalt salt in tartaric or citric acid an excess of ammonia is added, the addition of potassium ferricyanide will cause a very dark red colouration in the solution. Mr. Skey says that the colour thus produced by the ferricyanide is so intense that it will reveal the presence of cobalt in solution when all other tests fail, its delicacy being about four times greater than that of ammonium carbonate. A solution of cobalt prepared as indicated above, so as only to contain $\frac{1}{5000}$ part of cobalt, when placed in a $\frac{3}{4}$-inch test-tube, is very distinctly coloured by the addition of a soluble ferricyanide, and even when diluted down so as to contain but 1 part of cobalt in 400,000 parts of the liquid, the colouration is still distinctly visible in a bulk of a few ounces.

(*B*) Mr. R. H. Davies, F.C.S., recommends the following modification of Mr. Skey's test:—When only the two metals—nickel and cobalt—are present in solution, add ammonia until the precipitated hydrates are redissolved (ammonium chloride does not appear to be essential), then potassium ferricyanide. If the amount of cobalt is large, a reddish-brown precipitate of cobalt ferricyanide will occur. This is soluble in excess of the ferricyanide solution, which must then be added until it has disappeared, and a deep red-brown liquid results. If only an exceedingly small quantity of cobalt be present, no precipitate, but a colouration merely (in itself evidence of this metal), will be observed upon the addition of ferricyanide. Potassium ferrocyanide must now be added, and here, again, a precipitate of nickel ferrocyanide will occur if much nickel salt be present. If the liquid remains clear, add hydrochloric acid, drop by drop, noting the effect. A precipitate (yellowish-white) upon the addition of from 6 to 12 drops, while the colour due to cobalt ferricyanide remains unchanged, and the liquid is still strongly alkaline, indicates nickel; while if none of this element be present no apparent effect will be produced by the hydrochloric acid until suddenly, on neutralisation, the colour disappears, and a yellowish-white precipitate of cobalt ferrocyanide is thrown down.

(*C*) For the detection of cobalt and nickel, Dr. G. Papasogli adds to an acid solution of the two metals a slight excess of a solution of potassium hydrate to precipitate the metals in the state of basic salts. The precipitate is allowed to settle, the alkaline liquid decanted off, and the deposit repeatedly washed to remove the excess of potash. A few drops of ammonium chloride and of ammonia are then added, and it is heated in a slight excess of potassium cyanide.

Care must be taken, as far as possible, not to stir the solution of the double cyanide, to prevent the absorption of atmospheric oxygen. If the double cobalt solution is converted into cobalti-cyanide, the addition of an alkaline polysulphide no longer produces the red colouration mentioned above.

The solution of the cyanides is then divided into two portions. To the first are added a few drops of the ammonium polysulphide, so that it may form a stratum above the cyanide solution. If in the place of contact of the two liquids there is observed a red colouration, this indicates the presence of cobalt. The reaction is independent of the presence of nickel, and is sensitive to the fourth and even the fifth decimal place if the solution is sufficiently concentrated.

In the other portion of the solution is immersed a small slip of zinc. If the liquid contains nickel there will be observed, besides the gaseous envelope, an intense red colouration, which shows itself over the whole surface of the slip, but especially at the lower part. The presence of cobalt does not interfere with this reaction, which is still produced even if the solution containing the cobalt has absorbed oxygen.

If the solution is concentrated the sensitiveness of the reaction extends to the fourth decimal place. The presence of ammoniacal salts in excess retards, or even hinders, the reaction.

The solution of potassium cyanide used should be concentrated, but an excess in quantity should be avoided, especially if the quantity of nickel is small. If an excess of the cyanide is used, then, on immersing the slip of zinc, there occurs suddenly a strong evolution of gas, which disperses the red colouration and makes it difficult to perceive the reaction.

To avoid this inconvenience, the author places in the solution to be examined a slip of platinum, joined at one extremity to a slip of zinc. The greater portion of the gas then envelops the platinum, and as the red colour forms only around the zinc it is less readily dispersed, and the reaction remains more sensitive.

(*D*) A method of separating nickel from cobalt, given some years since by Liebig, consists in boiling the mixed double cyanides of nickel and potassium and cobalt and potassium with mercury oxide. Nickel oxide is precipitated, while an equivalent quantity of mercury is dissolved in the cyanide. The method certainly gives good results, but is not free from objection. Long boiling is necessary before the precipitation is complete, and it is difficult to prevent bumping during ebullition. The

excess of mercury oxide must be separated from the nickel oxide by a special operation, and the nickel afterwards again precipitated by caustic alkali.

(*E*) These inconveniences may be completely avoided, according to Wolcott Gibbs, by employing, instead of the oxide alone, a solution of the oxide in the mercury cyanide. When this solution is added to a hot solution of the nickel and potassium double cyanide, the whole of the nickel is immediately thrown down as a pale green hydrate of the protoxide. Under the same circumstances, cobalt is not precipitated from the double cobalt and potassium cyanide. Mr. W. N. Hill, who has repeatedly employed this method and carefully tested it, has found that the separation effected is complete. No cobalt can be detected in the precipitated nickel oxide by the blowpipe, nor can the nickel be detected in the cobalt (finally separated as oxide) by Plattner's process with the gold bead. The solution of mercury oxide is easily obtained by boiling the oxide with a strong solution of the cyanide, and filtering. The hydrated nickel oxide precipitated may be filtered off, washed dried, ignited, and weighed. The cobalt is more readily and conveniently estimated by difference when the two metals have been weighed together as sulphides.

(*F*) Mr. T. H. Henry has mentioned another objection to Liebig's process referred to above. The potassium cyanide employed should be free from cyanate, and as the commercial salt always contains cyanate, Liebig proposed instead the employment of hydrocyanic acid and caustic potash. Mr. Henry fuses commercial potassium cyanide, for a few minutes, with a little pure charcoal, and, when cold, dissolves it in water, and uses this solution instead of the pure salt or the mixture of hydrocyanic acid and potash. The rest of the operation may be carried out as directed by Liebig (boiling the solution with mercury oxide), or by Dr. Gibbs's modification, as described in the preceding paragraph. Mr. Henry says that he believes this process to be one of the most elegant, accurate, and expeditious in the whole range of analytical chemistry.

(*G*) Dr. Phipson gives the following method of isolating minute quantities of nickel in cobalt chloride. A few grains of that salt are dissolved in water, and the whole of the cobalt precipitated, with the nickel, by potassium xanthate employed in slight excess, and previously dissolved in a little distilled water. A few drops of ammonia are then added, just sufficient to render the liquid slightly alkaline, and the dark green cobalt xanthate is collected on a filter. The whole of the nickel is in the filtrate, and the whole of the cobalt in the filter. The nickel in the filtrate is precipitated by a few drops of ammonium sulphide.

(*H*) G. Delvaux separates the two metals, by two known methods permitting the exact estimation of the two oxides, and the preparation of the two metals in a state of purity. The two fundamental processes

are, firstly that of Pisani, who uses caustic potash in presence of an ammoniacal liquid, in which are dissolved the two metals, with exclusion of air. The nickel oxide is precipitated alone in bulk, but always carries down with it more or less of cobalt oxide. The second method is that of Terreil, who precipitates cobalt in an acid solution in a state of roseo-cobaltic hydrochlorate. The cobalt oxide is peroxidised by means of permanganate. We suppose that the two bodies, cobalt and nickel, have been obtained by known methods, either as pure oxides or pure sulphides, free from all foreign matter. The mixed oxides or sulphides are dissolved in aqua regia containing a large proportion of hydrochloric acid. The solution is largely diluted with water and saturated with ammonia in excess. Permanganate is then added until the solution remains rose-coloured for some time. Pure potash is then added, when the nickel is precipitated as hydroxide, carrying with it manganese oxide, derived from the permanganate. The precipitate is washed by decantation and filtered; redissolved in hydrochloric acid, and treated again with ammonia, permanganate, and caustic potash. The washing-waters which contain the cobalt are collected, saturated with acetic acid, and precipitated by sulphuretted hydrogen. The mixture of nickel and manganese oxides is redissolved in hydrochloric acid, and the solution saturated with ammonia. The solution is exposed to the air for some time, and the manganese oxide is by degrees entirely precipitated. It is filtered off, the filtrate is saturated with acetic acid, and the nickel thrown down by means of sulphuretted hydrogen. The process may be employed on the large scale for obtaining nickel completely free from cobalt.

(*I*) M. P. Dirvell founds a method on the following facts:—

1. If there be added to the aqueous solution of cobalt nitrate or sulphate an excess of cold saturated solution of phosphorus salt, mixed with a solution of ammonium bicarbonate from which no ammoniacal odour is emitted, a bluish precipitate is formed in the liquid. When the mixture is slowly warmed the equivalent of carbonic acid in excess at first escapes; then, by boiling for a few seconds, a very distinct ammoniacal odour is perceptible. At this moment the boiling is discontinued, and from 2 to 3 c.c. of ammonia added to the liquid. The precipitate is for the most part dissolved, and it is only necessary to warm gently to 100° to obtain a precipitate of a beautiful purple, inclining to violet, which is rapidly deposited. It loses no ammonia at 100°, and is transformed at a red heat into pyrophosphate.

2. A solution of the corresponding nickel salts treated in the same manner gives only a pure blue liquid, which is not rendered turbid by heat.

3. By mixing the two above-mentioned reagents in excess with a solution containing cobalt and nickel, and treating in the same manner, the red precipitate of ammonio-cobaltic phosphate is again obtained, while the remaining blue liquor contains the whole of the nickel. By

this means the cobalt in the nickel sulphate of commerce can be detected.

It is better to make this separation for the qualitative research of the two metals in assay-flasks, when evaporation is slow. For the quantitative separation prepare the reagents in the following manner: 1·3 gramme of phosphorus salt is digested in the cold in 250 grammes of water; 2·3 grammes of effloresced ammonium carbonate are dissolved in the same quantity of water, and the solution saturated with carbonic acid till all ammoniacal smell is gone.

After having separated the two oxides in the customary way, and having reduced them by hydrogen, they are weighed, dissolved in nitric acid, and the acid solution evaporated to dryness in a water-bath. The residue is redissolved in about 50 c.c. of water, to which is added a quantity of phosphorus salt equal to 30 times the weight of the two metals, and to which a volume of ammonium bicarbonate equal to that occupied by the phosphate has previously been added. Then operate as has already been indicated, care being taken to frequently shake the flask containing the liquid, especially after the addition of the ammonia.

If the boiling has inadvertently been too prolonged, causing the evaporation of the blue liquid containing the nickel on the sides of the vessel, and the consequent precipitation of a little nickel, it is easily ascertained by the colour of the cobalt precipitate, which will, in this case, be paler. It can also be compared with the moist ammonio-cobaltic phosphate, which is kept in a bottle to act as a test. In this case the clear blue liquor is drawn off, the red precipitate dissolved in only as much dilute phosphoric acid as is absolutely necessary (it is even better to leave a little precipitate undissolved), then the operation is continued with ammonium bicarbonate and ammonia.

In all cases the precipitate is washed in cold water, weighed on a tared filter at 100°, or calcined; 100 parts of the calcined precipitate contain 40·4 of cobalt. With regard to the blue liquid separated by filtration, sulphuretted hydrogen completely precipitates the nickel. The precipitate is calcined in a crucible with some sulphur, and weighed in the state of sulphide.

Detection of Cobalt in the Presence of Nickel

Vögel's process [1] has been found by S. R. Benedict to be very sensitive, and will detect 0·5 per cent. of cobalt in nickel solutions. A saturated solution of ammonium sulphocyanide is added, then a mixture of amyl alcohol and ether added, and the solution shaken. If cobalt be present, the alcohol-ether layer has a blue colour.

The detection of traces of nickel in an excess of cobalt is a more difficult problem. The most delicate method, up to the present time,

[1] *Ber.* 1878, vol. xii. p. 2314.

is probably the one suggested by Parr,[1] which depends upon the fact that freshly precipitated nickelic hydroxide will liberate iodine from potassium iodide, while cobaltic hydroxide will not. The procedure is as follows :—Bromine water is added to the solution, which is then warmed, next an excess of sodium carbonate added, and the solution brought to boiling. Both the cobalt and nickel are oxidised and precipitated in the trivalent condition by this treatment. The precipitate is well washed upon a filter, and hot potassium iodide poured upon it. Free iodine in the filtrate is evidence of the presence of nickel. This test is not as delicate as Vögel's method for cobalt, yet it will detect nickel in many commercial cobalt salts.

The following mode of estimating cobalt in New Caledonian ores has been worked out by Thomas Moore [2] (Nouméa).

Two and a half grammes of the pulverised and dried mineral are dissolved in concentrated hydrochloric acid, and evaporated until the solution becomes syrupy ; water is now added to dissolve all soluble matter, leaving only a residue of silica and chromite ; 100 cubic centimetres of a saturated solution of ammonic chloride are now added, and the whole then diluted with cold water in about 400 cubic centimetres. A weak solution of ammonia (1 part strong ammonia and 15 parts water) is now carefully added with constant and vigorous stirring, until the liquid takes a deep red colour, indicating the formation of basic ferric compounds. The solution must be clear and free from precipitated oxide of iron, which is easily distinguished from the turbidity caused by the silica in suspension. From this point the neutralisation is completed by the careful addition, drop by drop, of a 5-per-cent. solution of sodic carbonate until the supernatant fluid is perfectly clear and transparent. To arrive exactly at this condition it is preferable to stop the addition of the sodic carbonate when the solution has only a slight yellow tint, as a little extra stirring invariably causes this to disappear. At this stage the solution, which possesses a distinct acid reaction, but is nevertheless free from iron or alumina, is transferred to a half-litre flask and diluted to the mark ; then, after a thorough mixing by shaking, filtered through a ribbed filter ; 400 cubic centimetres of the clear filtrate are now exactly measured off into a flask of about 600 cubic centimetres capacity, 20 cubic centimetres of a saturated solution of sodic acetate and 10 cubic centimetres of acetic acid added, and the whole then raised nearly to the boiling-point. A current of sulphuretted hydrogen is then passed through the solution, allowing the gas to pass until the contents of the flask are nearly cold ; the sulphides of cobalt, nickel, and zinc will then be found to have been completely precipitated free from impurities, and may now be filtered off, washed with water containing sulphuretted hydrogen, then dried and ignited. The ignited oxides and any sulphide which may

[1] *Journ. Am. Chem. Soc.* 1897, vol. xix. p. 314.

[2] *Chemical News*, Aug. 10, 1900.

remain attached to the sides of the flask are now dissolved in strong hydrochloric acid with the aid of a drop or two of nitric acid and evaporated twice to dryness with hydrochloric acid, so as completely to get rid of all nitric acid, the residual chloride dissolved in from 5 to 10 cubic centimetres of water, and allowed to become cold. The solution of the metals thus obtained may, through careless neutralisation, contain a little iron, so that for greater security it is always better to add a slight excess of an emulsion of oxide of zinc, and filter off any trace of ferric oxide which may be thrown down.

The filtrate, which is now entirely free from iron, is diluted to about 50 cubic centimetres, and well mixed with from 10 to 15 cubic centimetres of a 10-per-cent. solution of hydrogen peroxide, and then with 10 cubic centimetres of a 10-per-cent. solution of potassic or sodic hydrate; the cobalt is immediately precipitated as sesquioxide, Co_2O_3, while the nickel is simply thrown down as the green hydrated monoxide. The mixed precipitate is now boiled for about a minute, so as to ensure the complete decomposition of the excess of hydrogen peroxide, allowed to cool, and then transferred to a stoppered bottle and digested with an excess of potassic iodide and hydrochloric acid until the decomposition is complete; then the iodine thus set free is titrated in the usual manner with sodic hyposulphite, $I \times 0{\cdot}46511 = Co$. The potassic or sodic hydrate employed in this process must be previously examined for impurities which can liberate iodine from potassic iodide; samples containing nitrites, for example, are not uncommon.

The separation and estimation of small quantities of cobalt in presence of nickel is effected as follows by Thomas Moore [1] (Nouméa).

The solution containing the chlorides of the two metals should not have much free acid, and if, as is usually the case a little iron is present, it should be eliminated by precipitation with a slight excess of zinc oxide, and filtered off. The filtrate is now diluted to from 300 to 400 cubic centimetres with water, one drop of hydrochloric acid added, and raised to the boiling-point or nearly so; now add sufficient bromine water, and then not too much zinc oxide; a large excess only hinders the subsequent filtration, but is not otherwise detrimental. The solution is now boiled for about five minutes, or until the greater part of the bromine is expelled; then filter, and wash the precipitate thoroughly with boiling water. The precipitate is now washed as perfectly as possible from the filter into a beaker glass, the trace adhering to the filter-paper being dissolved off by very weak hydrochloric acid containing a little sulphurous acid; the filtrate, which need not exceed 5 cubic centimetres, being received in a capsule, evaporated to dryness, then dissolved in a few drops of water, and added to the main precipitate. The precipitate is now well boiled to thoroughly disintegrate it, and then allowed to become cold. When cold, 5 to 10 cubic centimetres of peroxide of hydrogen, which have been rendered strongly alkaline with

[1] *Chemical News*, Aug. 17, 1900.

caustic soda, are added, the mixture well stirred, and then boiled for two or three minutes to destroy the excess of peroxide, then allowed to cool, after which it is digested for five minutes in a stoppered bottle with potassic iodide and hydrochloric acid, and the iodine thus set free titrated by means of a very weak solution of sodic hyposulphite; $I \times 0{\cdot}46511 = Co$.

E. Pinerua,[1] of the Laboratory of the University of Valladolid, Spain, bases the separation of nickel from cobalt, nickel from iron, and cobalt from aluminium, on the insolubility of the chlorides of nickel and aluminium, and the great solubility of cobalt and iron, in a solution of ordinary ether saturated with hydrochloric acid gas at a low temperature.

The hydrated chlorides (0·3 gramme to 0·4 gramme) of the metals, nickel and cobalt, nickel and iron, cobalt and aluminium, are dissolved in the smallest possible quantity of water, and to the solution are added 10 or 12 cubic centimetres of fuming hydrochloric acid and 10 cubic centimetres of ordinary ether (D. 15 C.=0·725), or, better still, anhydrous ether. This must be well shaken, and through the resulting homogeneous liquid a current of hydrochloric acid gas is passed continuously until complete saturation, at the temperature of melting ice with which the beaker or test-tube should be surrounded. During this operation the nickel is precipitated in the state of heavy, crystalline, yellow chloride, and the cobalt remains in solution with an intense blue colour (Engel's acid chloride). In the presence of iron, which under these conditions would give a bright yellow solution, the colour becomes green.

Most of the commercial chlorides of nickel and cobalt, *soi-disant* pure, are really very impure. By using this process for precipitating the nickel, on the commercial chlorides of cobalt, the resultant liquid is of a bluish-green instead of a pure blue colour, indicating the presence of iron.

The precipitated chloride is yellow, but sometimes the remaining liquid is of a light yellowish-green colour, indicating the presence of iron and cobalt.

The precipitate of chloride of nickel is washed by decantation, with ether saturated with hydrochloric acid gas, at a low temperature, collected on a filter, and thoroughly washed again on the filter; it can then be weighed, and the nickel estimated in the ordinary manner (such as sulphate, for example) with very accurate results.

The same method of procedure can be utilised for the separation of aluminium and cobalt; the former metal is completely precipitated in the state of insoluble chloride, as it is when in the presence of iron, using the analogous method of Hanriot and Rothe, as modified by F. A. Gooch and F. S. Havens.[2]

[1] *Chemical News*, April 23, 1897.

[2] 'Method for the Separation of Aluminium from Iron,' by F. A. Gooch and F. S. Havens. *Chemical News*, vol. lxxiv. p. 296.

The cobalt remains like the iron in solution; and the insoluble chloride of aluminium, washed with ether saturated with hydrochloric acid gas, can be estimated with great accuracy.

To effect the separation of nickel from iron, it is necessary to wash the chloride of nickel many times with ether to eliminate the chloride of iron which is redissolved, and the operation must be repeated several times.

Separation of Nickel and Cobalt from Manganese

(*A*) Wolcott Gibbs effects the separation of manganese from nickel and cobalt (and zinc also if present) in the following way:—To the neutral or nearly neutral solution of the chlorides, sodium acetate is to be added in excess, together with a few drops of free acetic acid. The solution is then to be boiled, and a rapid current of sulphuretted hydrogen passed through it while boiling, and continued for half an hour. Every trace of cobalt, nickel, or zinc, is precipitated in the form of sulphide, while the whole of the manganese remains in solution. The precipitate is to be thrown on a ribbed filter and quickly washed with cold water saturated with sulphuretted hydrogen. It is easily washed, and though the cobalt sulphides and nickel precipitated in this manner are far more easily oxidised than when precipitated by boiling sodium sulphide from boiling solutions, they will be found to present no difficulty as regards oxidation upon the filter. Manganese may then be estimated in the filtrate by boiling with hydrochloric acid and precipitating in the usual manner with sodium carbonate. The mixed sulphides upon the filter—supposing, for the sake of generality, that all three are present—are to be dissolved in hydrochloric acid, and the metals converted into double cyanides by means of an excess of potassium cyanide, after which the zinc may be precipitated by means of sodium sulphide, as recommended by Wöhler.

(*B*) When perfectly pure potassium cyanide is not at hand, the following process will be found particularly convenient:—Sodium acetate is to be added to the solution of the mixed chlorides, after which the vapour of hydrocyanic acid, generated in a flask from sulphuric acid and potassium ferrocyanide, is to be passed directly into the solution. Zinc cyanide is immediately precipitated more or less completely as a perfectly white powder. A solution of sodium sulphide is then to be added as long as a precipitate is formed, after which the zinc sulphide is to be separated by filtration. Cobalt and nickel remain in solution as double cyanides. The same process may be used to separate manganese from cobalt and nickel, sodium sulphide under these circumstances throwing down a pure flesh-red precipitate. It is easy to see that zinc and manganese together may be separated from cobalt and nickel by the same process and at one operation. No manganese

cyanide appears to be formed when hydrocyanic acid is passed into a solution containing a manganese salt, acetic acid, and sodium acetate.

The nickel and cobalt sulphides are thrown down from boiling solutions by a boiling solution of sodium sulphide in an insoluble form, so that, in fact, even strong hydrochloric acid scarcely exerts upon them an appreciable action. This process has been applied to the separation of cobalt and nickel from zinc and manganese by Mr. Perkins, and gives results which are very satisfactory, especially for qualitative purposes; the manganese and zinc sulphides precipitated under the same circumstances being readily soluble, even in dilute acid.

Electrolytic Separation of Cobalt from Iron [1]

For determining both metals Classen advises that the solution of the double oxalates should be electrolysed as directed for iron. In this way are ascertained both the joint weight of iron and cobalt, and the quantity of iron. When this weight has been ascertained the residue is dissolved in dilute sulphuric acid (covering the metal with dilute sulphuric acid and gradually adding concentrated acid until the liquid becomes hot) and the iron is titrated with permanganate in the platinum capsule. In order to compensate the red colour of the cobalt sulphate the needful quantity of nickel sulphate is previously added. The end of the reaction is easily perceived.

Or the residue of iron and cobalt may be dissolved in hydrochloric acid, the iron oxidised with hydrogen peroxide, expelling the excess by ebullition, and titrating with stannous chloride.

Electrolytic Separation of Nickel from Iron

Classen's method for separating nickel and iron is the same as the one just described for the separation of cobalt and iron.

Nickel and iron separate out in the form of a fine white alloy which can scarcely be distinguished from platinum. The alloy is exceedingly resistant to acids and is only very slowly attacked by dilute sulphuric or hydrochloric acid.

In order to determine the iron in the alloy the deposit is heated in the capsule with concentrated hydrochloric acid, and if the iron is to be titrated with permanganate the solution is reduced with nascent hydrogen. It is simpler to oxidise the solution with hydrogen peroxide, and after expulsion of the excess to titrate the ferric chloride formed with stannous chloride.

Electrolytic Separation of Cobalt and Nickel from Iron [2]

G. A. Le Roy proposes the following method:—The solution of the metallic sulphates containing the iron in the ferric state is mixed with

[1] For details of operations see chapter on Electrolytic Analysis. [2] Ibid.

a minimum of citric acid (to prevent precipitation by ammonia), and then is added a large excess of a concentrated solution of ammonium sulphate containing free ammonia. If the liquid is electrolysed with a current evolving 5 c.c. of detonating gas per minute, the metals are deposited at the negative electrode. When their weight has been determined, the metals are covered with a strongly ammoniacal solution of ammonium sulphate, the capsule is connected with the positive pole of the battery, and electrolysed with a current of about 1·5 c.c. of detonating gas per minute. Nickel and cobalt are deposited on the platinum in connection with the negative pole, and the iron is converted into ferric hydroxide, which partly adheres to the capsule and is partly suspended in the liquid.

Separation of Nickel and Cobalt from Iron

(*A*) F. Field separates nickel and cobalt from iron peroxide by precipitating the latter with lead oxide. In the case of nickel and iron, the nitrates are evaporated nearly to dryness, and after the addition of water, lead oxide (litharge) is added, and the whole boiled for ten minutes or a quarter of an hour. The iron is entirely precipitated, the nickel and lead nitrates remaining in solution. After filtration, which can be effected with great readiness, dilute sulphuric acid is added, and on standing for sixteen hours the lead sulphate is filtered off, and the nickel precipitated and estimated in the usual manner. The filter containing the excess of litharge and peroxide is digested in dilute sulphuric acid, filtered and washed. The filtrate is precipitated by potash.

It may here be remarked that nickel oxide can be more readily estimated by precipitation as peroxide by means of sodium hypochlorite than as oxide by caustic potash. Nickel peroxide, after boiling the solution in which it is suspended, separates as a rather dense precipitate, and can be easily washed, while the great difficulty of freeing the bulky gelatinous protoxide from potash is well known. The alkali, indeed, adheres with remarkable pertinacity to this substance, and if not added with considerable caution, and other circumstances attended to, very protracted washing is necessary. In employing sodium hypochlorite, it is requisite to have an open vessel, a beaker for instance, as the peroxide is liable to form flakes upon the sides of the glass, which are difficult to remove from a narrow-necked flask. The peroxide is heated to whiteness and the nickel weighed as protoxide.

Cobalt can be separated from iron in precisely the same manner as nickel. Many analyses have shown that no trace of cobalt is precipitated from its solution on boiling with lead oxide, and even when the iron is in considerable excess—50 to 1 for example—the separation is complete. The solution of cobalt freed in this manner from iron contains no trace of that metal, gives no shade of blue with potassium ferrocyanide, nor can iron be recognised by any known test.

(*B*) Iron sesquioxide may be perfectly separated from cobalt and nickel by boiling the neutral or nearly neutral solutions with sodium acetate, provided that the following precautions are observed:—The solutions from which the iron is to be precipitated must be dilute; half a litre of the solution should not contain more than 1 grain of the sesquioxide. The quantity of sodium acetate should be sufficient to convert by double decomposition all the bases present into neutral acetates. The acetate should be added to the metallic solution when cold, and the whole should then be heated together and boiled for a short time. It is not necessary to filter upon a water-bath funnel, but the beaker containing the solution should be kept nearly at the boiling-point during filtration, and a ribbed filter should be employed. It is especially necessary, where nickel is present, to add a few drops of free acetic acid to the solution, to prevent the formation of basic acetates of the protoxides. It is best, whenever possible, to have all the bases present in the form of chlorides. The iron upon the filter, in the form of basic acetate, must, whenever an absolutely complete separation is necessary, be redissolved in hydrochloric acid, and again be precipitated by boiling with the acetate after rendering the solutions nearly neutral by means of sodium carbonate. In this manner only it is possible to separate the last traces of the stronger bases. Finally, the basic iron salt, after washing, must be redissolved in hydrochloric acid, and precipitated by boiling with ammonia in the usual manner, to free it completely from alkali.

(*C*) T. Moore recommends that if the solution contains much free acid, this should be got rid of by evaporation and dissolving the residue in water. To the solution so obtained a quantity of ammonium sulphate should be added, sufficient to form a double sulphate with the nickel and cobalt present. Dilute to about 150 c.c., and then add rather a large excess of oxalic acid, and stir well. If a precipitate forms, more ammonium sulphate must be added until a clear solution is obtained. Ammonia is now added in considerable excess; stir, heat gently for a few minutes, and filter; wash well with water containing ammonia; or dilute to 500 c.c., and after allowing the precipitate to settle, withdraw a given portion of the clear upper stratum of liquid, which, after a further addition of ammonium sulphate (to lessen the resistance of the solution to the electric current), is ready for electrolysis or any other method of estimating the nickel or cobalt the chemist may desire.

Separation of Nickel from Iron

T. Moore adopts the following process for the assay of nickel ores, &c., when it is necessary to estimate that metal only. The solution of the two metals is freed, as far as possible, from acids; glacial phosphoric acid (sodium pyro-phosphate may also be employed) is added until the precipitate first formed commences to dissolve, and then an

excess of potassium cyanide, which will dissolve the remainder and form a red or yellow solution according to the amount of phosphoric acid added. Heat the solution and keep boiling for a minute or two, adding more cyanide at intervals until a drop of potassium hydrate ceases to give a precipitate. After the solution has become cold, render very distinctly alkaline with potassium hydrate, then throw down the nickel by the addition, in considerable excess, of a strong solution of bromine in potassium hydrate, warming the liquid to facilitate the precipitation. Filter off the black precipitate and wash well out, dissolve it off the filter in warm dilute sulphuric acid, and after saturating with ammonia deposit the nickel electrolytically from the warm solution. Any cobalt present remains with the iron, but manganese will be found in the nickel solution completely or partly deposited on the opposite pole as oxide according to the amount present.

Separation of Nickel or Cobalt from Zinc

A very good plan for separating nickel from zinc is given by Wöhler as an illustration of the method of analysing German silver (an alloy of nickel, zinc, and copper) :—The copper having been separated from the other metals (see Copper), the liquid, after being filtered and reduced by evaporation to a small bulk, is treated with excess of caustic potash, and then with hydrocyanic acid, until the precipitate which is at first formed is completely redissolved with a yellow colour. In this liquid, which contains double cyanides, the zinc is precipitated in the state of sulphide, by means of potassium protosulphide (not ammonium sulphide). After some hours' digestion, and when the precipitate is completely deposited, it is filtered off, and, after boiling the liquid with aqua regia, the nickel is precipitated as oxide by caustic potash. This oxide must be calcined after it is dried.

Separation of Nickel, Cobalt, and Iron, from Zinc

P. von Berg has attempted the separation of zinc from iron, cobalt, and nickel, by passing sulphuretted hydrogen into a formic or monochloracetic solution. In presence of only 3 c.c. of free formic acid (sp. gr. 1·2) and 360 c.c. water he obtained zinc sulphide free from any ponderable traces of iron. It is necessary to filter immediately after the treatment with sulphuretted hydrogen, as, if it is allowed to stand, some zinc sulphide is deposited. The liquid should be heated to 50° or 60°. After the solutions are duly diluted and heated they are mixed with a quantity of sodium formate approximately equal to half the equivalent of the zinc sulphate present, and with the proportion of free formic acid (sp. gr. 1·2), and a slow current of sulphuretted hydrogen is then introduced until it becomes predominant. A large excess of sodium formate is to be avoided. As soon as the precipitate has

partially settled it is filtered, the precipitate washed with sulphuretted hydrogen water to which about 1 per cent. of free formic acid has been added, and the zinc sulphide is determined in the known manner. Zinc may also be successfully precipitated from a monochloracetic solution. The author proceeds in a very similar manner to that already described. As soon as the precipitation is completed and sulphuretted hydrogen predominates, he filters at once without waiting for the liquid to become clear. Any portion of precipitate adhering to the side of the beaker is at once brushed off with a feather before it can dry. The precipitate is washed with sulphuretted hydrogen water, to which a little monochloracetic acid has been added.

Electrolytic Separation of Cobalt and Zinc from Manganese [1]

Classen finds that cobalt and zinc are little disposed to be reduced in a heated liquid, as on applying a current of about 10 c.c. (a strength which easily effects reduction in the cold) the metals are deposited in a spongy state, and not adhesive. If it is therefore required to separate the above two metals from manganese, the electrolysis of the solution of the double salts (obtained as above) is effected at an ordinary temperature. If the proportion of manganese is small, the reduction is at once rapid and accurate. If the proportion is greater, the reduction is more tedious. In order to effect a complete separation we are compelled to dissolve the deposited peroxide in oxalic acid, without interrupting the current, and to allow the current to act again. For this purpose we proceed as directed in the separation of aluminium and iron.

Electrolytic Separation of Cobalt, Nickel, Zinc, and Iron, from Aluminium [2]

Classen finds that if a solution containing the above metals is mixed with a large excess of ammonium oxalate, and submitted in the cold to a current of from 10 to 12 c.c. of detonating gas, there are first iron, cobalt, nickel, or zinc, or all four metals, deposited at the negative electrode, while the aluminium remains in solution as long as the quantity of ammonium oxide is larger than that of the ammonium carbonate formed. When, ultimately, a precipitation of aluminium hydroxide occurs, the solution is almost free from the other metals. A small quantity of the solution is tested from time to time with ammonium sulphide by means of a capillary tube, and the current is interrupted as soon as the reaction ceases to appear.

For performing the experiment, the aqueous or faintly acid solution of the sulphates (chlorides are less suitable), neutralised with ammonia

[1] For details of operations see chapter on Electrolytic Analysis. [2] Ibid.

if needful, is mixed with an excess of ammonium oxalate, so that the total volume of the liquid is from 150 to 175 c.c., adding (with the application of a gentle heat if needful) so much solid ammonium oxalate that there may be from 2 to 3 grammes ammonium oxalate to 0·1 gramme of the metals. When the temperature of the solution is not higher than 40° it may be at once electrolysed.

It is not well to pass the current longer than is necessary for the reduction of iron, cobalt, nickel, or zinc. Otherwise, much aluminium is deposited as hydroxide on the negative electrode and cannot be removed. In such a case we are compelled to dissolve the aluminium hydroxide by acidulation with oxalic acid, and, if too much acid has been added, to electrolyse until the last traces of the metals which have passed into solution are reduced.

Without interrupting the current the oxalic acid is gradually poured upon the glass which covers the platinum capsule until no further effervescence takes place and the aluminium precipitate is dissolved.

If the quantity of the aluminium is not greater than that of the other metals, this method at once gives good results. In the contrary case the precipitate of hydroxide is redissolved without interrupting the current, by the cautious addition of oxalic acid, and the solution is electrolysed again until the metals which have to be separated are completely deposited.

According to Classen's further experiments [1] the separation can be at once effected if care is taken that the ammonium oxalate is not unnecessarily decomposed. This end may be obtained by adding a large excess of ammonium oxalate, electrolysing in the cold, and not employing currents which decompose the double oxalates violently. If a current of 10 to 12 c.c. detonating gas is used, no aluminium hydroxide is deposited. In order to determine the aluminium in the liquid decanted from the iron, cobalt, &c., it is heated in a porcelain capsule to expel ammonia, the precipitate is filtered off, and the aluminium hydroxide is converted into Al_2O_3 by ignition.

As regards the reduction of the aluminium oxide to metal, for a quantitative determination of the latter, the author remarks that experiments in that direction have proved fruitless.

Electrolytic Separation of Cobalt, Nickel, Zinc, and Iron, from Manganese and Aluminium [2]

The separation can be effected in a solution of the double oxalates, proceeding as directed for the separation of cobalt and zinc from manganese. After the reduction is completed, the solution containing the precipitate of manganese is boiled with an excess of soda-lye, a few

[1] *Berichte*, vol. xviii. p. 1795.

[2] For details of operation see chapter on Electrolytic Analysis.

c.c. of sodium hypochlorite or hydrogen peroxide are added, and the peroxide of manganese is at once filtered off.

In the filtrate after acidification with hydrochloric acid, the aluminium is precipitated as hydroxide with ammonia, and determined as aluminium oxide in the usual manner.

Electrolytic Separation of Cobalt, Nickel, Zinc, and Iron, from Chromium [1]

If a solution containing chromium as oxide or as chromium ammonium oxalate and mixed with an excess of ammonium oxalate is submitted to electrolysis, the chromium salt is entirely converted into a chromate. In the simultaneous presence of iron, cobalt, &c., these metals are first deposited as such upon the negative electrode. The metals are then characterised by a peculiar lightness.

After completion of the precipitation, the liquid is boiled to decompose the ammonium carbonate, the chromic acid is reduced to oxide by boiling with hydrochloric acid and alcohol, and the chromium is precipitated as hydroxide by means of ammonia. The hydroxide is converted into Cr_2O_3 in the well-known manner, and determined as such.

Electrolytic Separation of Cobalt, Nickel, Zinc, and Iron, from Chromium and Aluminium [2]

Classen finds that the separation is effected as in the above case. For determining aluminium in presence of chromium, the decanted liquid is boiled until the smell of ammonia has become very faint, the aluminium hydroxide is filtered off, and the chromium is deposited in the filtrate as directed in the previous instance.

Electrolytic Separation of Cobalt, Nickel, Zinc, and Iron, from Manganese, Chromium, and Aluminium [3]

Classen proceeds substantially as above. When the yellow colour of chromic acid has appeared the liquid is boiled to decompose the ammonium hydrocarbonate, precipitated in heat with soda-lye with the addition of a little sodium hypochlorite, or hydrogen peroxide. The precipitate of manganese peroxide always contains an admixture of chrome. After filtration and washing it is dissolved in hydrochloric acid, and the precipitation is repeated with soda-lye and an oxidising agent. The chrome is determined in the filtrate as directed above.

[1] For details of operation see chapter on Electrolytic Analysis.
[2] Ibid. [3] Ibid.

Electrolytic Separation of Cobalt, Nickel, Zinc, and Iron, from Uranium [1]

According to Classen the separation of uranium depends on the same principle as that of aluminium. For its execution a large excess of ammonium oxalate is required in order to keep the uranium in solution as a double oxalate until the accompanying metals are reduced. The current must correspond to about 10 or 12 c.c. of detonating gas per minute. With stronger currents it may happen, especially if the quantity of ammonium oxalate is insufficient, that the uranium may be deposited as hydroxide, in consequence of a strong rise of temperature in the liquid and the consequent decomposition of the ammonium hydrocarbonate as it is formed.

The solution of uranium, after the determination of the metals, is freed from oxalic acid by prolonged electrolysis, and the ammonium carbonate is lastly decomposed by heat. The uranium deposit is in a state of very fine division, and to render it fit for filtration it is mixed with nitric acid, heated until it is completely dissolved, and precipitated with ammonia. The uranium hydroxide is converted into uranous oxide by ignition in a current of hydrogen.

Electrolytic Separation of Cobalt, Nickel, Zinc, and Iron, from Chromium and Uranium [2]

Classen finds that the separation depends on the elimination of iron, cobalt, nickel, or zinc, as metals, from the solution of the double oxalates by means of the current, and on the oxidation of the chromium oxide to chromic acid. The uranium is thus separated out as hydroxide while the chromium remains in solution as ammonium chromate. In order to render practicable the quantitative separation of chromium and uranium the electrolysis must be continued until the complete oxidation of the oxalic acid. The electrolysed liquid is boiled to decompose the ammonium hydrocarbonate formed, and is then allowed to stand for six hours. The chromium is determined as above directed in the filtrate freed from uranium.

Separation of Nickel or Cobalt from Manganese, Iron, Zinc, and Uranium

Clemens Zimmermann, after pointing out that the usual procedures are either very tedious or questionable as to accuracy, gives his method for separating zinc from other metals of the group by means of ammonium sulphocyanide. To the liquid in question, which, in addition to the zinc salt, may contain any number of the other metals of the fourth group, iron and uranium, if present, being in the

[1] For details of operation see chapter on Electrolytic Analysis. [2] Ibid.

state of ferric and uranic salts, he adds, if its reaction is acid, sodium carbonate till a slight turbidity appears, neutrality being the main condition for success. An excess of a solution of ammonium sulphocyanide, not too dilute, is then added, the sides of the vessel are rinsed with water at 60° to 70°, preferably in an Erlenmeyer flask, and a very moderate stream of sulphuretted hydrogen is introduced repeatedly, but not for very long, till the odour of this gas does not disappear after the liquid has stood for some time. During the introduction of the gas the appearance of a milky-white precipitate is first perceived, and after a considerable time zinc sulphide is separated in flocks which continually become denser. The beaker is now exposed to a gentle heat till the precipitate has settled and the liquid has become clear, which may require six hours. It is then filtered, the white zinc sulphide is washed with water containing sulphuretted hydrogen and ammonium sulphocyanide, and dried. This precipitate contains all the zinc, free from the other heavy metals of the group. When dry it may be ignited in a current of hydrogen according to Rose's process, or it may be dissolved in hydrochloric acid, evaporated to dryness in a weighed platinum capsule on the water-bath, mixed with an excess of elutriated mercuric oxide, pure and free from alkali, evaporated to dryness, and ignited. Zinc oxide remains, perfectly pure and without loss, and is weighed when cold.

In the filtrate from the zinc sulphide the sulphocyanides are first destroyed by means of nitric acid, which at the same time peroxidises any ferrous or uranous salts present. This operation is best effected in a roomy, long-necked flask, which is heated on the water-bath, and nitric acid is added by degrees in small portions until the liquid no longer becomes red, followed by decolouration. Any yellow cyanogen persulphide formed is filtered off. If the acid is added too rapidly, the liquid may be projected from the flask.

In order to separate the iron present from nickel and cobalt, the solution, which may contain ferric salts along with nickel or cobalt salts, or both, is mixed with an excess of ammonium sulphocyanide, when the blood-red colour of iron sulphocyanide appears; a dilute solution of sodium carbonate is then added, drop by drop, till the red colour just disappears. All the iron is thus precipitated as ferric hydroxide, none of it remaining in solution, and no cobalt or nickel being thrown down. The precipitate is allowed to settle, filtered, washed with boiling water to which a little ammonium sulphocyanide has been added, dried, ignited, and weighed. The filtrate is treated as has been directed for the filtrate from zinc sulphide. The author separates cobalt and nickel by Liebig's method with ferric oxide.

For the separation of iron and uranium, the liquid, in which the metals must have been peroxidised, is brought to a boil, mixed with an excess of ammonium sulphocyanide, and aqueous sodium carbonate is added, exactly as above directed for the separation of iron from cobalt

and nickel. The same process is further followed for the removal of the iron, which is found free from the slightest trace of uranic compounds.

The filtrate, which contains uranic oxide in solution, is first treated with nitric acid to destroy the sulphocyanogen, then neutralised with ammonia, and mixed with ammonium sulphide; the precipitate of uranium oxysulphide is boiled, by which it is resolved into sulphur and uranous oxide; it is then filtered, dried, and ignited. Lastly, the uranium is either weighed as uranoso-uranic oxide, or converted into uranous oxide by very strong ignition in a current of hydrogen gas, maintained until the product is cold. The precipitation of uranic oxide by ammonia is greatly promoted by the addition of ammonium chloride, without which it does not take place in dilute solutions.

Separation of Nickel, Cobalt, or Manganese, from Thallium

Add sodium sulphite in excess to the solution, so as to be certain that all the thallium is in the state of proto-salt, then add excess of sodium carbonate and boil. The thallium will remain in solution, while the other metals will be precipitated. Filter off and add potassium iodide to the filtrate; this will precipitate insoluble thallium iodide in the form of a yellow powder. When the thallium is present in traces only, it is better to add potassium iodide direct to the liquid, without separating the other metals with sodium carbonate.

Separation of Cobalt from Gallium

(*A*) However slight the proportion of cobalt, caustic potash does not give very good results, in consequence of the relatively considerable entanglement of gallium in the oxide precipitated. Sensible traces of gallium may be detected in cobalt oxide which has been precipitated with excess of potash five times in succession, and this when operating upon a liquid containing merely 0·005 gramme gallium in 2 to 3 grammes of cobalt oxide. Yet, after the seventh potassic treatment, there no longer remains any gallium in the cobalt oxide. The process is therefore only fit for removing small quantities of cobalt mixed with much gallium; the small precipitate of cobalt oxide is then freed from the last traces of gallium by one of the other methods. The potassic filtrates often retain a trace of cobalt, which tinges them blue; exposure to the air decolourises these solutions in one or two days in the cold, or in one hour with heat, brown cobalt oxide being deposited.

(*B*) Barium and calcium carbonates effect at first merely an imperfect separation of gallium and cobalt. Even in the cold, after a contact of six hours, the precipitates contain notable quantities of cobalt oxide. Contrary to what happens with the zinc salts, a little more cobalt oxide is found in the precipitate with the calcium than in that

with the barium salt. The inconvenience of the precipitation of a certain quantity of cobalt oxide in presence of barium and calcium carbonates is diminished by the separation which is naturally effected between gallium and cobalt, when boiling with ammonia or treatment with cupric hydrate is employed to eliminate calcium and barium salts.

In the reaction of calcium carbonate in heat, after sulphurous reduction, there are also deposited notable quantities of cobalt oxide, which, nevertheless, are entirely eliminated if the operation is repeated once or twice, and also on ammoniacal ebullition or treatment with copper hydrate for the removal of lime. Prolonged boiling after supersaturation with ammonia enables us to separate gallium from cobalt very conveniently. It is necessary to operate upon a very acid liquid, so as to produce a sufficient quantity of ammonium chloride, taking care to boil previously, so as to destroy the cobalt per-salts. The ammonia is not added until after the liquid has begun to boil. The purpuro-cobaltic salts, which are sometimes formed in small quantity, are dissolved and carried away in the washing-waters. The gallium oxide thus obtained almost always retains traces of cobalt which are eliminated on repeating the operation.

(*C*) Excellent results are obtained either by means of cupric hydrate or of metallic copper and cuprous oxide. Sensible traces of cobalt, however, remain in the first copper precipitates ; but they are easily removed by one, or at most two repetitions.

Separation of Nickel from Gallium

(*A*) Nickel oxide precipitated by an excess of boiling potash retains gallium more energetically than does cobalt oxide. With a liquid containing 0·005 gramme gallium and 2 to 3 grammes nickel oxide, a very notable proportion of the gallium is found in the precipitate after the seventh treatment with potash. This procedure is consequently applicable only in cases of a small quantity of nickel mixed with much gallium. The galliferous nickel oxide is then analysed by one of the other methods.

(*B*) If we have mixtures containing little gallium and a large mass of protoxides, such as those of cobalt, nickel, manganese, zinc, &c., it is almost always very advantageous to begin by precipitating at a boil all the gallium sesquioxide by means of an alkali, along with a small fraction of the protoxides. The detection of the gallium then becomes easier, since it bears upon a small bulk of matter. The action of calcium and barium carbonates in the cold, as well as that of calcium carbonate in heat after sulphurous reduction, requires the same remarks as in the case of the separation from cobalt. It has likewise been found that a little more nickel oxide is rendered insoluble with calcium carbonate than with barium carbonate.

CHAPTER VII

SILVER, MERCURY, COPPER, LEAD, BISMUTH

SILVER

Preparation of Pure Silver

THE subject of the preparation of pure metallic silver has been studied in so exhaustive a manner by Professor Stas in his researches on the relations existing between atomic weights, that there is little left for any other investigator to do in connection with this subject. In the following pages is given an abstract of the processes which he found most successful.

Preparation of Silver from Silver Chloride.—Experience has shown that silver chloride, free from copper and iron, can be obtained directly by pouring a cold solution of silver nitrate, diluted with 30 times its weight of water, into a slight excess of hydrochloric acid, washing the precipitate with cold distilled water, and then digesting the chloride, dried at the ordinary temperature, and finely powdered, in aqua regia. When well washed after this treatment, the chloride does not retain the slightest trace of either copper or iron; while, so long as the silver chloride is in a curdy form, it retains in its pores, like coagulated albumen, some of the bodies which were dissolved in the liquid from which it was precipitated. Silver chloride, however, when dried at the ordinary temperature and finely powdered, very easily yields to aqua regia foreign metals which contaminate it. But whatever may be the purity of silver chloride, it produces a metal which always contains silicium and iron when it is reduced by Gay-Lussac's method—that is to say, by ignition with a mixture of chalk and charcoal.

Silver chloride, purified by the above process, mixed with its own weight of pure dry sodium carbonate, containing a tenth part of pure potassium nitrate, when heated in a white unglazed porcelain crucible, with the precautions recommended by Berzelius for avoiding intumescence, yields an ingot of silver. This ingot, fused again with a tenth of its weight of pure nitre and borax, and then run into an ingot-mould lined with pipeclay, gives a bar of silver which retains scarcely

any appreciable traces of foreign matters. This process requires great care, for when the mixture of chloride and carbonate is heated, if the temperature is raised too much at first, the mixture fuses, bubbles up, and is in danger of running over. To effect with safety the reduction of silver chloride in a white unglazed porcelain crucible, the latter should be placed inside a clay crucible. The most convenient plan for performing this operation is the following:—Fill up the space between the two crucibles with calcined pipeclay, powdered and mixed with 5 per cent. of fused and powdered borax. Under the influence of the heat the borax fuses and solders the whole together. When the silver chloride is reduced, the whole can be handled and the melted silver poured out as if it were one crucible. The great bulk which has to be heated before reaching the porcelain crucible prevents it cracking, and avoids loss of silver.

As the reduction by heat of silver chloride with sodium carbonate is a most delicate operation, when performed in large quantities, this reduction is effected under the influence of a solution of caustic potash and sugar of milk, as first proposed by Levol.

To procure potash and sugar of milk free from heavy metals, add to a concentrated solution of potassium hydrate, previously boiled, a slight excess of a solution of potassium sulphydrate to precipitate traces of dissolved metals.

After the deposit of the metallic sulphides, decant the alkaline solution and add it to freshly precipitated silver oxide, to deprive it of sulphur; after a sufficient digestion and rest, separate the excess of silver oxide and the silver sulphide that has been produced. By the same means the heavy metals contained in an aqueous solution of sugar of milk are eliminated.

The silver chloride contained in a large porcelain jar is digested at a temperature of from 70° to 80° C. with a mixture of solutions of potassium hydrate and sugar of milk, until all the chlorine is separated from the silver. The metallic silver, which is grey, is washed with water until the excess of alkali has disappeared, then digested with pure dilute sulphuric acid, and lastly washed with ammoniacal water. After being dried, 5 per cent. of its weight of borax is added, containing 10 per cent. of sodium nitrate, and then, with necessary precautions, it is fused in a Paris crucible.

The fused metal may then be poured into a mould coated with a paste of mixed calcined and uncalcined kaolin. The bars of silver, first cleaned with sharp sand, are then heated to redness with caustic potash prepared from tartar; the adhering kaolin having been dissolved, the bars are washed in pure water.

Preparation of Silver by Liebig's Process.—This process consists of reducing in the cold, by means of pure milk sugar, a pure concentrated ammoniacal solution of silver nitrate, to which pure potash has been added, until fulminating silver begins to be

precipitated. After a short time a violet precipitate is formed, which is transformed into a mirror of silver, if the solution does not contain more than 10 per cent. of nitrate. If, on the contrary, it contains much more metal, the silver remains as a violet precipitate. This precipitate, after being washed with water, is digested with aqueous ammonia, which removes the copper, if the silver contained any. When dried, it preserves its violet colour, and constitutes a peculiar modification of silver. Heated to 300° or 350° C., the metal becomes incandescent, and then assumes its proper colour, being of a dead white. To reduce it to bars fuse it with a certain quantity of pure nitre and borax, and run it into an ingot-mould lined with pipeclay. This always gives the metal of a uniform purity. It must be borne in mind that it is not only necessary for the metal obtained by any process always to possess the same properties; it is also necessary for it to be absolutely identical with pure silver prepared by other methods. For it may happen—and this is the case in the reduction of pure silver chloride by Gay-Lussac's process—that the operation of reduction communicates to the metal as much impurity as has been separated by solution and precipitation.

Preparation of Silver by Precipitation with Phosphorus.—An excellent, although very slow, method for preparing perfectly pure silver is by acting on a 1-per-cent. solution of silver nitrate with finely divided phosphorus. This action is very slow, but the metal after having remained for a long time in an excess of solution of silver, and then being digested in ammoniacal water, yields, after fusion with purified nitre and borax, silver absolutely pure.

Preparation of Silver by Reduction of the Chloride in the Wet Way.—Dissolve at the boiling-point a silver coin in very dilute nitric acid. The silver nitrate produced, after having been evaporated to dryness and fused, is kept at its point of fusion as long as any oxygen compounds of nitrogen are given off. The nitrate mixed with nitrite is dissolved, when cool, in the smallest possible quantity of cold water, and the solution, after resting forty-eight hours, is filtered through a double filter to separate all the matter that might have remained in suspension. The limpid solution, diluted with 30 times its volume of distilled water, is precipitated by an excess of pure hydrochloric acid. The silver chloride formed is, when deposited, washed by decantation, first with water acidulated with hydrochloric acid, and then with pure water.

This washing is performed by shaking the chloride violently each time in large stoppered bottles, with the necessary quantity of liquid.

It is then spread upon a cloth that has been washed with hydrochloric acid, strongly compressed, and left to dry spontaneously. When perfectly dry it is finely powdered and digested for several days in aqua regia. It is then again washed in distilled water.

Preparation of Pure Silver by Reduction of its Ammoniacal Solutions. — This method furnishes pure silver more easily and promptly than any other known way; and it has the special advantage of giving it in a state of great purity. It is based upon the complete reduction which ammoniacal solutions of silver compounds undergo when added to ammoniacal cuprous sulphite, or to a mixture of ammonium sulphite and any ammoniacal copper salt. At the ordinary temperature this reduction takes place slowly, with deposition of black, blue, or grey silver, according to the dilution of the liquids. Above a temperature of 60° C. the reduction is almost instantaneous, and the silver is precipitated in a state of division corresponding to the dilution of the liquid; its colour varying from grey to pure white.

A silver coin is dissolved in dilute boiling nitric acid; the solution of silver and copper nitrates is evaporated to dryness, and the saline mass fused. This fusion is necessary to destroy the platinum nitrate, which is often formed in dissolving silver coins.[1] After cooling, the nitrates are taken up by an excess of ammoniacal water. The ammoniacal solution is left to rest for forty-eight hours. The limpid liquid is filtered through double filter-paper, and then diluted with distilled water until it contains no more than 2 per cent. of its weight of silver.

Neutral ammonium sulphite is obtained by mixing ammonia with sulphurous acid. To ascertain the quantity of sulphite required for the complete precipitation of the silver from the ammoniacal solution of silver and copper nitrate, heat to the boiling-point a definite volume of solution of ammonium sulphite, and ascertain the volume of the solution of silver and copper which is decolourised by this salt. Experiment has proved that, as soon as the ammonium sulphite, sufficiently heated, is not coloured blue by the cupric oxide dissolved in the ammonia, there remains no trace of silver dissolved in the liquid, because in this case all the copper exists in the cuprous state, the presence of which is incompatible with that of any compound of silver dissolved in ammonia.

The quantity of ammonium sulphite necessary for the precipitation of the liquid having been ascertained, add it to the argentiferous solution, and after being well mixed leave it to itself for forty-eight hours in a closed glass flask, to prevent the contact of the air. At the end of this time about a third of the silver will be reduced, at the ordinary temperature, and is precipitated in the form of a shower of crystallised silver, of a greyish-white colour and very brilliant.

The decanted blue liquid, in quantities of 10 litres at a time, is then put into a water-bath at a temperature of from 60° to 70° C. The time required to cause the elevation of temperature is quite sufficient for the complete reduction of the remainder of the silver in solution, and for the reduction of the cupric sulphite to the state of cuprous sulphite,

[1] Silver coins frequently contain iron, nickel, and traces of cobalt, platinum, and gold.

especially if care be taken to have sufficient excess of solution of ammonium sulphite. The liquid in which the reaction takes place becomes quite colourless if the copper contains neither nickel nor cobalt. If it contains nickel, it takes a slight green tint ; it takes, on the other hand, a reddish tinge if cobalt is present.

The silver being separated out, decant the liquid when cold, and wash separately the silver precipitated from the cold and the warm solutions. This washing is performed by decantation with ammoniacal water ; it is continued as long as the washing waters are perceptibly coloured blue by exposure to air, or are precipitated by barium chloride. The silver is afterwards left for several days in concentrated ammonia, and then washed in pure water.

If the solution from which the silver is precipitated has been diluted until it contains no more than 2 per cent. of silver, the ammonia left in contact with this metal is not coloured even after several days' digestion. There is no longer any copper for the ammonia to dissolve ; it dissolves silver instead, for this metal is feebly attacked by the alkali under the influence of air, as is easily proved by evaporating liquid ammonia which has remained for several days in contact with turnings of pure silver. The liquid always leaves a black shining mirror of silver nitride by its spontaneous evaporation.

By fulfilling all the conditions above described, and especially by carrying the dilution of the ammoniacal solution of the silver and copper nitrates to 2 per cent. of silver, we obtain silver of great purity. When the precipitated silver is required in bars, fuse it with 5 per cent. of its weight of calcined borax containing 10 per cent. of sodium nitrate, as mentioned in the case of the silver reduced from the chloride by potash and sugar of milk. Larger quantities may also be fused with the air-hydrogen blowpipe in a crucible of pure porcelain, or in an oxyhydrogen gas furnace in crucibles of marble-lime.

Purification of Silver by Distillation

(*A*) Pure silver may be fused in air at a temperature sufficiently high to volatilise it, without becoming at all stained or discoloured, and without giving off coloured vapour. This fact has been taken as a basis by Professor Stas, in order to ascertain the purity of the silver prepared by either of the processes already given. He describes his experiment as follows :—About 400 grammes of silver reduced from its chloride, placed in a crucible of lime from white marble, itself enclosed in a refractory crucible, were submitted to the hissing flame produced by the combustion of ordinary coal gas with pure oxygen. The silver fused without becoming in the least discoloured. It was then heated until it boiled violently. The silver first gave to the flame the sodium character ; but in a short time the yellow colour disappeared, and, so long as the silver did not boil, no discolouration appeared, although the

metal gave off vapour in considerable quantity. After the silver boiled a pale blue vapour was produced, which occasionally bordered upon purple. Some chemists assign a green colour to the vapour of silver. The green colour observed arose indisputably from the copper contained in the silver submitted to the experiment. The purple colour is attributed to the existence of strontium or lithium in the marble used for the preparation of the quick-lime crucible.

This vapour stained the lime a deep yellow, which colour, however, disappeared on the application of heat. When, by this process of refining, the silver had lost all volatile matter, and when the fixed but oxidisable materials that it might contain must have united with the lime, it was poured from a good height, and in a thin stream, into distilled water, where it took the form of pure white, almost spherical globules. The crucible presented no trace whatever of a metallic oxide or silicate.

(*B*) The same treatment was applied to the pulverulent silver prepared by the cuprous ammoniacal sulphite, and identical phenomena presented themselves, excepting always the intense yellow colour of the flame, which was produced when the silver reduced from the chloride was heated to near its boiling-point.

Before submitting the silver under experiment to the action of the oxyhydrogen gas-flame care must first be taken to expose the lime-crucible to the heat of the oxyhydrogen blowpipe, so as to eliminate as much as possible from the lime the volatile substances that give a particular colour to the flame; all marbles contain notably sodium, and many contain strontium and lithium.

(*C*) Having been struck by the facility with which silver may be boiled violently, and distilled in the flame of oxyhydrogen gas, Professor Stas was led to experiment on the distillation of silver both for the object of obtaining it absolutely pure, and also to ascertain if silver refined by the methods already described still retains any traces of fixed bodies capable of uniting with lime.

For this purpose, in a block of lime prepared from white marble, from 25 to 30 centimetres in length, by 10 centimetres width and height, there was made a circular cavity 3 centimetres in diameter and 2 centimetres in depth, in communication with an inclined plane also 3 centimetres in width, by at most half a centimetre in depth, and serving to condense the vapour of silver. This inclined plane was terminated by a reservoir acting as a receiver for the liquid metal. About 50 grammes of refined silver were placed in the cavity, first heated to whiteness by the application of a jet of coal-gas burning in a suitable excess of compressed air, and the block was covered with a plate of lime from white marble, 5 centimetres in thickness, pierced with two inclined circular openings, one corresponding to the circular cavity, the other to the little reservoir at the end of the inclined plane. Through one of the openings of the plate was passed a large

oxyhydrogen blowpipe, furnished with very thick ends of platinum to avoid their fusion and the transportation of the metal. When the interior of the cavity had been heated to the boiling-point of silver, not more than ten or fifteen minutes were required to distil the whole of the silver. The 50 grammes were volatilised without leaving in the cavity of lime, which was used as the retort for distillation, the slightest appreciable residue to the eye assisted by a glass. The distillation of silver is such a simple operation to manage that nothing could be easier than to procure a kilogramme of distilled silver, if the apparatus was proportioned to the mass. In the operations above described, *at least* half the silver used was, however, lost. It was, in fact, carried away in the state of pale blue vapour by the current of oxyhydrogen gas, although this was very moderate, and without too great an excess of oxygen: it was diffused through the surrounding atmosphere, the transparency of which it affected, while imparting to it a very sensible metallic taste. The apparatus was also very imperfect; vapour of silver escaped in quantities by the opening intended to carry off the products of combustion, and all round between the block and the thick plate serving as a cover to it. Their surfaces, indeed, were not sufficiently well smoothed to fit very exactly. Wherever the vapour of silver passed it left a light or dark yellow stain, like that left by the vapour of litharge. The condensation of the vapour of silver takes place the more readily the less excess of oxygen the oxyhydrogen gas contains.

All the different samples of silver prepared by any of the above-described methods were subsequently fused, and cast in an ingot-mould lined with white pipeclay. To detach the pipeclay, the surfaces of the bars were rubbed with sharp white sand. They were then heated to dull redness and covered over with caustic potash, which was kept in a fused state for at least a quarter of an hour. The adherent pipeclay being in this manner attacked, the bars were suddenly plunged into water. The silicate formed on the surface being thus detached, the bars, after a second scrubbing with sharp sand, were fit for use. These bars, before being employed, were treated with boiling hydrochloric acid, washed first in cold aqueous ammonia, then in pure water, and finally heated to redness on plates of pure silver. It having been necessary for the silver to be in the form of small lumps from 2 to 25 grammes in weight, in the form of sheet, and in a certain state of division to make up weights previously calculated, the small lumps were obtained by cutting the ingots with a chisel on an anvil of polished cast-steel. The turnings and filings obtained from the ingots by means of a lathe and file furnished the finely divided silver. To separate the iron adhering to the silver when cut with the chisel, lathe, or file, these different forms of the metal were digested in a close vessel for twenty-four hours, and at a temperature of 60° to 80° C., first with strong hydrochloric acid, and then with pure ammonia. The silver was finally washed with absolutely pure water, heated to redness

on a plate of pure silver, and immediately put into bottles with well-fitting stoppers. Having found that silver, after rolling, contained iron, which was absent before rolling, the precaution was taken to have all the silver which was required in the form of sheet rolled between two plates of pure silver. It is only at the expense of the surfaces of the two plates which touch the cylinders of the mill that the surface of the inner plate could be protected from contamination with all foreign metal. The laminated silver was heated to redness in the air, and enclosed while very warm in a well-stoppered bottle.

Ascertaining the Purity of Silver.—Professor Stas gives a very simple plan for ascertaining the purity of silver. The pure metal remains melted in the air at a sufficiently high temperature to volatilise it without being covered by any scum or colouration, and without giving a coloured vapour. Silver containing no more than the $\frac{1}{500000}$th part of iron, copper, or silicium becomes covered with a very strong and mobile scum, when it is fused before a blowpipe fed with a mixture of illuminating gas or hydrogen and an excess of air. Silver containing scarcely appreciable traces of copper when volatilising in an oxidising flame always gives a coloured flame. This assay may be performed on charcoal or white-burned pipeclay, or on porcelain, by means of a gas blowpipe or a simple eolipile. The scoria derived from the impurities in the metal always forms upon the surface of the flattened spheroid caused by the fusion. After cooling, the foreign matter is found adhering to the silver near the point of contact of the metal with the support.

According to Dr. Classen, silver is wholly precipitated by cadmium. When dealing with a nitric solution of silver, evaporate to dryness in the presence of sulphuric acid, dissolve the silver sulphate in boiling water, plunge into it a plate of cadmium, and the reduction of the silver takes place at once. The silver is deposited in a compact mass, easily washed with water; as it may contain a little cadmium, boil it in the acid liquid until no hydrogen escapes; wash it until the water contains no sulphuric acid; then dry and calcine; the silver, at first a black grey, takes the metallic lustre; it may then be weighed—the results are very exact.

The reduction of silver compounds by means of cadmium goes on very quickly, and as cadmium is but slightly soluble in dilute acids, the same piece of metal will serve for several operations, without even losing the metallic lustre of the surface. Freshly precipitated silver chloride may be reduced in the same way.

Electrolytic Separation of Silver[1]

(*A*) Dr. Classen finds that silver forms with ammonium oxalate a white precipitate of silver oxalate, not soluble in an excess of the precipitant. This behaviour may be used for separating silver from those

[1] For details of operation see chapter on Electrolytic Analysis.

metals which form soluble double salts with ammonium oxalate. From its solution in potassium cyanide, silver separates out with characteristic properties very suitable for quantitative determinations (Luckow's method). If insoluble silver compounds have to be analysed (oxalate, chloride, &c.), they are dissolved in potassium cyanide; soluble compounds are mixed with a quantity of potassium cyanide, sufficient for the formation of the double salt.

In order to obtain the silver in a compact state we use a current corresponding to 1·5 or 2 c.c. of detonating gas per minute. After complete reduction the liquid is at once decanted off, the silver is first purified by repeated washing in water, the water is removed by means of alcohol, the residue is dried in the air-bath and weighed.

(*B*) In carrying out this method according to F. Rüdorff, we add to the solution, which may contain as much as 0·3 gramme of silver, a slight excess of potassium cyanide, dilute with water to 100 c.c., and electrolyse with a battery consisting of from 3 to 6 Meidinger elements. The end of the reaction is ascertained by means of hydrogen sulphide. The deposit is washed in water and dried in the air-bath at 100°.

(*C*) J. Kruting mixes the solution of the silver salt to be precipitated with a slight excess of ammonia, adds ammonium sulphate, and electrolyses with a current of 2 c.c. of detonating gas per minute. Towards the end of the operation the current is strengthened to 5 c.c. of detonating gas.

(*D*) The following experimental conditions have been ascertained in the Munich laboratory for the above process. The solution, which must contain at most 0·5 gramme of silver, is mixed with 20 per cent. by volume of ammonia (sp. gr. 0·96), and 5 per cent. ammonium sulphate (1 : 10) is heated and electrolysed with a current of N.D. 100= 0·02–0·05 ampère. The precipitate may be washed after the current is interrupted, but with great care for the entire removal of the ammonium sulphate.

(*E*) Fresenius and Bergmann have ascertained that a compact deposition of the silver may be effected from a liquid containing nitric acid. They add to the solution of silver about 20 c.c. nitric acid (sp. gr. 1·2), dilute with water to about 200 c.c. and electrolyse with a current yielding from 2 to 2·5 c.c. of detonating gas per minute.

(*F*) According to the results of the Munich laboratory it is advantageous to add to the solution (which may contain as much as 0·4 gramme silver) 3 vol. per cent. of nitric acid, to heat and to electrolyse with N.D. 100=0·04–0·05 ampère. In order to avoid loss the silver must be carefully washed without interrupting the current.

An insufficient quantity of nitric acid occasions the formation of peroxide.

Volumetric Estimation of Silver

(*A*) It would be out of place here to describe the well-known Gay-Lussac process for the assay of silver by the wet way. It is necessary however, to draw attention to some improvements introduced into this process by Professor Stas, by which the errors incidental to the old process are entirely obviated. The operation is conducted in the following manner:—The silver, after having been heated to redness in a crucible of the same metal and properly cooled in the air, is weighed and introduced into a white-glass flask, with the stopper well ground in with emery, and having very thick sides to enable it to withstand an internal pressure of at least 10 atmospheres. Then pour upon the metal 10 times its weight of pure nitric acid at 25° Baumé. Put in the stopper and fix it solidly in its place by the aid of strong cord. Then surround the flask with wire gauze, and place it in a bath where its temperature is raised to 45° or 50° C. At the end of twenty-four or thirty-six hours all the silver will have dissolved without any trace of gas developing itself, and consequently without anything escaping from the flask. Indeed, the nitrogen binoxide, as fast as it is produced, reduces the nitric acid to the state of nitrous or hyponitric acid, which at this temperature remains perfectly dissolved in the large excess of nitric acid employed. If the temperature of the bath does not exceed 50°, there is nothing to fear. Upwards of 100 solutions of silver in a closed flask have been made, employing from 3 to 50 grammes of silver at a time, without any accident taking place. Twice only, the temperature of the bath rising much too high, two flasks which were immersed in it yielded to the internal pressure and produced a rather violent explosion. The plan of dissolving the silver in a close vessel has been adopted because the method of solution in open vessels, such as is adopted in the assay rooms of the Mint, causes a slight loss of silver. Moreover, the constant presence of silver in the washing-waters of the gas, arising from the solution of the metal in the ordinary way, sufficiently points to the necessity of effecting this solution either in a close vessel or in an apparatus in which the escaping gases may be washed. It ought to be added, however, that the loss experienced upon a gramme of silver never affects the accuracy of the assay of silver in the Mint, owing to the much more considerable and unavoidable errors of experiment.

The remainder of the description is given in Professor Stas's own words:—'The solution of the metal having been effected, and the flask well cooled, I introduce such an amount of pure water that, with the acid already added, the total weight of the liquid becomes at the minimum 35 times, and at the maximum 50 times, the weight of the silver employed. I now carry the flask into a room only lighted with gas. After having conveniently inclined it, I introduce it into a tube, sealed

up at one end, fixed to a rod of platinum, and containing the chloride weighed with the greatest accuracy that my balances will admit of. I then drop the chloride into the solution of silver, and wash the tube out several times with water, so as not to lose the traces of chloride which may remain adhering to it. After having tightly closed the flask, and enveloped it in caoutchouc, I shake it, until the liquid, at first turbid, becomes perfectly clear. I then proceed to the assay of the silver remaining unprecipitated. For this purpose I have prepared with the greatest care the decimal solutions of salt and silver, such as are employed in the laboratories of the Mint.

'On the other hand, I have myself manufactured pipettes, tubes which when empty, in a vertical position, would furnish me 10, 5, 4, 3, 2, 1, or $\frac{1}{2}$ a cubic centimetre of decimal solution. I also constructed burettes which, when placed in a vertical position, would deliver drops exactly equal to the twentieth of a cubic centimetre. The burette itself and the tubes of $\frac{1}{2}$, 1, and 2 centimetres, are subdivided into twentieths of a cubic centimetre. The small burette consists of a graduated tube of 4 or 5 millimetres internal diameter, drawn out to a point so as to expose an opening of about 1 millimetre in diameter, and fused to a larger open tube, the aperture of which is covered with a piece of vulcanised caoutchouc folded over the side of the tube, and more or less strongly bound to it, according as it is wished to deliver the drops more or less rapidly; my burettes would only give 5 or 6 per minute.

'It is absolutely necessary to hold the burettes in a vertical position, for the same instrument which furnishes with the greatest accuracy 20 drops per cubic centimetre only delivers 17 or 18 when it is inclined 45°; in a position of 10° or 15° no more than 16 or 17 drops are required to make a centimetre.

'To perform the assay, I have also the following arrangement:— In a long narrow box, the anterior portion of which is furnished with yellow glass, and the posterior portion lighted by a gas lamp, I arrange a perfectly spherical glass globe containing a saturated solution of the double potassium and sodium chromate, so as to concentrate the rays and obtain a cone of yellow light. I then place the flask containing the assay in such a position that the surface of the liquid may be traversed by the beam of yellow light. To make an observation, I place myself so that the eye makes an angle of 60° with the luminous ray traversing the flask. When this artifice is employed, a liquid containing 2 milligrammes of silver per litre produces a yellow, opaque, and dull precipitate of silver chloride, when half a centimetre of decimal solution is allowed to fall carefully upon its surface; when the quantity of silver is reduced to 1 milligramme, the precipitate of chloride is yellow, opaque, and brilliant; when the liquid is diminished in strength, so that it contains no more than the twentieth of a milligramme of silver per litre, there is still produced an appreciable cloud

upon the addition of a corresponding quantity of decimal solution. It is only necessary to wait sufficiently long, without touching the flask, to be certain of it. Nevertheless, in these assays I have only worked to tenths of a milligramme.

'In all my experiments I have continued adding decimal salt solution as long as I have seen a cloud produced on the surface of the liquid after standing fifteen minutes. When I have arrived at the extreme limit, and have just passed it, I add 5 cubic centimetres of decimal solution of silver. After well shaking, I neutralise three-quarters of the excess of silver, so as to obtain immediately upon agitation a clear liquid approaching very nearly the extreme limit. When there was a difference between the results of two assays, a difference that has never exceeded $\frac{2}{10}$ or $\frac{3}{10}$ of a milligramme, I always took the minimum result.

'Those who have made many assays by the wet way will have noticed that the interior sides of a flask in which they have for some time shaken silver chloride produced by successive precipitation, become covered with a kind of varnish of chloride, appear greasy, and so lose their transparency. To obviate this inconvenience when it occurs, I remove, by means of a pipette, a portion of the liquid after it has been agitated and become limpid by standing sufficiently, and transfer it to a bottle having parallel glass sides, and ascertain in this second bottle the presence of silver or salt in excess. The liquid in this bottle was always added to the first whenever it was found necessary to continue the operation.

'The assay presents another difficulty which may lead one greatly into error when not forewarned of it.

'A liquid from which almost all the silver has been precipitated by a saline solution, but which still contains between 1 and 2 milligrammes of silver per litre, is precipitated equally upon the addition of a decimal solution of silver or of salt. In this case, however, there is a very evident difference in the resulting turbidity. The precipitate occasioned by the decimal salt solution in the assay containing 1 or 2 milligrammes of silver in the state of nitrate is always opaque, yellow, and brilliant; while the precipitate formed upon the addition of silver nitrate to the same liquid is whitish and translucent. I account for this anomaly by the slight solubility of silver chloride in the alkaline nitrate in solution, and which precipitates in the presence of a silver solution richer than itself. I have, notwithstanding, always added decimal salt solution until precipitation ceases.

'Such is the method of assay which I have adopted for all my estimations by means of double decomposition.'

(*B*) In a note published subsequent to the above researches, Professor Stas shows how one of the difficulties in the wet assay of silver can be avoided. He says that the Gay-Lussac process is open, under certain conditions, to a source of error arising from the solubility of silver chloride in the very liquid to which its origin is due. This

solution, whatever its mode of production may be, is precipitated equally by a decimal solution of silver and by hydrochloric acid or an alkaline chloride. The extent to which this precipitation ensues is uncertain. At the ordinary temperature there may be a variation of from 1 to $\frac{1}{6000}$ in 100 c.c. of the liquid. Practically, it is quite possible, while preserving the simplicity of the wet method of assay, to substitute a bromide, or hydrobromic acid, for a chloride, or hydrochloric acid. This absolutely removes those anomalies which have been observed to be attendant on the use of a chloride or hydrochloric acid.

(*C*) Professor J. Volhard proceeds as follows :—The alkaline sulphocyanides produce in silver salts a curdy precipitate as insoluble in water as silver chloride. The red solution of ferric sulphocyanide produces the same precipitate, and is decolourised at the same time. If potassium or ammonium sulphocyanide is added to the solution of a silver salt mixed with a ferric salt, a red colouration appears, which is immediately decolourised, and does not become permanent until all the silver is precipitated. This indication is extremely sensitive, and the amount of silver is easily deduced from the quantity of sulphocyanide solution consumed in producing a permanent colouration if the strength of the sulphocyanide is known. This process is much more sensitive than that of Mohr, who employs potassium chromate as indicator, and can be used for the estimation of all bodies which are completely precipitated by silver nitrate from an acid solution. It is merely requisite to add silver nitrate in excess, and estimate the excess of silver remaining after precipitation. To prepare the standard solution of ammonium sulphocyanide—a salt too hygroscopic to be weighed directly—we dissolve about 8 grammes in a litre of water. On the other hand, 10 grammes of fine silver (or 10·8 if the solution is to correspond to the atomic weight) is dissolved in nitric acid and diluted with water to 1000 c.c. To 10 c.c. of this solution add 5 c.c. of ferric sulphate (at 50 grammes ferric oxide per litre), and dilute with 150 to 200 c.c. of water. The sulphocyanide solution is then dropped in with a burette till a permanent red colouration appears. If *e.g.* 9·6 of the sulphocyanide have been required, 960 c.c. of this solution is then diluted to make up 1 litre, when each c.c. will correspond to 10 milligrammes of silver. To assay an alloy of silver 1 gramme is dissolved in nitric acid, the solution evaporated in the water-bath, 5 c.c. of ferric sulphate and 200 c.c. of water added, and the sulphocyanide run in. Every $\frac{1}{10}$ of a c.c. used expresses $\frac{1}{1000}$ of silver. The presence of copper within certain limits is without influence. If it amounts to 80 per cent. the precise point of saturation is difficult to seize, either because the blue colour masks the red colouration, or because the cupric solution has an action upon the sulphocyanide. It will be necessary to ascertain if the sulphocyanide undergoes any change in keeping, and if the

presence of certain metals renders the result doubtful. Finally, this method requires simplifying for alloys rich in copper and poor in silver. This simplification may be found, perhaps, in the following reaction: When to a mixed solution of copper and silver, potassium ferrocyanide is added, the brown precipitate of copper ferrocyanide does not appear till all the silver has been thrown down.

Separation of Silver Chloride and Iodide

Silver chloride, when treated with ammonium sulphocyanide in an ammoniacal liquid, is readily and completely converted into silver sulphocyanide, while silver iodide remains untouched.

Silver cyanide is converted into sulphocyanide by hydrosulphocyanic acid so rapidly that dissolved silver cannot be titrated with sulphocyanide solution in presence of silver cyanide. But if the silver cyanide be precipitated from a given quantity of prussic acid by an excess of silver solution, there is no difficulty in titrating the excess of silver in the filter with sulphocyanide solution.

Extraction of Silver from Burnt Pyrites

(*A*) In the manufacture of sulphuric acid, iron and copper pyrites are burnt in kilns supplied with a limited amount of air, the products of combustion being thence conducted into leaden chambers, as in the case of vitriol manufactured from ordinary brimstone.

The resulting residue, or 'burnt ore,' was formerly to a large extent smelted for copper, and, from the great amounts of iron oxide present, acted as a valuable flux for the more siliceous ores of that metal. It may be taken as containing on the average about 4 per cent. of copper and 18 dwts. of silver to the ton.

For several years past a large proportion of the burnt ore produced in the various chemical works of this country has been worked by what is known as 'the wet process of extraction.'

By this process the burnt ore is first finely ground and sifted, and subsequently roasted with common salt until, by the oxidation of the metallic sulphides present, a portion of alkaline salt is converted into sodium sulphate, while the copper is, on the contrary, transformed into a soluble chloride. The copper salt is subsequently removed by repeated washings, and the copper precipitated by iron in the metallic state. It has long been known to those engaged in this business that the copper precipitate produced, contains not only a notable quantity of silver, but also distinct traces of gold. No attempt, however, to separate the precious metals, and to turn them to profitable account, had been made until Mr. F. Claudet patented a process for the separation of silver from ordinary copper liquors by the addition of a soluble iodide.

(*B*) The amount of silver present in burnt ore seldom exceeds 18 dwts. per ton ; but as the whole of this is never obtained in solution, it follows that, dealing with such minute quantities, in order to obtain satisfactory commercial results, the process employed should be both cheap and expeditious.

The vats, in which the burnt ore which has been roasted with salt is lixiviated, generally receive some eight or nine successive washings either with water or with water acidulated by hydrochloric acid, and of these only the first three contain a sufficient amount of silver to be worth working. For the purpose of removing the soluble salts from the ground and washed ore, hot water is employed, and as a large proportion of the sodium chloride used remains undecomposed, it acts as a solvent for the silver chloride produced during the process of furnacing.

(*C*) The several operations for the extraction of silver are conducted in the following manner ; and as the first three washings contain nearly 95 per cent. of the total amount of that metal dissolved, these alone are treated :—

The liquors are first run into suitable wooden cisterns, each of a capacity of about 2700 gallons, where they are allowed to settle. The yield of silver per gallon is now ascertained by taking a measured quantity, to which are added hydrochloric acid, potassium iodide, and a solution of lead acetate. The precipitate thus obtained is thrown upon a filter, and, after being dried, is fused with a flux consisting of a mixture of sodium carbonate, borax, and lampblack. The resulting argentiferous lead is passed to the cupel, and, from the weight of the button of silver obtained, the amount of that metal in a gallon of the liquor is estimated.

The liquor from the settling vat is now allowed to flow into another of slightly larger capacity, while at the same time the exact amount of a soluble iodide necessary to precipitate the silver present is run into it from a graduated tank, together with a quantity of water equal to about $\frac{1}{10}$ the volume of the copper liquor. During the filling of the second tank its contents are constantly stirred, and, when filled, a little lime-water is added, and it is allowed to settle for forty-eight hours. The supernatant liquors are, after being assayed, run off, and the tank again filled, when the precipitate collected at the bottom is, about once a fortnight, washed into a vessel prepared for its reception.

This precipitate is chiefly composed of lead sulphate, silver iodide, and copper salts, from which the latter are readily removed by washing with water acidulated by hydrochloric acid. Thus freed from copper salts, the precipitate is decomposed by metallic zinc, which completely reduces the silver iodide, and, to a certain extent, also the lead sulphate The result of this decomposition is :—

1st. Zinc iodide, which, after being standardised, is employed in subsequent operations to precipitate further quantities of silver.

2nd. A precipitate rich in silver, and also containing a valuable amount of gold.

The results of nearly six months' experience of this process at the Widnes Metal Works show that ½ ounce of silver and 1½ grain of gold may be extracted from each ton of ore worked, at a total cost, including labour, loss of iodide, &c., of 8*d.* per ton, or 1*s.* 4*d.* per ounce, of silver produced. If from this amount be deducted 6*d.*, the value of the 3 grains of gold contained in each ounce of silver, the cost of production, per ounce of silver, will be reduced to 10*d.* and the expense of working a ton of ore to 5*d.* This leaves a profit of about 2*s.* on each ton of ore worked.

The value of the precious metals extracted from each ton of ore treated is certainly not large, as the amount originally contained is very small. With richer ores, however, more satisfactory results would be obtained; but when it is stated that some of the copper extraction works operate on 30,000 tons of ore annually, it becomes evident that a profit of 2*s.* per ton is a most important consideration in a business in which competition has rendered care and economy absolutely necessary.

Detection of Alkalies in Silver Nitrate

M. Stolba dissolves the salt in the smallest possible quantity of water; the liquid is filtered, and hydrofluosilicic acid is added drop by drop. If this produces a turbidity, an alkaline salt is present. If the liquid remains limpid, it is mixed with an equal volume of alcohol which will precipitate the slightest traces of alkali if present.

Separation of Silver from Gallium

(*A*) In a very acid nitric solution the silver is removed by a slight excess of hydrochloric acid.

(*B*) Sulphuretted hydrogen completely removes the silver contained in nitric solutions moderately acid, or in strongly acid hydrochloric liquids.

Separation of Silver from Thallium

(*A*) Sulphuretted hydrogen in an acid solution precipitates the silver. If the two metals have been precipitated together as chlorides, boil the mixture in nitro-hydrochloric acid; this will dissolve out the thallium in the form of sesquichloride. Dilute with water, boil, and filter while hot. Wash the residue on the filter with hot dilute hydrochloric acid. From the solution thallium sesquichloride separates, on cooling, in the form of orange-yellow crystals.

(*B*) Silver and thallium chlorides can also be separated by boiling in water. When hydrochloric acid, or a soluble chloride, is added to a solution of the thallium protoxide or one of its soluble salts, a white

curdy precipitate of thallium protochloride is thrown down, scarcely to be distinguished at first sight from silver chloride. When boiled in water it dissolves like lead chloride, and separates again on cooling; the crystals, however, are much smaller and less brilliant than those of lead chloride. One part of the chloride dissolves in 283·4 parts of water at 60° F., and in 52·5 parts of boiling water. When boiled in nitric acid or aqua regia, it is converted into the sesquichloride, which separates, on cooling, in yellow crystalline scales. It is soluble in 380·1 times its weight of water at 60° F., and in 52·9 parts of boiling water. Pure water produces a slight decomposition into teroxide and protochloride, which, however, may be prevented by the addition of a drop of nitric or hydrochloric acid. From the slight solubility of the chlorides, in even boiling water, it is evident that this method of separating thallium from silver is tedious, and is very liable to leave thallium behind.

(*C*) The best method of separating silver and thallium, when together as chlorides or iodides, consists in reducing the metals by the addition of a rod of pure zinc to the mixture. When the reaction is complete, remove the zinc, and wash with hot water till the washing-waters are free from chlorine. Then heat with dilute sulphuric acid, which dissolves the thallium and leaves the silver.

Separation of Silver from Manganese

P. Jannasch and H. Kammerer[1] dissolve the mixture of silver and manganese in moderately strong nitric acid.

The solution is poured into a mixture of 20 cubic centimetres water, 50 hydrogen peroxide, and 40 concentrated ammonia, and the whole is covered and heated upon the water-bath for ten to twelve minutes, whereupon the precipitate of hydrated manganese peroxide, which rapidly deposits, is filtered off. The precipitate is most carefully washed, firstly with a mixture of 8 parts by volume of water, 17 of hydrogen peroxide, and 17 of strong ammonia, and finally with hot water, incinerated, and lastly ignited before the blast until the weight is constant. The filtrate, containing all the silver, is heated on the water-bath until the ammoniacal odour disappears, acidified with concentrated nitric acid, and the silver is separated as chloride in the ordinary manner.

The separation of manganese and silver proceeds extremely easily and smoothly. A single precipitation of the manganese is sufficient, as the precipitate on examination was found free from traces of silver. In more complicated mixtures—*e.g.* an alloy of silver, bismuth, manganese, and nickel—the new process is decidedly to be preferred to a preliminary precipitation of the silver.

[1] *Chemical News*, Aug. 23, 1895.

MERCURY

Test for Mercurial Vapours.—M. Merget recommends paper steeped in the ammoniacal solution of silver nitrate or palladium chloride as reagents for mercurial vapours much more sensitive than gold-foil. This test-paper is very sensitive: a slip of sheet-copper plunged into a liquid containing 1 part of mercury in 10,000 remained bright after immersion, but if exposed to the ammoniacal silver-nitrate paper it occasioned a characteristic black spot. He finds that, even when solidified, mercury emits vapours in appreciable quantity.

Blowpipe Test for Mercury.—T. Charlton first obtains the sublimate either by heat alone or by anhydrous fusion mixture, and then, instead of adding nitric acid and solution of potassic iodide, simply drops into a tube a small grain of iodine. If this is quickly done the tube will still be warm enough to volatilise the iodine. If the tube has been allowed to cool before adding the iodine, then it will be necessary to apply a gentle heat, to cause the iodine to volatilise. As soon as the iodine comes in contact with the mercury sublimate a bright scarlet mass is formed, which is very characteristic of mercury.

Electrolytic Separation of Mercury [1]

(*A*) According to Dr. Classen, the metal can be easily precipitated from the solution of the mercuric salt, which is mixed with an excess of ammonium oxalate. It is reduced with a current of about 2 c.c. of detonating gas per minute. If the mercury exists in solution as chloride, the electrolysis is continued until the mercurous chloride disappears from the positive electrode.

From the solution of a mercury salt acidified with nitric acid the mercury is deposited at the negative electrode, in the form of a mirror of small globules, on applying a current of about 0·2 to 0·5 c.c. detonating gas per minute. The metal adheres very firmly to the sides of the capsule, and can be washed without loss.

Still, to prevent re-solution the washing must be effected without interrupting the current. The metal is purified with water and absolute alcohol, dried for a short time over sulphuric acid in the desiccator, and weighed.

(*B*) In the laboratory of the Munich High School the following experimental conditions have been ascertained:—If no metal is in solution except mercury, we add 1 to 2, or even 5 per cent. of its volume of nitric acid (sp. gr. 1·30), and electrolyse at the ordinary temperature with N.D. 100=1 ampère, or N.D. 100=0·5 ampère, according as mercury is present alone or not. The maximum quantity

[1] For details of operation see chapter on Electrolytic Analysis.

of mercury is 2 grammes. The precipitation is complete in about two hours.

(*C*) F. Rüdorff adds to the solution, which may contain 0·3 gramme mercury, about 5 drops of nitric acid (sp. gr. 1·2) or dilute sulphuric acid (1 : 10), dilutes with water to 100 c.c., and electrolyses with 2 to 6 Meidinger elements. The precipitation requires about fourteen hours. When it is completed he adds about 10 drops of sodium acetate, and washes after interrupting the current.

(*D*) According to A. Brand, the solution of the mercuric salt (mercurous compounds must first be converted into the mercuric state) is mixed with a slight excess of sodium pyrophosphate, and the precipitate formed is dissolved in ammonia or ammonium carbonate. From this solution about 1 gramme of mercury is deposited in from five to six hours by a current which evolves about 2 c.c. detonating gas per minute.

(*E*) According to G. Vortmann, mercury can be readily deposited from an ammoniacal solution. The aqueous solution is mixed with tartaric acid, and an excess of ammonia is added.

(*F*) F. Rüdorff uses 0·5 gramme tartaric acid in 10 c.c. ammonia (sp. gr. 0·91), dilutes to 100 c.c., and electrolyses with the current of from 2 to 6 Meidinger elements.

(*G*) G. Vortmann proposes the following method for the determination of mercury:—From the solution in potassium iodide. The solution of the mercuric compounds is mixed with an excess of potassium iodide diluted with water, and electrolysed as already indicated. As regards the removal of the iodine from the positive electrode, refer to the process described under Bismuth.

(*H*) Edgar F. Smith precipitates mercury from its solution in potassium cyanide. The mercuric solution, which may contain about 0·2 gramme mercury, is mixed with 0·25 to 2 grammes potassium cyanide, diluted with water to 175 c.c., and electrolysed with a current of 0·2 c.c. detonating gas. The metal, reduced in this manner, must be washed only with water, and not alcohol, since on washing with the latter the grey films are detached. Vortmann observed a similar phenomenon after reduction from an alkaline solution of the double potassium iodide containing soda-lye.

(*I*) Insoluble mercury compounds may be readily electrolysed by suspending them in water acidulated with a little hydrochloric acid, or in a dilute solution of sodium chloride (about 10 per cent.), and electrolysing as usual. The mercury in the cinnabar at Almaden is determined according to this process, as proposed by Dr. Classen.

Electrolytic Estimation of Mercury

F. W. Clarke puts a solution of mercuric chloride, slightly acidulated with sulphuric acid, into a platinum capsule connected with the

zinc pole of a Bunsen bichromate battery of 6 elements. The wire at the end of the carbon pole terminates in a thin slip of platinum foil which dips into the solution. At first mercurous chloride is deposited, which gradually takes the metallic state, and after the lapse of an hour there is nothing in the capsule but globules of pure mercury covered with a solution in which ammonia occasions not the slightest turbidity. This liquid is withdrawn with a pipette, and water poured in its place once or twice before separating the connection with the battery. The liquid is then decanted off and the mercury washed first with water, then with alcohol, and lastly with ether, and is then dried under the air-pump.

Estimation of Mercury by Distillation

(*A*) In estimating mercury by distillation it is necessary, especially if the metal is in the state of chloride or sulphide, to take certain precautions, without which a portion of the sulphide or chloride would volatilise without decomposition. H. Rose gives the following directions for carrying out the operation: Introduce into a glass tube capable of resisting fusion, closed at one end, and measuring from 35 to 50 centimetres in length, a column of sodium bicarbonate, then one of quicklime, and then a well-blended mixture of the mercurial compound and quicklime, and, finally, a column of quicklime. The open end of the tube is drawn out and bent round so as to enter a small flask containing water. The tube is heated as if for an organic analysis, commencing at the open end and finishing with the sodium bicarbonate. The operation ended, cut the bent end of the tube, collect all the mercury in the flask, dry with paper, and afterwards over sulphuric acid, and then weigh it.

The quicklime must not be replaced by lime hydrate. That would occasion all the inconvenience of an analysis of a sulphuretted combination of mercury. The water, acting on the calcium sulphide, would form sulphuretted hydrogen, which, by dissolving in the water of the receiver, would, in time, transform a portion of the reduced mercury into sulphide. It is even advisable in this case to replace the sodium bicarbonate by magnesium carbonate.

Combinations containing mercury iodide are not entirely decomposed when treated as above. Biniodide and proto-iodide are condensed in the extremity of the tube simultaneously with the metallic mercury.

To analyse these combinations recourse must be had to metallic copper, the operation being similar to that with quicklime.

(*B*) All compounds of mercury when dry and intimately mixed with three times their bulk of ordinary anhydrous fusion mixture ($K_2CO_3 + Na_2CO_3$) yield, under the influence of heat, metallic mercury, which condenses on the cooler portions of the tube above the assay. This metallic sublimate, when unmixed with other matters (metallic or

otherwise) and in large quantity, usually shows distinctly enough its characteristic globules; but when impure or small in amount the globular character is not at all evident, and it may then be quite easily mistaken for arsenic alone, and sometimes, though rarely, for antimony. If the substance which is undergoing examination gives with, if not without, the aid of flux a metallic sublimate, pour into the tube 2 drops of concentrated nitric acid, and immediately afterwards a single drop of a fairly strong solution of potassium iodide in water. The nitric acid decomposes the potassium iodide, and the iodine is liberated in fumes which act on any mercury in the sublimate or in the assay, and instantly produce the unique scarlet mercury iodide, which is largely thrown up against the sides of the tube. The antimony tri-iodide, produced in like manner, is brownish in colour, and becomes yellowish after exposure to the air for some little time. The arsenic tri-iodide is yellow, and this, as in the case of mercury, forms at once; but if the bottom of the tube containing the excess of nitric acid be heated slightly, the fumes from that body quickly decompose the iodide, and a spongy dark grey mass of arsenic is driven all round the upper part at least of the tube. In the same way the nitric acid quickly decomposes the antimony iodide, while it does not act nearly so rapidly on the mercuric iodide. Mr. A. Johnstone shows in the following table how this test would be applied in the ordinary course of blowpipe analysis:—

Detection of Mercury in Minerals

(*a*) Heat the powdered substance in a small piece of hard glass tubing (say with a $\frac{1}{4}$-inch bore) closed at one end.

1. A metallic sublimate is produced. Proceed further by *b*.

2. A non-metallic sublimate is formed. Heat a fresh portion of the substance mixed with about three times its bulk of fusion mixture. A metallic sublimate forms. Proceed further by *b*.

3. There is no evidence of the slightest volatilisation other than water. No mercury is present in the mineral.

(*b*) Pour into the tube containing the metallic sublimate and assay 2 drops of strong nitric acid, then at once 1 drop of potassium iodide solution, and heat the bottom of the tube a little. A scarlet mass forms and remains on the sides of the tube. Mercury is present in the body tested.

Detection of Very Minute Quantities of Mercury

When mercury occurs in very minute quantities the metallic sublimate described above may not be perceptible on the sides of the glass tube. In this case, when only the merest traces of mercury are looked for in the substance, proceed as follows:—Place in the closed tube, as already detailed, the mixture of powdered substance and flux,

and introduce on the end of a stout wire a small piece of gold leaf, which should be held just over the surface of the mixture. Now apply heat for a minute or so. Any mercury present will be volatilised, and the vapour will combine with the gold to form a whitish amalgam. Take out the wire with the gold leaf on its end after sufficient heat has been applied to the mixture in the tube. Touch the surface of the leaf which faced the assay with a single drop of concentrated nitric acid, and on the top of this add immediately a drop of potassium iodide solution; the fine scarlet iodide will at once appear very distinctly on the amalgamated surface of the gold leaf if any mercury was present in the body subjected to examination.

Electrolytic Detection of Mercury

(*A*) Dr. C. A. Kohn says that mercury is best separated from its nitric-acid solution on a small closely wound spiral of platinum wire. The solution to be tested is acidified with nitric acid and electrolysed with a current of from 4 to 5 c.c. of detonating gas per minute. The deposition is effected in about half an hour. The deposited metal is then removed from the spiral by heating the latter gently in a test-tube, when the mercury forms in characteristic globules on the upper portion of the tube. As a confirmatory and very characteristic test a crystal of iodine is dropped into the tube, and the whole allowed to stand for a short time, when the presence of mercury is indicated by the formation of the red iodide; 0·0001 gramme of mercury in 150 c.c. of solution can be clearly detected.

(*B*) Wolff has applied this test under similar conditions, using a special form of apparatus, through which the solution to be tested is allowed to pass slowly, and in which a silver-coated iron electrode is employed as the anode.

Estimation of Mercury in the Form of Protochloride

(*A*) M. de Bonsdorff proposes to precipitate mercury as protochloride by alkaline formates. This method may lead to completely erroneous results, as alkaline formates do not invariably reduce mercury bichloride. The affinity of mercuric chloride for alkaline chlorides is so great that when these bodies are present the ordinary reactions of mercury are not produced. When a liquid contains much hydrochloric acid, an alkali does not precipitate mercuric oxide from it. Sulphuric and nitric acids have the same effect. Such a mercuric solution, containing a large excess of potash, is not precipitated by ammonium sulphide unless the base has been previously supersaturated with an acid.

(*B*) The best method for estimating mercury is to precipitate it in the state of protochloride by phosphorous acid. When the liquid

contains free hydrochloric acid, the temperature may be raised to 60° C., without the mercury protochloride being reduced to the metallic state by phosphorous acid. The precipitated protochloride is not immediately formed in very weak liquids; it is necessary to leave the mixture undisturbed for twelve hours. The chloride deposits itself readily, especially when the liquid is sufficiently acid. The precipitate is to be collected on a filter, washed with cold, or even hot water, and dried at 100°. This process is very applicable to cases where the liquid contains much nitric acid. Only the solution must then be diluted with a sufficient quantity of water.

Electrolytic Separation of Mercury from Silver[1]

Both metals are precipitated quantitatively from a solution acidified with nitric acid. The sum of the mercury and silver is then determined; the former is volatilised by heat and the silver weighed again.

Separation of Mercury (Per-salts) from Silver

Add a sufficient quantity of hydrochloric acid to the diluted solution. After the deposition of silver chloride, decant the supernatant liquid; then heat the chloride precipitate with a small quantity of nitric acid, add some water and a few drops of hydrochloric acid, and then filter. Precipitate the mercury from the filtered liquid by phosphorous acid, according to Rose's process, already described (page 291, *B*).

Separation of Mercury from Zinc

This separation may be readily effected by precipitating the mercury in the state of protochloride by phosphorous acid, in the presence of free hydrochloric acid. The process may be carried out as previously described.

Electrolytic Separation of Mercury from Iron, Cobalt, Nickel, Zinc, Manganese, Chromium, and Aluminium

Classen finds that the separation depends on the precipitation of mercury in a solution acidified with nitric acid, from which the other metals are not separated.

Separation of Cadmium from Mercury

To the solution of the mixed metals add excess of hydrochloric acid and then phosphorous acid. This precipitates the mercury in the form of protochloride. Filter off, and to the filtrate add sodium carbonate, which will precipitate the cadmium as white carbonate. This is washed, dried, and converted by ignition into brown oxide.

[1] For details of operation see chapter on Electrolytic Analysis.

Care must be taken to remove as much of the precipitate from the filter as possible before calcining it.

Separation of Thallium from Mercury

Mercury frequently accompanies thallium in the flue dust from pyrites burners. From mercury per-salts the gradual addition of potassium iodide effects a ready separation. If much mercury is present, the precipitate is almost pure scarlet, but on further addition of potassium iodide drop by drop, the mercury iodide dissolves and leaves the insoluble yellow thallium iodide.

Sulphuretted hydrogen passed through an acid solution of the two metals precipitates the mercury as sulphide. This, however, carries a little thallium down with it.

Separation of Gallium from Mercury

Of the following methods the first must be especially recommended as exact and rapid.

(*A*) The hydrochloric solution, distinctly acid, is treated with an excess of hydrogen sulphide.

(*B*) The mercury may be reduced by zinc, or preferably by copper, in a liquid kept slightly acid. The reduction of mercury is more rapid than that of bismuth ; it is complete, and the precipitate contains no gallium. The formation of a deposit of cuprous chloride is not an inconvenience.

(*C*) Potassium ferrocyanide may be used for the separation of gallium from mercury in a very acid solution. The precipitate, if carefully washed with hydrochloric water, retains no mercury.

(*D*) Chemical treatises generally teach that the precipitate formed by potash in mercuric salts is insoluble in an excess of the reagent. Nevertheless, potash cannot serve for the separation of gallium from mercury, since the alkaline liquid retains notable quantities of mercury. That part of the mercuric oxide which is precipitated on boiling is free from gallium.

Separation of Mercury from Bismuth

P. Jannasch and E. von Cloedt separate mercury from bismuth, lead and manganese, by hydrogen peroxide in alkaline solutions.[1]

As an initial point for their experiments the authors used pure metallic bismuth and mercuric oxide. The weighed quantities were heated in a covered porcelain capsule with 10 cubic centimetres of concentrated nitric acid. The mixture, containing an excess of nitric acid, is slowly poured into a mixture of 25 to 30 cubic centimetres of concentrated ammonia, 25 cubic centimetres of hydrogen peroxide at

[1] *Chemical News*, Aug. 9, 1895.

3 to 4 per cent., and 50 cubic centimetres of water. There ensues a brisk effervescence of escaping oxygen, and the bismuth subsides as a yellowish-grey deposit of hydrated peroxide. It is then dissolved on the filter in dilute hot nitric acid, again precipitated as before, filtered, and weighed in a platinum crucible as bismuth peroxide.

The pure hydrogen peroxide should be used as fresh as possible, since its solutions on prolonged standing seem to attack sensitive kinds of glass, and may thus be contaminated with silica.

If the first deposit of bismuth is washed with extreme care, a single precipitation is sufficient for accurate separation.

For the determination of the mercury the entire ammoniacal filtrate is evaporated down for the complete expulsion of the excess of ammonia, strongly acidified with sulphurous acid, the liquid poured into a larger beaker, diluted to at least 300 cubic centimetres, and lastly precipitated at a moderate heat with sulphuretted hydrogen. The further treatment of the mercury sulphide, and its weighing, are effected in the usual way.

Separation of Mercury from Lead

The separation is effected by pouring the solution of the nitrates, acidified with nitric acid, into the ammoniacal oxidising liquid. The results are very satisfactory. It must be observed that, prior to filtration, the lead precipitate is allowed to stand for some time (thirty minutes to one hour), with occasional stirring, as otherwise traces of lead may remain in solution. The lead hydro-peroxide is filtered off, well washed with cold water, dissolved on the filter in dilute nitric acid (equal to about 10 cubic centimetres of the concentrated acid), with a simultaneous addition of hydrogen peroxide, and precipitated again in the same manner.

Separation of Mercury from Manganese

The separation of these metals is effected with great ease, which appears the more remarkable as manganese—in consequence of its tendency, when in the state of peroxide, to carry other oxides down with it—is apt to frustrate the smooth course of an analysis. The mixture is dissolved in 50 parts water and 10 parts of concentrated nitric acid. This mixture is added to a liquid of 30 hydrogen peroxide, 30 strong ammonia, and 50 water. After heating for thirty minutes in a covered beaker on the water-bath, the precipitate is filtered and washed with a mixture of water, ammonia, and hydrogen peroxide, and finally with hot water. The precipitate may be ignited in a platinum or porcelain crucible, either while still moist or after a partial drying. The coarser particles are carefully crushed, and the ignition is continued until the weight becomes constant.

Separation of Mercury from Molybdenum and Tungsten by Means of Hydrazine

1. Separation of Mercury from Molybdenum

0·2 to 0·3 gramme of finely powdered molybdic acid is dissolved in water to which excess of ammonia containing a few drops of soda solution has been added. The solution is warmed on the water-bath to drive off excess of ammonia, and 2 to 3 grammes of tartaric or citric acid are added. Then mercury chloride is added, any turbidity being dissolved by means of a few drops of hydrochloric acid, and the solution is diluted to 100 cubic centimetres. It is then warmed to about 80°, with addition of a warm solution of 2 grammes of hydrazine sulphate in 30 to 45 cubic centimetres of concentrated ammonia. After heating for a quarter of an hour, with frequent stirring, it is allowed to stand for three or four hours, and then filtered. The precipitate of mercury is separated off, converted into sulphide, and determined as such, while the molybdenum in the filtrate is determined as trisulphide by the addition of ammonium sulphide, according to a method previously described by Jannasch.

2. Separation of Mercury from Tungsten

No tartaric or citric acid is added, but otherwise the method is essentially the same as the above. 10 to 15 cubic centimetres of fuming nitric acid are added to the filtrate, which is then evaporated to 50 cubic centimetres, when tungstic acid separates out as a fine yellow precipitate, which may be dried and weighed.

COPPER

Detection of Traces of Copper

According to Drs. Endemann and Prochazka, if to a dilute solution of a copper salt concentrated hydrobromic acid is added, a dark brownish or violet colour is at once produced.

This reaction is so delicate that $\frac{1}{100}$ of a milligramme of copper can be detected with certainty. One drop of a solution containing this small quantity of copper is brought on a watch-glass, one drop of hydrobromic acid is added, and the solution is then allowed to evaporate slowly by standing the glass on a warm place. When the whole has been concentrated to about one drop, this will distinctly show a rose-red colour. The colour then produced is about three or four times as distinct as the one which is obtained by the addition of potassium ferrocyanide. Of other metals examined in this direction, they find

that only iron is apt to interfere with this reaction, and then only when it is present in considerable quantity.

This reaction may also be utilised as a colorimetric test for the quantitative estimation of small quantities of copper.

The following is a very delicate test for copper. A zinc-platinum element is formed of two thin wires, which is then placed in the solution to be tested. Should there be much copper present, almost immediately the platinum becomes covered with a blackish deposit; but if the solution is very dilute it is necessary to leave the wires in for some hours, when probably the platinum will be only slightly, if at all, coloured. The platinum wire is now removed, washed with water, and exposed, without previous drying, for a few moments to the action of hydrobromic acid and bromine vapour, obtained by heating a small quantity of potassium bromide with strong sulphuric acid. The deposit becomes deep violet. The colour may be more easily recognised by rubbing the platinum wire upon a piece of porcelain.

Mr. R. C. Woodcock has experimented on the delicacy of this reaction. He dissolves metallic copper in nitric acid, and then dilutes the solution until 8 c.c. contains 0·0000008 gramme of copper; 8 c.c. are then taken, and a drop of dilute hydrochloric acid added, the zinc-platinum element placed in the solution, and left for nineteen hours, after which time the copper can just be detected by applying the above test.

Electrolytic Reduction of Copper [1]

(*A*) Classen gives the following description of the method for the reduction of copper from a solution containing an excess of ammonium oxalate. 'A weak current only must be used, as otherwise the metal is deposited in a spongy state at the negative electrode. As it is not always practicable to obtain the copper in a compact state from the solution of this double salt, I have no longer employed this method, and as far back as 1888 I made experiments for determining this metal from a solution of the acid double oxalate. The solution of copper is mixed with a solution of ammonium oxalate (saturated in the cold) and the electrolysis is undertaken with a current corresponding to 3 or 4 c.c. of detonating gas. When the separation of the copper is in progress and the original deep-blue colour of the solution is decreasing, a solution of oxalic acid (saturated in the cold) is added. The poorer the solution appears to be in copper the more freely oxalic acid may be added, up to about 25 or 30 c.c. In the analysis of substances poor in copper, oxalic acid may be added to the liquid quite at the commencement of the electrolysis, while in concentrated solutions of copper the electrolysis must be undertaken in a liquid as neutral as possible, as otherwise sparingly soluble copper oxalate may be produced by the free oxalic acid.

[1] For details of operation see chapter on Electrolytic Analysis.

'After the decomposition is complete, the liquid is decanted off the capsule, repeatedly washed with alcohol, dried in the air-bath, cooled, and weighed.

'The deposit of copper is of a bright red colour, adheres very firmly, and is in no respect inferior to that obtained from a nitric solution. The chief advantage of the process lies in its rapid execution. If the liquid is kept during the decomposition at from 40° to 50°, it is easy to obtain, in from three to four hours, about 2 grammes of copper as a fine adhesive deposit. No trace of copper can be detected in the supernatant liquid.'

(*B*) In a solution mixed with nitric acid, copper can be also deposited quantitatively, as Luckow has shown. The separation can be effected quite as easily and with more certainty in a liquid acidified with sulphuric acid. Precipitation from acid liquids has the defect that the copper must be washed without interrupting the current, whereby a larger quantity of liquid is obtained, and hinders the determination of other metals present in solution.

(*C*) The reduction of copper from a nitric solution presupposes a certain quantity of nitric acid and the absence of chlorides. To about 200 c.c. of liquid which contains the copper as sulphate we add 20 c.c. nitric acid[1] of specific gravity 1·21, and electrolyse with a current which yields 3 to 4 c.c. detonating gas per minute in the voltameter (N.D. 100=1 ampère, if no other metal but copper is present in solution, otherwise =0·5 ampère).

Chlorides must not be present. If antimony, arsenic, or bismuth is present, portions of these metals appear in the deposit of copper.

The presence of chlorides occasions a spongy deposit. In order to compensate for their influence and to effect a dense deposition of copper, we add from 2 to 3 grains of ammonium nitrate and 20 c.c. ammonia (sp. gr. 0·01) diluted with water to 100 c.c., and electrolyse with a battery of from 4 to 6 Meidinger elements. After completing the reduction, the liquid is acidified with diluted acetic acid, the capsule, filled to overflowing with water, poured out, the last residues of water removed by inverting the capsule, which is then dried at 100° in the air-bath.

(*D*) For separating copper in an ammoniacal solution, Rüdorff at the Munich Laboratory proceeds as follows. He adds ammonia in slight excess, so that the precipitate first formed redissolves, and adds further from 20 to 25 c.c. of ammonia (sp. gr. 0·96), supposing that the quantity of copper in solution reaches 0·5 gramme. If there is 1 gramme copper in solution the quantity of ammonia is increased to 30 or 35 c.c.

In this liquid he further dissolves from 3 to 4 grammes ammonium

[1] This large quantity of nitric acid is necessary only if the copper has to be simultaneously separated from the other metals. If no metal is present in solution except copper, from 1 to 2 c.c. nitric acid suffice.

nitrate, and electrolyses with a current of N.D. 100=2 ampères. The washing must be effected without interrupting the current.

A solution containing free nitric acid may also be used for the separation of those metals which in presence of this acid are not reduced nor deposited as peroxides at the positive electrode—*e.g.* cobalt, nickel, zinc, cadmium, iron, manganese, and lead. It must be remembered that the nitric acid is gradually converted into ammonia; therefore, in case of a prolonged action of the current, nitric acid must be added from time to time. Copper, even in the presence of small quantities of antimony and arsenic, may be precipitated from its solution in ammonium oxalate, or from one containing free nitric acid. If the quantity of the two latter metals is at all considerable, arsenic and antimony are deposited along with copper on prolonged action of the current, when in consequence the negative electrode assumes a more or less dark colour. In order to be able to determine the copper in such cases, the dry electrode is ignited for a short time, when the copper is oxidised and the antimony and arsenic are volatilised. The residual oxide is dissolved in nitric acid, and the electrolysis is repeated.

Electrolytic Detection of Copper

0·00005 gramme of copper can be very readily detected by electrolysing an acid solution in the usual way. Dr. C. A. Kohn uses a spiral of platinum wire as the cathode, and the presence of the metal is confirmed by dissolving it in a little nitric acid and testing with potassium ferrocyanide.

Quantitative results in solutions containing 0·001 gramme of metal are thus obtained with considerable accuracy, and the method, as in the case of lead, is of use for the detection of minute quantities of the metal in water. The advantages of electrolysis over the colorimetric methods usually employed in such cases are twofold. In the first place, concentration is not necessary, owing to the delicacy of the test; and secondly, the erroneous results that are obtained in all colorimetric processes, due to the influence of the varying constituents present in the solution tested on the accuracy of the reaction, are entirely obviated.

Precipitation of Metallic Copper in Quantitative Analyses

The estimation of copper in the state of oxide, simple as the operation appears, is, nevertheless, always more or less faulty, and the results are not sufficiently exact. After the copper oxide has been precipitated by potash and calcined, the filter in which the oxide is retained, and from which it is impossible to detach it, reduces a portion of the copper. The metal must therefore be re-oxidised. But calcining in a vessel open to the air, or even in a current of pure oxygen, will not completely re-form the oxide. The oxygenation of the metal remains

imperfect, however long the reaction may be continued. Recourse must now be had to nitric acid, whose oxidising action is perfect; but another inconvenience then arises. When the copper nitrate is decomposed, some of the oxide is carried off in the stream of nitrous vapours. This phenomenon is shown very visibly by experimenting in a small glass flask holding 100 c.c. with a neck 7 or 8 centimetres long. However carefully the decomposition of the nitrate may be conducted, the interior of the flask and its neck are entirely covered with an impalpable powder of cupric oxide, some even escaping from the flask in appreciable quantities.

On very carefully experimenting in a comparatively large and well-closed platinum crucible there is a notable loss. Thus, according to some experiments of MM. Millon and Commaille, 1·3305 gramme of pure copper gave but 1·6605 gramme of oxide instead of 1·6675 gramme.

To obviate these difficulties copper should be estimated in the metallic state. The oxide is precipitated by potash, and the precipitate, washed with hot water and dried, is burnt, with the filter, in a large platinum capsule. The residue of this calcination does not adhere to the sides of the capsule. It is placed in a platinum vessel, where it is reduced by a current of pure hydrogen.

According to Th. Weyl, copper reduced in hydrogen retains a certain quantity of this gas, falsifying the results of the analysis. This inconvenience may be avoided by reducing copper oxide by the vapours of formic acid.

Precipitation of Copper as Sulphide

This would be an excellent form in which to estimate copper were it not that, on the ignition previous to weighing it, the sulphide oxidises and loses sulphur, the result being a mixture of disulphide, sulphate, and oxide. David Forbes has shown that this difficulty can be got over in a similar manner to the case of nickel (see page 245). The weight of sulphur in the copper sulphide and of oxygen in the oxide being identical, a mixture of sulphide and oxide in varying proportions may be weighed and calculated as if it were pure oxide or pure sulphide. It is only necessary, therefore, to remove the small quantity of sulphuric acid in the ignited copper sulphide. This is effected by adding a small amount of ammonium carbonate to the incinerated sulphide as soon as it is cold, and then carefully heating until all the ammoniacal salts are expelled. Some attention must be paid to the details of the operation, as the copper sulphide, especially in cases where free sulphur has been precipitated along with it, is very apt to cake together or even fuse during the incineration (if this is not very carefully conducted), and, consequently, it is less easily acted on by the air during incineration; this must be avoided, and the oxide should also not be allowed to absorb hygrometric moisture before or during weighing.

Estimation of Copper as Sulphocyanide

A. Guyard employs a reagent obtained by dissolving in water equal weights of ammonium sulphocyanide and bisulphite. This mixture keeps well, and can be used several months after its preparation, provided it is not left exposed to the air for any length of time; but, should a slight alteration take place in its composition, this would be of little consequence.

A mixture of equal weights of potassium sulphocyanide and sodium bisulphite answers equally well; in fact, it keeps still better than the former mixture, and the only objection to its use is its being composed of fixed salts.

The important property of this reagent consists in forming, in solutions of copper acidulated with hydrochloric acid, an abundant white precipitate of copper sub-sulphocyanide which is completely insoluble.

The only precaution to take to ascertain the presence of copper in a solution is to neutralise any nitric acid which might be present, with an excess of ammonia, and then to acidulate the solution with a slight excess of hydrochloric acid.

When the white precipitate of copper sub-sulphocyanide is thoroughly washed—and this is the case when free from chlorides, which adhere more strongly to the precipitate than sulphocyanides—and thoroughly dried, it contains 52·30 per cent. of copper.

As in chloride solutions, the only metal precipitated by the reagent is copper; it affords an easy means of separating this metal from all others, and of estimating it with promptitude and with the greatest accuracy. The drying of the precipitate being the longest part of the operation, whenever it is required to make a rapid estimation the process can be modified as follows. The washed copper sub-sulphocyanide is detached while wet from the filter; the filter is burnt, and its ashes are mixed with the precipitate, which is digested for some time with an excess of ammonium sulphide. By this means copper sulphide is obtained. It is filtered and thoroughly washed; it is then dried very rapidly in a small porcelain crucible and calcined. This being done, a little excess of pure flowers of sulphur is thrown into the crucible, which is then carefully covered, and all the sulphur is driven off at a dull red heat. After cooling, the residue of copper sulphide presents the constant formula Cu_2S, and it contains exactly four-fifths of its weight of copper.

Estimation of Copper in Bar Copper and in Native Copper

Twenty grains of the metal are dissolved in nitric acid, and if the solution is quite clear, the copper is estimated exactly as in the former example. If, on the contrary, a precipitate of antimony or tin oxides is manifest in the liquor, it should be dissolved by adding a little

hydrochloric acid, or a fresh lot of metal should be dissolved in aqua regia. This being done, the estimation of copper is proceeded with exactly as previously stated.

For complete analysis 100 grains are dissolved in nitric acid or in aqua regia. The solution, supersaturated with ammonia, is reacidulated with a slight excess of hydrochloric acid, and the liquid is then added. With the precaution already indicated, and in general when the precipitation is complete, the supernatant liquid assumes a pink or red colour due to iron sulphocyanide. The liquid is then filtered on a double filter (this precaution is useful because copper sulphocyanide is apt to pass through single filters), and the precipitate is well washed. The filtrate, mixed with a little more hydrochloric acid, is boiled until no smell of sulphurous acid from the reagent can be detected: it is then submitted to analysis.

Lead, arsenic, and antimony will generally be found. Even coppers leaving no residue in nitric acid, contain antimony which can be detected and estimated when separated in this way. The same remark applies to tin, which exists more often than might be supposed. Bismuth, nickel, and zinc are three metals which exist very frequently also in copper. Cobalt is often found, and silver and iron are nearly always present.

Sulphur, which exists frequently, must be estimated in a special operation.

Estimation of Copper in Pyrites and other Copper Ores, and in Slags

The sulphocyanide reagent proves much less useful in the analyses of these minerals and slags than in those of the former products, for the reason that ordinary methods answer well when applied to them. Indeed, it is not advisable to use the reagent at first to effect the separation of copper, unless this metal exists in large quantity, and is alone to be estimated. However, if uniformity in the estimation of copper was an object, no objections would be raised against using the reagent, which separates the copper with equal perfection, whatever substances accompany it. But for analytical purposes it would be best to precipitate, by sulphuretted hydrogen, copper and the group of metals which are precipitated with it, and thus to separate them from the large proportions of iron and of earthy matters which may be present.

The precipitated sulphides being redissolved in nitric acid or in aqua regia, this solution can be submitted to analysis, and, in most cases, the reagent can be employed with advantage in this part of the operation, and if copper is the most abundant metal of all, it will prove as useful as ever. If, on the contrary, copper formed only a small fraction, it would be best not to use the reagent at all, but to apply the ordinary methods of separation.

Some pyrites and certain earthy minerals contain about equal proportions of bismuth and copper. In these instances it is best to separate bismuth first, to avoid all possibility of this metal being precipitated by water and mixed up with copper. The same remark applies to cases where antimony is present in large proportions.

As a general rule, when a metal, such as lead, silver, antimony, or bismuth, exists in large proportions, and when this metal can be easily separated from copper, it is best and safest to effect its separation at once.

There are instances in which the separation of copper is not only difficult but imperfect with ordinary methods. Such is the case when copper exists in a liquid with palladium, vanadium, molybdenum, and cadmium. In these instances no better means of separation can be resorted to than to use the mixed sulphocyanide and bisulphite reagent (page 300), which effects all these separations with the greatest perfection.

Volumetric Estimation of Copper

Mohr's method of estimating copper, by adding a standard solution of potassium cyanide to an ammoniacal solution of copper, Herr Fleck says, offers two objections: the quantity of cyanide necessary to destroy the blue colour varies according to the quantity of ammonia the liquid contains, and at the end of the operation it is difficult to tell the exact moment at which the blue colour disappears.

To remedy these inconveniences, Herr Fleck proposes to dissolve the copper compound in ammonium carbonate instead of ammonia. He shows that an excess of this salt does not interfere with the reaction. In the second place he adds a drop of potassium ferrocyanide to the blue liquor, and then at the moment the cupro-ammoniacal compound is destroyed the liquid becomes red.

Estimation of Copper with Potassium Ferrocyanide

(*A*) When the copper ore, after having been acted upon by acids, is treated with excess of ammonia in order to precipitate the iron oxide, that substance invariably retains larger or smaller quantities of the copper oxide. The quantity thereof so retained varies according to the larger or smaller quantity of copper contained in the ores. It is therefore necessary to repeat the treatment with ammonia at least twice, sometimes even three and four times, so as to obtain a complete separation of copper from iron.

(*B*) In order to obviate the loss of time which is caused by these operations, M. Maurizio Galetti, Chief Assayer and Chemist to the Royal Assay Office at Genoa, proposes to convert into acetate the small quantity of copper oxide which accompanies the precipitate of iron oxide. This can be effected by two different methods, dependent on

the fact whether the iron oxide is removed by filtration (previous to the use of standard solution of potassium ferrocyanide), or is left in the ammoniacal liquid. The operations are conducted as follows :—

1. Suppose a copper pyrites be submitted to analysis. Take 1 gramme of the previously very carefully pulverised and dried ore. Treat it first with concentrated nitric acid, boiling to incipient dryness in order thereby to free the sulphur from any small particles of ore which are at first taken up by it. Add 10 c.c. of hydrochloric acid, boil down to about half that bulk, dilute with distilled water, and add ammonia in large excess; boil the liquid, and next add acetic acid until it assumes an emerald-green colour. After the liquid has been well stirred, boil again for about two minutes, and again add ammonia in excess. It is then poured out of the flask into a suitable glass vessel, and the flask is rinsed out with a sufficient quantity of distilled water to bring the bulk of the liquid up to $\frac{1}{2}$ litre. This having been done, it is very cautiously and gradually acidified with dilute acetic acid. Any considerable excess of this acid should be avoided. As soon as the basic iron acetate has subsided, the precipitation of the copper by means of the standard solution of potassium ferrocyanide is proceeded with.

Since the copper oxide, which might have adhered to the iron oxide, has been converted, by the process just described, into a soluble salt, it cannot fail to be completely precipitated by the potassium ferrocyanide solution. When an estimation of copper has to be made in ores which are rather poor (that is to say, contain less than 6 per cent. of copper), it is preferable to add to the nitric acid solution 0·1 gramme of pure copper, which quantity has to be deducted afterwards from the results obtained. This precaution is required in order to prevent the presence of a large quantity of iron oxide from vitiating the results of the analysis of poor ores. When ores contain up to 12 per cent. of copper, a quantity of 1 gramme of the ore should be taken ; but for richer ores 0·5 gramme is sufficient. It is always advisable to make a control analysis with pure copper when testing the ores.

2. The second modification is carried out in the following manner.

(*C*) After the second addition of ammonia to the liquid, it is filtered and the precipitate is washed with a dilute and boiling solution of acid ammonium acetate. This solution is prepared by saturating 20 grammes of pure acetic acid with ammonia, and adding thereto 15 grammes of pure acetic acid in 585 grammes of water. When the washing of the iron oxide is carefully done, the copper salt, which tenaciously adheres to the iron oxide, is entirely removed therefrom ; but it will require about 400 grammes of the liquid, the preparation of which has just been described.

The normal solution of copper for standardising the potassium ferrocyanide should be prepared as follows :—

0·2 gramme of pure copper is dissolved in nitric acid ; excess of

ammonia is added ; the liquid is next acidified with acetic acid, then diluted with 400 grammes of acid ammonium acetate, and the whole brought up to 500 grammes. To this solution 20 c.c. of the standard solution of potassium ferrocyanide are added, when the liquid should not contain any excess either of copper or of ferrocyanide.

The standard solution of potassium ferrocyanide to be used for the estimation of copper is made by dissolving 50·225 grammes of ferrocyanide in as much distilled water as will suffice to make the solution weigh exactly 1 kilogramme.

If the copper ores contain zinc, nickel, and cobalt, the copper should be first separated from these metals, either by precipitating the copper from its solution by means of zinc, or as copper sulphide by means of sodium thiosulphate.

Estimation of Copper with Sodium Sulphide.—An ammoniacal solution containing $\frac{1}{10000}$ of copper reacts distinctly on moist, recently precipitated zinc sulphide—the zinc dissolving, while the copper is precipitated in the form of sulphide. Zinc sulphide decomposes instantly in a hot ammoniacal solution of copper.

(*A*) Starting from this reaction, Dr. C. Kunsel proposes the following volumetrical method for the estimation of copper.

He prepares pure sodium sulphide by saturating a solution of caustic soda free from carbonate, with sulphuretted hydrogen, and driving off the excess of the gas. The solution is then diluted so that a cubic centimetre precipitates a centigramme of copper.

A known weight of pure copper is dissolved in nitric acid, the solution supersaturated with ammonia, diluted, and heated to boiling. The solution of sodium sulphide is then added to the hot solution of copper, stirring continually until a drop of the mixed solutions no longer colours zinc sulphide brown. Zinc sulphide for indicating the complete precipitation of the copper is prepared in the following way. Zinc is dissolved in hydrochloric acid, the solution is supersaturated with ammonia and is then boiled with a little zinc sulphide to remove the lead which is always present in commercial zinc. The ammoniacal solution of zinc, now free from lead, is filtered and decomposed with sodium sulphide, a small quantity of zinc being allowed to remain in solution. The moist zinc sulphide, with excess of zinc solution, is then spread evenly upon several layers of filter-paper. When the paper has absorbed most of the solution, the moist white layer of zinc sulphide is ready for use.

The ore or alloy, free from arsenic, is dissolved in hydrochloric acid with the addition of some nitric acid, and, when necessary, is evaporated to dryness, the deposit dissolved in hot water, and filtered to separate silica. Any iron may be removed from the mixed chlorides by the addition of ammonia. The solution freed from iron is then rendered strongly ammoniacal, heated to boiling, and the standard solution of sodium sulphide added (with continual shaking) until a drop

of the mixed solutions no longer acts on zinc sulphide, *i.e.* until all the copper is precipitated. The number of cubic centimetres of the standard solution is then read off and the amount of copper calculated.

(*B*) The following volumetric methods may be occasionally useful. F. Weil bases a method on the following principles.

(1) That with an excess of free hydrochloric acid, and at boiling heat, the presence even of the smallest quantity of copper chloride may be detected by the greenish-yellow colour of the solution, this colour being the stronger and more prominent the more free hydrochloric acid is present.

(2) The aqueous solutions of copper chloride, which contain free hydrochloric acid, become, while boiling, upon the addition of tin protochloride, instantaneously converted into colourless solutions of copper protochloride. The reaction is quite finished as soon as, by the addition, drop by drop, of the tin protochloride, the green colour of the copper perchloride is changed to the colourless copper protochloride. Even a single drop of tin protochloride added in excess can be readily detected by the addition of a single drop of a solution of corrosive sublimate, which produces a precipitate of white mercury protochloride. It is clear, therefore, that the quantity of the solution of tin protochloride, which is required for the perfect decolouration of the copper solution, will indicate the quantity of the copper present in the solution. If it contains iron along with the copper, the iron will have to be estimated in a separate portion of the solution by means of potassium permanganate; while, in the estimation of the copper, the quantity of tin protochloride equivalent to, and converted by the iron into iron perchloride, has to be deducted.

Preparation and Keeping of the Solution of Tin Protochloride.—Take about 6 grammes of tinfoil (this material ought first to be tested for its purity), dissolve in 200 c.c. of pure hydrochloric acid at a boiling heat, with the addition of some pieces of platinum wire; the tin solution thus obtained is diluted to 1000 c.c. by the addition of distilled water, and is poured into a wide-mouthed glass bottle, after which the solution is covered over with a layer of petroleum. This bottle is provided with a glass syphon-tube and stopcock attached, and also with a funnel-tube for replenishing the solution. This solution, although kept under petroleum, and thereby protected from the action of the air, only keeps sufficiently steady and unaltered for a single day, so that the liquid has to be tested and accurately titrated every morning, before using it for the estimation of copper in solutions wherein the quantity of that metal is unknown.

Titration of Tin Protochloride with Pure Copper.—Take chemically pure, recrystallised, pulverised copper sulphate, deprived of adhering moisture by pressing between filter-paper; weigh off 7·867 grammes (equal to 2 grammes of pure metallic copper), dissolve in distilled water, and dilute to 500 c.c.; keep this solution as a normal

solution of copper in a glass-stoppered bottle. Take of this solution by means of a pipette, 25 c.c. (equal to 0·1 gramme of pure copper), pour this quantity into a flask capable of containing 100 c.c.; add 5 c.c. of pure hydrochloric acid, which causes the blue liquid to become deep-green; and next boil the liquid upon a sand-bath; then take a burette divided into c.c. and tenths; fill it with the solution of tin protochloride up to zero, and immediately after pour rapidly into the boiling copper solution sufficient of the tin salt to cause the same to become very nearly decolourised. After this the tin solution is added, drop by drop, until the copper solution is as clear and colourless as distilled water; as soon as this point has been reached, add with a pipette again 5 c.c. of pure hydrochloric acid, and, if by this addition the slightest green colouration is produced, tin protochloride is added, drop by drop, until the decolouration is complete; after this, the quantity of tin solution employed is read off. If it is desired to make sure that the end of the reaction is properly reached (a precaution which is quite unnecessary if 10 c.c. of hydrochloric acid have been added), 1 c.c. of the colourless solution is taken, by means of a pipette, and poured into a test-tube; this tube is placed in cold water to promote the rapid cooling of the contents; and, after cooling, there is added to the solution one drop of a concentrated aqueous solution of mercury chloride. If this does not bring about a turbidity or precipitate, it is best to add to the contents of the flask another drop of tin protochloride solution; this having been done, the testing of the contents of the flask by means of mercury chloride, as just mentioned, is repeated, and if a turbidity or precipitate ensues, the quantity of tin solution applied is read off, care being taken to deduct therefrom $\frac{1}{20}$ of a c.c. Every 16·2 c.c. of the tin solution correspond to 0·1 gramme of metallic copper.

Titration of any Compound of Copper not containing either Iron or Nickel.—Take 4 grammes of the metal, either reduced to powder or at least cut (not filed) to a convenient size; dissolve in strong nitric acid contained in a long-necked flask; expel the excess of this acid by boiling with excess of sulphuric acid or with hydrochloric acid in case silver is contained in the substance taken for assay; next, water is added, and the bulk of the liquid brought to from 250 to 500 c.c., according to the presumable quantity of copper present, care being taken to mix the liquid thoroughly, and thereby render it uniform throughout. It is not absolutely required to remove by filtration insoluble substances, such as silica, lead sulphate, stannic acid, antimonic acid, silver chloride, and the like, since these substances settle readily to the bottom of the tall cylindrical jar employed for containing the liquid, while the assay is being made. The tin solution is added after the addition, as above stated, of some 5 or 10 c.c. of hydrochloric acid.

Titration of a Compound of Copper which also contains Iron.—The weighing off of the substance, its solution in acid, and the

titration of 25 c.c. of the joint solution of the two metals, is performed as described above, with this difference, that the operation of adding the tin solution is performed with the solution of the metals contained in a flask of a capacity of at least 250 c.c. After the total quantity of tin solution required at the first titration has been noted, the titration of the iron is executed in the following manner. From 25 to 50 c.c. of the sulphuric acid solution are diluted with a large quantity of water, and placed in a flask of 250 c.c. capacity; to this liquid, metallic zinc and platinum wire are added, and left in the solution until it is perfectly colourless; the entire quantity of copper, tin, lead, arsenic, antimony, &c. which might be present is precipitated in the metallic state; the colourless liquid is then decanted, and the iron volumetrically estimated by means of potassium permanganate.

Observation on the Titration of Compounds of Copper containing Iron.—If the operator does not happen to have ready at hand a titrated permanganate solution for the estimation of the iron, the titration of the liquid containing copper and iron can be readily performed in the following manner. Precipitate, as above mentioned, by the aid of zinc and platinum, all the copper, &c., decant the supernatant liquid, wash the precipitated metal (or metals) with distilled water, and dissolve these in sulphuric acid, and estimate next in 25 c.c. of that solution (after previous addition of from 5 to 10 c.c. of pure hydrochloric acid) the copper directly by titration with tin perchloride solution, without the necessity of estimating the iron at all.

Titration of a Compound of Copper which contains Nickel.—Since the green colour of the nickel salts prevents the complete and perfect decolouration, by stannous chloride, of a solution which contains copper and nickel together, titration by means of the tin salt, as described, can be employed, but the end of the reaction must be tested for by the use of the solution of corrosive sublimate. In preference, however, to this, the following method may be employed.

(*A*) The substance to be tested (about 4 grammes) is dissolved in nitric acid, or, if need be, in nitro-hydrochloric acid; next, the greater part, but not all, of the acid is saturated with sodium carbonate; then add, after having diluted the liquid with cold water, an excess of freshly precipitated barium carbonate, to which some ammonium chloride is added, and which together are suspended in water. This milky liquid is thoroughly stirred through the metallic solution; by this proceeding a precipitate ensues, which contains all the copper as hydrated oxide, and, if present, the iron also as hydrated oxide, while the nickel remains in solution. The precipitate is first washed by decantation, next collected on a filter, thoroughly washed, and, after having been redissolved in hydrochloric acid, titrated as above described. The presence of arsenic or its compounds does not in the least interfere with the process; while, if cobalt happens to be present —which will, however, be only rarely the case—the treatment is the

same as for nickel. By a series of test experiments, and by comparison with gravimetrical analysis, the process above described is found to be thoroughly reliable and to give accurate results.

(*B*) For the volumetric estimation of copper, M. P. Casamajor precipitates copper and lead from alkaline solutions by a titrated solution of sodium sulphide. This was the reagent used by Pélouze for the volumetric estimation of copper in a process published some thirty years ago in the *Annales de Chimie et de Physique*. In the process of Pélouze copper is dissolved in a large excess of ammonia, by which an intensely blue liquid is obtained, and a titrated solution of sodium sulphide is added, until the blue colour disappears.

Instead of using an excess of ammonia, M. P. Casamajor uses an alkaline tartrate dissolved in an excess of caustic soda. This liquid is the same which, added to a titrated solution of copper sulphate, forms Fehling's solution. It is prepared by dissolving 173 grammes of Rochelle salt in 480 c.c. of caustic soda of specific gravity 1·14, and adding water to form 1 litre of solution. This alkaline solution is added to the copper solutions in slight excess of the quantity sufficient to dissolve the copper to a deep blue-coloured liquid, and the porcelain dish is heated so that the liquid is carried to nearly the boiling-point. The titrated solution of sodium sulphide is then added until no turbidity is produced by the addition of 1 drop.

In this manner of proceeding the blue colour of the solution is not taken into account. The dark brown colour which follows the addition of the reagent is the only guide. The first addition of the alkaline sulphide gives rise to an intense black-brown precipitate. As soon as this is formed, the liquid in the dish is thoroughly stirred with a glass rod. This has the effect of agglomerating the copper sulphide into coarse curds, which settle to the bottom of the dish, leaving the liquid clear and almost colourless. If, after settling, the liquid should not be sufficiently clear, it should be vigorously stirred again until the desired effect is obtained. After every addition of sodium sulphide the liquid should be thoroughly agitated until it becomes clear. The degree of turbidity produced is a guide as to the quantity of reagent to use. At the beginning the brown cloud is very intense, and it is useless to await the complete clearing up of the liquid before adding more of the reagent. Towards the end the brown cloud is comparatively slight, and the reagent should be added drop by drop. The liquid in the dish should be stirred, so as to clear it up entirely before adding a drop of the reagent.

By thorough stirring the copper sulphide agglomerates in thick heavy curds, which settle rapidly, leaving the surface of the dish very clean, as seen through the clear liquid. On this clean white surface the faintest cloudiness is easily seen. A liquid containing 1 part of copper in 30,000 parts of solution will give a distinct brown turbidity by the addition of 1 drop of the reagent.

Assay of Copper Pyrites

The following method of treating copper pyrites has been found more advantageous than the ordinary process of oxidising the mineral with aqua regia, and subsequently evaporating the solution repeatedly with hydrochloric acid, or with sulphuric acid, to expel the last traces of nitric acid. It is thus described by Mr. F. P. Pearson in the *Chemical News* :—

Place a weighed quantity of the powdered mineral, together with some potassium chlorate, in a porcelain dish. (Five grammes of a variety of a pyrites containing about 18 per cent. of copper was found to be enough for one analysis; and a quantity of potassium chlorate equal to a small teaspoonful was added to the ore.) Invert a small glass funnel with bent stem in the dish above the pyrites, and pour upon the latter rather more ordinary strong nitric acid than would be sufficient to completely cover the powder. Place the dish upon a water-bath, and, from time to time, throw into it small quantities of potassium chlorate. The doses of the chlorate must be repeated at frequent intervals, until free sulphur can no longer be seen in the dish. If necessary, add nitric acid also from time to time, to replace that lost by evaporation.

As a general rule, it is safer and more convenient to heat the mixture on a water-bath than upon sand, though the oxidation of sulphur can be effected more easily and quickly when the mixture of nitric acid and chlorate is heated to actual boiling than at the temperature obtainable by means of a water-bath. When the last particles of sulphur have been destroyed, remove the inverted funnel from the dish, rinse it with water, and collect the rinsings in a beaker by themselves. Allow the liquid in the evaporating-dish to become cold, pour upon it a quantity of ordinary strong hydrochloric acid rather larger than the quantity of nitric acid taken at first, evaporate the mixed solution to dryness, and heat the dry residue to render the silica insoluble, in case any be present.

Pour water upon the cold residue, and, without filtering the liquor, wash the contents of the dish into the beaker which contains the rinsings of the funnel. Heat the liquid in the beaker nearly to boiling, add to it about 25 c.c. of a strong aqueous solution of ferrous sulphate slightly acidulated with sulphuric acid, and keep the mixture at a temperature near boiling for four or five minutes, in order to destroy the small quantity of nitric acid which may have escaped decomposition in spite of the evaporation with hydrochloric acid.

The ferrous salt seldom or never acts instantaneously, but the reducing action proceeds rapidly and perfectly satisfactorily when once begun. If need be, add more of the ferrous solution, little by little, until the entire contents of the beaker become dark-coloured or almost black, and no more gas is disengaged.

In order to be sure that all the nitric acid has been reduced, it is as well, after the mixture of liquid and solution of ferrous sulphate has been duly heated, to place a drop of the mixture upon porcelain, and test it with potassium ferrocyanide. In general, however, the colouration of the liquor in the beaker, due to the formation of nitrous or hyponitric acid, will be a sufficient indication that the iron sulphate has done its work. The nitrous fumes quickly disappear from the liquid at a subsequent stage of operations when metallic iron is immersed in the solution.

When enough of the ferrous sulphate has been added, filter the mixed solution into a wide beaker, precipitate the copper in the metallic state upon a sheet of iron in the usual way, and ignite the copper in a porcelain crucible, in a current of hydrogen, before weighing.

By means of the ferrous salt, the last traces of nitric acid may be got rid of far more quickly, conveniently, and certainly than by the old system of evaporating the pyrites solution with several successive portions of hydrochloric acid. By treating the pyrites with potassium chlorate and nitric acid, it is easy to oxidise and dissolve every particle of the sulphur in the mineral, so that no portion of the latter can escape decomposition by becoming enveloped in free sulphur. When aqua regia is used, on the other hand, or a mixture of potassium chlorate and hydrochloric acid, a certain proportion of sulphur almost invariably remains undissolved, and might easily enclose portions of the mineral, so as to protect them from the solvent action of the acids.

Estimation of Copper in the Mansfeld Ores by Dr. Steinbeck's Process

(*A*) This method embraces three distinct operations, viz.: 1. The extraction of the copper from the ore. 2. The separation. 3. The quantitative estimation of that metal.

1. The Extraction of the Copper from the Ore.—A proof centner, equal to 5 grammes of pulverised ore, is put into a flask, and there is poured over it a quantity of from 40 to 50 c.c. of crude hydrochloric acid, of a sp. gr. of 1·16, whereby all carbonates are converted into chlorides, while carbonic acid is expelled. After a while there is added to the liquid in the flask 6 c.c. of a normal nitric acid, prepared by mixing equal bulks of water and pure nitric acid of 1·2 sp. gr. As regards certain ores, however, specially met with in the district of Mansfeld, some, having a very high percentage of sulphur and bitumen, have to be roasted previous to being subjected to this process; and others, again, require only 1 c.c. of nitric acid instead of 6. The flask containing the assay is digested on a well-arranged sand-bath for half an hour, and the contents only boiled for about fifteen minutes, after which the whole of the copper occurring in the ore, and all other metals, are in solution as chlorides. The blackish residue,

consisting of sand and schist, has been proved by numerous experiments to be either entirely free from copper, or at the most only 0·01 to 0·03 per cent. has been left undissolved.

The extraction of the copper from the ore, according to this method, is complete, even in the case of the best quality of ore, which contains about 14 per cent. of metal; while, at the same time, the very essential condition for the proper and complete separation of the metal, viz. the entire absence of nitric acid or any of the lower oxides of nitrogen, is fully complied with.

2. The Separation of the Copper.—The solution of metallic and earthy chlorides, and some free hydrochloric acid, obtained as just described, is separated by filtration from the insoluble residue, and the liquid run into a covered beaker of about 400 c.c. capacity: in this beaker has been previously placed a rod of metallic zinc, weighing about 50 grammes, and fastened to a piece of stout platinum foil. The zinc to be used for this purpose should be as much as possible free from lead, and at any rate not contain more than from 0·1 to 0·3 per cent. of the latter metal. The precipitation of the copper in the metallic state sets in already during the filtration of the warm and concentrated liquid, and is, owing chiefly to the absence of nitric acid, completely finished in from half to three-quarters of an hour after the beginning of the filtration. If the liquid be tested with sulphuretted hydrogen, no trace even of copper will be detected; the spongy metal partly covers the platinum foil, partly floats about in the liquid, and, in case either the ore itself or the zinc applied in the experiment contained lead, small quantities of that metal will accompany the precipitated copper. After the excess of zinc (for an excess must be always employed) has been removed, the spongy metal is repeatedly and carefully washed by decantation with fresh water, which need not be distilled, and care is taken to collect together every particle of the spongy mass.

3. The Quantitative Estimation of the Precipitated Copper. To the spongy metallic mass in the beaker, wherein the platinum foil is left, since some of the metal adheres to it, 8 c.c. of the normal nitric acid are added, and the copper is dissolved by the aid of moderate heat, as copper nitrate; in the event of any small quantity of lead being present, it will of course be contaminated with lead nitrate.

When copper ores are dealt with which contain above 6 per cent. of copper, which may be sufficiently judged from the larger bulk of the spongy mass of precipitated metal, 16 c.c. of nitric acid, instead of 8, are employed for dissolving the spongy metallic mass. The solution thus obtained is left to cool, and next, immediately before titration with potassium cyanide, mixed with 10 c.c. of normal solution of ammonia, prepared by diluting one volume of liquid ammonia, sp. gr. 0·93, with two volumes of distilled water.

In the case of ores which yield over 6 per cent. of copper, and

where a double quantity of normal nitric acid has consequently been used, the solution of copper in nitric acid is diluted with water and made to occupy a bulk of 100 c.c.; this bulk is then divided exactly into two portions of 50 c.c. each, and each of these separately mixed with 10 c.c. of the liquid ammonia solution just alluded to, and the copper therein volumetrically determined. The deep blue-coloured solution of copper oxide in ammonia only contains besides, ammonium nitrate, any lead which might have been dissolved having been precipitated as hydrated lead oxide, which does not interfere with the titration with potassium cyanide. The solution of the last-named salt is so arranged that 1 c.c. thereof exactly indicates 0·005 gramme of copper. Since, for every assay, 5 grammes of ore have been taken, 1 c.c. of the titration liquid is, according to the following proportion—5 : 0·005 :: 100 : 0·1—equal to 0·1 per cent. of copper; it hence follows that, by multiplying by 0·1 the number of the c.c. of potassium cyanide solution used to make the blue colour of the copper solution disappear, the percentage of copper contained in the ore is immediately indicated.

As may be imagined, at the laboratory of the mine-owners at Eisleben, such a large number of assays are daily executed that, in this case, there can be no reason to fear a deterioration of the cyanide solution, of which large quantities are used and often fresh made; but for security's sake, the solutions are purposely tested for control at least once every week. According to the described plan, six assays can be made within four hours; and during a working day of from seven and a half to eight hours, twenty assays have been often quite satisfactorily made by the umpires, as well as by the workmen at Eisleben.

Special Observations on this Method.—Dr. Steinbeck considered it necessary to test his method specially, in order to see what influence is exercised thereupon by (1) ammonium nitrate, (2) caustic ammonia, (3) presence of lead oxide. The copper used to perform the experiments for this purpose was pure metal, obtained by galvanoplastic action, and was ignited to destroy any organic matter which might accidentally adhere to it, and, next, cleaned by placing it in dilute nitric acid. Five grammes of this metal were placed in a litre flask and dissolved in 266·6 c.c. of normal nitric acid, the flask and contents gently heated, and, after cooling, the contents diluted with water, and thus brought to a bulk of 1000 c.c. exactly. Thirty c.c. of this solution were always employed to test and titrate one and the same solution of potassium cyanide under all circumstances. When 5 grammes of ore, containing on an average 3 per cent. of copper, are taken for assay, that quantity of copper is exactly equal to 0·15 gramme of the chemically pure copper. The quantity of normal nitric acid taken to dissolve 5 grammes of pure copper (266·6 c.c.) was purposely so taken as to correspond with the quantity of 8 c.c. of normal nitric

acid which is employed in the assay of the copper obtained from the ore, and this quantity of acid is exactly met with in 30 c.c. of the solution of pure copper.

As regards No. 1 and No. 2 (see above), the influence of double quantities of ammonium nitrate and free caustic ammonia (the quantity of copper remaining the same), and the action of dilute solution of potassium cyanide thereupon, will become elucidated by the following facts.

(*a*) Thirty c.c. of the normal solution of copper, containing exactly 0·15 gramme of copper, were rendered alkaline with 10 c.c. of normal ammonia, and are found to require, for entire decolouration, 29·8 c.c. of potassium cyanide solution ; a second experiment, again with 30 c.c. of normal copper solution, and otherwise under identically the same conditions, required 29·9 c.c. of cyanide solution. The average of the two experiments is 29·85 c.c.

(*b*) When to 30 c.c. of the normal copper solution first 8 c.c. of normal nitric acid are added, and then 20 c.c. of normal ammonia solution, instead of only 8, whereby the quantity of free ammonia and of ammonium nitrate is made double what it was in the case of the experiments spoken of under (*a*), there is required of the same cyanide solution 30·3 c.c. to produce decolouration. A repetition of the experiment, under exactly the same conditions, gave 30·4 c.c. of the cyanide solution employed ; the average of both experiments is, therefore, 30·35 c.c.

The difference between 30·35 and 29·85 is equal to 0·5 c.c., and that figure is therefore the coefficient of the influence of double quantities ; and supposing this to happen with the ores in question, it would only be equivalent to 0·05 per cent. of metallic copper. It is hence clear that slight aberrations of from 0·1 to 0·5 c.c. in the measuring out of 8 c.c. of normal nitric acid, used to dissolve the spongy copper, and of 10 c.c. of normal ammonia, in order to render that nitric acid copper solution alkaline, are of no consequence whatever for the technical results to be deduced from the assay ; it should, moreover, be borne in mind that the quantities of free ammonia and of ammonium nitrate in the actual assay of ores, for which always a quantity of 5 grammes of ore is taken, vary according to the richness or poverty of the ores in copper ; and the quotations of the following results of experiments prove that the influence of these substances is only very slightly felt in the accuracy of the results.

Eight c.c. of the normal nitric acid have been found to contain, by means of a series of experiments, 1·353 gramme of anhydrous nitric acid ; and this quantity of acid is exactly neutralised by 7·7 c.c. of normal ammonia solution, which contains 0·6515 gramme of ammonium oxide ; and 10 c.c. of the said normal solution contain 0·846 gramme of ammonium oxide.

One gramme of metallic copper requires, for complete oxidation,

0·2523 gramme of oxygen, and this quantity of oxygen is given off by 0·5676 gramme of anhydrous nitric acid; while, at the same time, nitrogen binoxide is disengaged. From these data can be calculated (1) the quantity of nitric acid which becomes decomposed when variable quantities of metallic copper are dissolved therein; (2) what quantity of nitric acid is left to form neutral ammonium nitrate; and (3) what quantity of free ammonia will be left after a portion of that alkali has been combined with, and therefore neutralised by, copper oxide and any remaining free nitric acid.

It is found that the quantitative variations between ores containing 1 per cent. or 6 per cent. of metal vary very little from the normal quantities exhibited by ores containing 3 per cent. of metal. The relation is as 1 : 2; and, for technical purposes, this has been proved not to be a disturbing quantity.

When, however, larger quantities of ammoniacal salts are present in the liquid to be assayed for copper by means of a titrated solution of potassium cyanide, and especially when ammonium carbonate, sulphate, and, worse still, chloride, are simultaneously present, these salts exert a very disturbing influence.

The presence of lead oxide in the copper solution to be assayed has the effect of producing, on the addition of 10 c.c. of normal ammonia, a milkiness along with the blue tint; but the presence of this oxide does not at all interfere with the estimation of the copper by means of the cyanide, provided the lead be not in great excess; and a slight milkiness of the solution even promotes the visibility of the approaching end of the operation.

Dr. Steinbeck, however, purposely made some experiments to test this point, and his results show that neither 50 nor 100 per cent. addition of lead exerts any perceptible influence upon the estimation of copper from its ores, or otherwise, by means of potassium cyanide. A small quantity of lead accidentally occurring will not, therefore, affect the results, the less so as, generally, no ores of both metals occur together wherein both are met in sufficient quantity to make it worth while working the ore for both metals at the same time.

Since it is well known that the presence of zinc very perceptibly influences the action of a solution of potassium cyanide, when applied to the volumetric estimation of copper, Dr. Steinbeck considered it necessary to institute some experiments, in order precisely to ascertain with what quantity of zinc present along with copper this influence commences to become perceptible. The solution of zinc employed was made by dissolving the metal in the smallest possible quantity of nitric acid; and 1 c.c. of that solution contained 0·001 gramme of zinc. The results of the experiments show that the presence of zinc does not interfere with the visibility of the end of the reaction, viz. the decolouration of the copper solution. They also prove that a small

quantity of zinc, less than 5 per cent. of the quantity of copper present, or 0·0075 gramme by weight of zinc, does not at all affect the action of the solution of potassium cyanide, but when the quantity of zinc increases, a very perceptible effect is seen upon the solution of cyanide; it is therefore necessary to bestow due care while washing the spongy copper, after it has been precipitated by means of zinc from its solution.

Since it has been ascertained that the action of solution of potassium cyanide in researches of this kind is also affected by an increased temperature of the solution of copper which is to be titrated therewith, it is strictly necessary never to operate with warm ammoniacal solutions of copper, but to suffer the same to cool down to the ordinary temperature of the air of the laboratory.

While 30 c.c. of copper solution, containing 0·15 gramme of copper and 10 c.c. of normal ammonia solution, required, at the ordinary temperature, 30 c.c. of cyanide solution, the same quantities required 28·8 c.c. of solution of cyanide between 40° and 45° C.; and at 45° C. 28·9 c.c. of the same solution, thus proving the injurious effect of warm solutions.

Estimation of Copper in the Mansfeld Ores by M. C. Luckow's Process

(*B*) This gentleman has applied to the quantitative estimation of copper a new method, based upon the precipitation of the metal in the metallic state from solutions containing either free sulphuric or nitric acids, by means of a galvanic current.

It is a great advantage of this method that, while the copper is precipitated, it is simultaneously separated from metals with which it is often found alloyed; some of these, such as tin and antimony, are separated by treatment with nitric acid in an insoluble form, while others, like silver, can easily be removed in the form of chloride. It is, at the same time, another advantage that the state in which the copper is obtained admits of its being accurately weighed and estimated, while a great number of operations, which require much time and various apparatus, are at the same time got rid of.

Although M. Luckow had previously discovered a method of electro-metallic analysis from liquids containing free sulphuric acid, his researches on the same subject, in the case of free nitric acid, belong to a recent period. These researches brought very unexpectedly to light the curious fact that even a weak galvanic current had the power of completely precipitating copper in a pure metallic state from nitric solutions, provided they did not contain more than 0·1 gramme of anhydrous nitric acid to the c.c. (nitric acid of 1·2 sp. gr. contains 0·32 gramme of anhydrous nitric acid to the c.c.), while it was found that the action was, at the same time, more regular, and less dependent

upon the power of the current than when free sulphuric acid was present. The following more commonly occurring metals are *not* precipitated by galvanic action from acid solutions :—zinc, iron, nickel, cobalt, chromium, the metals of the earths, and alkalies. The following are precipitated in the shape of peroxides, at the positive electrode : lead and manganese completely ; silver incompletely. When the solution contains traces of manganese, it becomes, in consequence of the formation of a trace of manganese peroxide, or of permanganic acid, deeply violet-coloured. This very sensitive reaction for manganese also takes place when small quantities of chlorine are present. The presence in the liquid of oxalic, lactic, and tartaric acids, and other readily oxidisable organic substances, and such protoxides as are readily peroxidised—for instance, iron protoxide—retard the formation of peroxides, as well as the occurrence of the reaction of manganese.

Mercury, silver, copper, and bismuth are precipitated at the negative electrode in the metallic state. When mercury is present in the solution simultaneously with copper, the former metal is separated before the latter, in the liquid metallic state. As soon, however, as the precipitation of copper commences, an amalgam of the two metals is formed when mercury is also present. Silver is precipitated almost simultaneously with copper ; bismuth only begins to be precipitated after the greater portion of the copper has been separated. A complete separation of silver only ensues when some such substance as tartaric or other similar acid is simultaneously present in the solution. The separation of the three last-named metals, by means of galvanic action, is, therefore, unsuccessful ; but, fortunately, there are many other means to accomplish this end completely.

(*c*) Metallic arsenic is only precipitated slowly, and long after the complete separation of copper, if arsenic acid happen to be present. The same remark applies to antimony, since it is well known that small quantities of antimonic acid are soluble in nitric acid.

The operations, according to Luckow's plan, are—1. Roasting the ore. 2. Solution of the roasted product. 3. Precipitation of the copper. 4. Weighing the copper.

1. **Roasting the Ore.**—Care should be taken to obtain a finely ground average sample of the ore. Then weigh off, in small porcelain capsules previously counterpoised, quantities of from 1 to 3 grammes ; these quantities are then placed on the inverted lid of an iron crucible on the inner surface of which the powdered ore is heated over the flame of a Bunsen gas burner. The powder may be carefully stirred up with a platinum wire, to promote the access of air during the roasting ; the ignition of bituminous matter and sulphur will be ended in about seven minutes. Ores which do not contain bitumen need not be roasted.

It has been already stated that in the case of poor copper ores (and those of the Mansfeld district are generally so), the quantities to be

weighed off for assay should not vary according to a presumed percentage of copper. Two grammes are therefore taken, and, instead of roasting the ore on the lid of an iron crucible, small porcelain crucibles are used for that purpose.

2. **Solution of the Roasted Product.**—The iron lid is allowed to cool, the roasted powder placed on a piece of glazed paper, and any powder adhering to the lid is removed by means of a camel's-hair brush on to the paper. The powder is next transferred to small beaker glasses, and about 2 or 3 c.c. of nitric acid, of 1·2 sp. gr., are added, along with about 10 to 15 drops of concentrated sulphuric acid. The beakers are then placed on a sand-bath, and moderately heated, at first; but when the contents have become nearly dry, the heat is increased, so as to evaporate and expel all sulphuric acid. The beakers should be covered with perforated watch-glasses. This operation requires from about three-quarters of an hour to one hour. The addition of sulphuric acid is made in order to increase the oxidising action of the nitric acid, and also to convert any lime which may happen to be present in the ore into a difficultly soluble salt. It is very useful, also, to add from 10 to 20 drops of hydrochloric acid to the mixture of the two acids just alluded to, since the rapidity of the evaporation is thereby increased and the occasional spirting about of the liquid is lessened.

The process just described may be modified, first by the use of porcelain capsules, the contents of which are easily transferred to beakers with flat bottoms, not higher than about two inches altogether. It is better, also, to use sulphuric acid, prepared with equal bulks of concentrated acid and water, and to measure off 4 c.c. for each assay; while for each assay, moreover, 6 c.c. of nitric acid and about 25 drops of hydrochloric acid are taken. Instead of covering the beaker with a perforated watch-glass, the upper part of a funnel is used, as represented in fig. 15; with this arrangement the sulphuric acid evaporates far more readily, and loss by spirting is prevented. The beaker is heated on a well-arranged sand-bath.

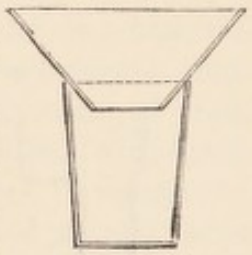


Fig. 15.

3. **Precipitation of the Copper.**—As soon as the beaker after removal from the sand-bath has become quite cool, the funnel which has been used as a cover is washed on both sides, with nitric acid of 1·2 sp. gr., diluted with six times its bulk of pure water; the sides of the beaker are next likewise washed, and it is then filled to about half its height with the same acid. A few drops of a concentrated solution of tartaric acid are added (this acid is best kept in solution in open vessels only slightly covered with a piece of paper); this having been done, the wire spiral, represented in fig. 16, is carefully placed in the beaker. This spiral consists of a piece of platinum wire about $\frac{1}{12}$ of an inch thick and $7\frac{1}{2}$ inches long, two-thirds of its length being so

wound that the straight end of the wire projects as if it were the axis of the centre of the spiral. The convolutions of the spiral are so large that they touch the sides of the beaker, while the straight portion just touches the centre of the bottom of the vessel.



Fig. 16.

When the heating has been carefully attended to, the acid liquid added to the contents of the beaker, after evaporation to dryness, will generally be quite clear ; if it happens to be turbid, 1 or 2 c.c. of a concentrated solution of barium nitrate may be added, and the thorough mixing of this saline solution with the acid contents of the beaker promoted, by gently moving up and down the platinum spiral just alluded to, and allowing the liquid to rest for a few minutes after. The copper present in the mass left at the bottom of the beaker gradually dissolves, and it is not actually requisite to wait before applying the galvanic current until it is all dissolved.

The next point is to place in the beaker the platinum foil, represented at fig. 17, of which the dimensions are—length, $2\frac{1}{2}$ inches ; width, $1\frac{1}{4}$ inch. The lower end of this platinum foil should be kept about $\frac{1}{16}$ of an inch apart from the convolutions of the spiral. When the beaker is only half filled with liquid, the platinum foil is immersed in the same for more than three-quarters of its height.



Fig. 17.

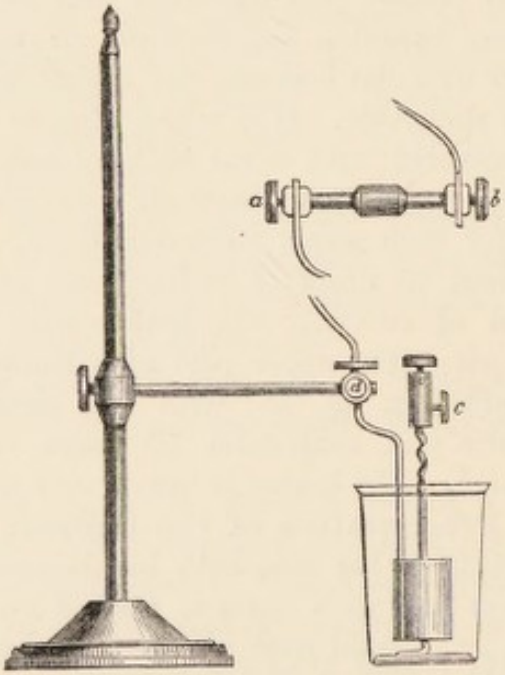


Fig. 18.

The wire fastened to this foil is fixed, by means of a screw, *a*, to the arm, *a b*, of the stand, represented at fig. 18 ; the other screw, *b*, serves to fasten a copper wire, proceeding from the zinc end of the galvanic battery. When the small screw clamp, *c* (fig. 18), has been fastened to the platinum wire placed in the beaker, another wire is fastened in the

top opening of the clamp, and this wire connected with the copper end of the battery, and the galvanic circuit thus closed. In a few moments after this has been done, the platinum foil, bent in the shape of the cylinder and placed inside the beaker, as before described, will be observed to become covered with a coating of metallic copper, while from the platinum spiral bubbles of gas escape, which facilitate, to some extent, the solution of the copper oxide in the dilute acid.

In order to ascertain whether the whole quantity of the copper has been precipitated, some more dilute nitric acid is added to the liquid in the beaker. If, in ten minutes after this, no more metallic copper is separated on the clean portions of the platinum foil, the operation is finished.

It must be here observed that continued practice has proved that the addition of a concentrated solution of barium nitrate acts injuriously on the process, as the metallic copper, which becomes separated, gets mixed with some insoluble barium sulphate, which increases the weight of the substance to be weighed.

The time occupied by the complete precipitation of the metal varies according to the force of the galvanic current. It takes from three to even eight hours. In order to make this point certain, all test assays are left for eight hours consecutively to the action of the galvanic current, experience having proved that, after that lapse of time, even with a weak current, the precipitation was so complete that all chemical reagents for detecting the presence of copper failed to discover the most minute trace of that metal.

4. **Weighing the Copper.**—The platinum cylinder to which the copper adheres, and the platinum wire spiral, are disconnected from the galvanic apparatus, the platinum cylinder carefully removed from the beaker and immediately plunged into a beaker filled with fresh cold water, and rinsed therein ; next washed with alcohol, by means of a washing-bottle, and then dried in a drying apparatus, and weighed after cooling. Since the platinum cylinder has been very accurately weighed *before* the experiment, its increase in weight will, of course, be that of the copper obtained.

Detection of Minute Traces of Copper in Iron Pyrites and other Bodies

(*A*) Although an exceedingly small percentage of copper may be detected in blowpipe experiments by the reducing process, as well as by the azure-blue colouration of the flame when the test-matter is moistened with hydrochloric acid, these methods fail in certain extreme cases to give satisfactory results. It often happens that veins of iron pyrites lead at greater depths to copper pyrites. In this case, the iron pyrites will almost invariably hold minute traces of copper. Hence the desirability, on exploring expeditions more especially, of some ready

test by which, without the necessity of employing acids or other bulky and difficult portable reagents, these traces of copper may be detected. The following simple method is due to Dr. E. Chapman, Professor of Mineralogy and Geology, Toronto, and will be found to answer the purpose. The test-substance, in powder, must first be roasted on charcoal, or, better, on a fragment of porcelain[1] in order to drive off the sulphur. A small portion of the roasted ore is then fused on platinum wire with phosphor salt, and some potassium bisulphate is to be added to the glass (without this being removed from the wire) in two or three successive portions, or until the glass becomes more or less saturated. This effected, the bead is to be shaken off the platinum loop into a small capsule and treated with boiling water, by which either the whole or the greater part will be dissolved; and the solution is finally to be tested with a small fragment of potassium ferrocyanide. If copper be present in more than traces, this reagent, it is well known, will produce a deep red precipitate. If the copper be present in smaller quantity—that is, in exceedingly minute traces—the precipitate will be brown or brownish-black; and if copper be entirely absent, the precipitate will be blue or green—assuming, of course, that iron pyrites or some other ferruginous substance is operated upon. In this experiment the preliminary fusion with phosphor salt greatly facilitates the after solution of the substance in potassium bisulphate. In some instances, indeed, no solution takes place if this preliminary treatment with phosphor salt be omitted.

(*B*) Another very delicate method of detecting traces of copper before the blowpipe by the employment of silver chloride will be found in a subsequent chapter.

Separation of Copper from Lead, Cadmium, Manganese, Mercury, Zinc, &c.

In G. Von Knorre's process the metals must be present as sulphates or chlorides. The solution, reduced if necessary to a small volume by evaporation, is neutralised with ammonia, if free mineral acids are present, and acidified with a few drops of hydrochloric acid. It is then heated almost to boiling-point, and there is added an excess (five parts to about one of the copper present) of nitroso-β-naphthol, previously dissolved in boiling acetic acid at 50 per cent. It is convenient to filter the hot solution of nitroso-β-naphthol through a moistened filter and

[1] In the roasting of metallic sulphides, &c., small fragments of Berlin or Meissen porcelain, such as result from the breakage of crucibles and other vessels of that material, may conveniently be used. The test-substance is crushed to powder, moistened slightly, and spread over the surface of the porcelain; and when the operation is finished, the powder is easily scraped off by the point of a knife-blade or small steel spatula. In roasting operations, rarely more than a dull-red heat is required; but these porcelain fragments may be rendered white-hot, if such be necessary, without risk of fracture.

let the filtrate flow into the hot solution containing the metals, stirring meanwhile.

After the liquid has stood for some hours in the cold the copper nitroso-naphthol is filtered off, and washed with cold water until a drop of the filtrate, if evaporated on platinum foil, leaves no solid residue. The washings, even then, have a yellow colour which does not affect the results. When dry, the filter and precipitate are placed in a capacious tared porcelain crucible, the filter is closed, the crucible is loosely covered, placed upon a sheet-iron plate, and cautiously heated with a small flame until vapours no longer escape. The temperature is then gradually raised, and the crucible is finally ignited with access of air until the carbon is burnt off, when the copper oxide can be weighed. If the quantity of copper nitroso-naphthol is considerable, pure oxalic acid or ammonium oxalate should be added to the precipitate on incineration in order to secure quiet decomposition. In presence of silver the copper precipitate is argentiferous.

Separation of Copper from Uranium

Sergius Kern proposes to precipitate the mixed solution of the two metals, very feebly acid, with potassium ferrocyanide, and treat the mixed precipitate with dilute hydrochloric acid. The uranium ferrocyanide dissolves while the corresponding copper compound remains undissolved.

Uranium ferrocyanide dissolved in hydrochloric acid, and boiled with a few drops of nitric acid, gives a green colouration. This reaction is proposed as a test for uranium salts

Separation of Copper from Mercury

Copper and mercury are conveniently separated by the addition of phosphorous acid to the dilute hydrochloric solution of the two metals. On standing for some time in the cold, the mercury is precipitated in the form of protochloride. The filtrate is heated to ebullition, and the copper oxide precipitated by caustic potash.

Electrolytic Separation of Copper from Mercury

According to Edgar F. Smith and Lee K. Frankel, we proceed as in separating zinc from cadmium. If the solution of the double cyanides is electrolysed with a current of 2 c.c. detonating gas per minute, the mercury is deposited alone. It must be cleansed with water alone. This method of separation yields satisfactory results only when the quantity of copper is smaller than that of mercury.

Separation of Copper from Thallium

When these two metals occur together analytically, they may be easily separated by adding to the acid solution sulphurous acid in

excess, and then potassium iodide; a dirty white precipitate will fall, consisting of copper subiodide and thallium iodide. On adding ammonia to the washed precipitate, the copper iodide rapidly dissolves, with absorption of atmospheric oxygen, to a deep blue liquid, while the thallium iodide is left behind as an insoluble yellow powder.

When potash is added to a solution of copper and thallium protoxides, copper oxide alone is precipitated.

Sulphuretted hydrogen in an acid solution also separates the copper, but as metallic sulphides are very liable to carry down thallium sulphide it is preferable to use other means of separation, if sulphuretted hydrogen can be avoided.

When present, even in small quantities, thallium diminishes the malleability and ductility of copper. Copper prepared by the cementation process frequently contains thallium. A specimen, for which the author is indebted to his friend the late Dr. Matthiessen, which had a conducting power for electricity of about 15 (that of pure copper being 100), was found to contain a comparatively large quantity of thallium; it is probable that the pre-eminently bad quality of this copper is thus to be accounted for.

Separation of Copper from Gallium

According to circumstances we may choose among the following methods, all of which are good, but the first is to be preferred whenever applicable.

(*A*) The hydrochloric solution, distinctly acid, is treated with a current of hydrogen sulphide. The copper sulphide is then treated with acidulated water containing hydrogen sulphide.

On ebullition, kept up for some minutes, potash throws down anhydrous cupric oxide containing no gallium. The separation is complete.

(*B*) In a solution kept slightly acid zinc easily throws down the copper without carrying the gallium along with it. It is much better to reduce the copper by means of the electrolysis of a sulphuric solution, quite free from chloride. The operation is performed in a platinum vessel, taking the usual precautions for the electrolytic estimation of copper.

(*C*) The separation may be effected by the prolonged boiling of a solution supersaturated with ammonia, provided that the copper is not very abundant, in which case the operation has to be several times repeated. The original hydrochloric solution must be very acid in order that it may afterwards contain a notable quantity of ammonium chloride.

Separation of Copper from Silver

The ordinary methods of separating copper from silver are too simple to require mention here. It may happen, however, that a rapid

and approximate separation of silver and copper nitrates is wanted without resorting to the process of precipitating the silver as metal or as chloride. Under these circumstances the following process will be useful. (It is supposed that the object is to prepare silver nitrate from silver coins which contain a large percentage of copper.) The alloy is dissolved in nitric acid ; the solution is filtered if necessary, and evaporated until it has the consistency of a thickish oil ; when this point is reached there is added to the solution very concentrated nitric acid free from hydrochloric acid. By this proceeding all the silver nitrate is precipitated, while copper nitrate remains in solution. One part of the concentrated metallic solution requires from three to four parts of nitric acid for the complete precipitation of the silver nitrate ; the more concentrated the nitric acid is the better, but acid of 1·25 sp. gr. answers the purpose. The solution of copper is decanted off and the silver nitrate washed with nitric acid.

A more exact but somewhat more troublesome method is to fuse the mixed nitrates. Copper nitrate decomposes much more readily than silver nitrate.

Electrolytic Separation of Copper from Silver [1]

(*A*) The neutral or slightly acid solution of a silver salt gives, if mixed with ammonium oxalate, a white precipitate insoluble in an excess of the precipitant. A copper solution, treated in the same manner, yields a soluble copper ammonium oxalate. We now add to the solution of both metals ammonium oxalate until the precipitate of silver oxalate appears of a pure white. It is then washed first with ammonium oxalate and afterwards with cold water and dissolved in potassium cyanide. The separation of the silver from this solution and the reduction of the copper in the filtrate are effected as already described.

(*B*) According to E. F. Smith, the separation from the solution of both metals may be effected by means of potassium cyanide. To about 0·4 gramme of the mixed metals there is added 4·5 grammes potassium cyanide ; the liquid is diluted to 200 c.c. and electrolysed with a current of from 0·1 to 0·4 c.c. detonating gas per minute. The silver is then deposited alone, free from copper.

The electrolysis takes about sixteen hours.

Separation of Copper from Nickel or Cobalt

(*A*) Obtain the metals in a slightly acid solution, and add sulphurous acid till the copper is entirely reduced to the state of sub-salt. Then precipitate with potassium sulphocyanide, and after allowing the precipitate to digest in the liquid for a short time, filter off the white copper sub-sulphocyanide.

[1] For details of operation see chapter on Electrolytic Analysis.

(*B*) The ordinary process for separating copper from nickel, founded on the precipitation of copper by sulphuretted hydrogen, leaves much to be desired on account of the facility with which copper sulphide after washing passes to the state of sulphate; and also because copper, during precipitation, always carries down with it considerable quantities of nickel, which passes to the state of sulphide in the precipitate. M. Dewilde has worked out a method of separating these metals based upon the property possessed by glucose of precipitating copper as a suboxide, when that metal exists in the form of tartrate dissolved by the aid of caustic potash. His process is as follows:—

Dissolve about 2 grammes of the alloy in hydrochloric acid containing a little nitric acid; evaporate off the excess of acid and dissolve the mixed chlorides in about 50 grammes of water. To the solution add about 4 grammes of cream of tartar. Heat slightly to facilitate solution, and add gradually a solution of caustic potash in alcohol. The first addition of alkali precipitates the copper and nickel oxides in the state of hydrates, but an excess of potash redissolves the whole, the copper and nickel tartrates being soluble in caustic potash. A blue solution is thus obtained, which after cooling is treated with a solution of pure glucose or inverted sugar, and boiled for one or two minutes. The copper is precipitated as a beautiful red suboxide sinking quickly to the bottom of the vessel; if, however, the glucose is added to a warm solution, the copper is precipitated in flakes which it is difficult to wash. The completion of the precipitation is ascertained by adding a further quantity of the glucose solution.

The precipitated copper suboxide is washed, dried, and ignited. It may be heated with nitric acid, and copper protoxide obtained by igniting the nitrate formed.

The filtrate containing the nickel is evaporated to dryness, the residue calcined, and then washed to remove the potassium carbonate. As the incineration can never be complete, on account of the presence of this salt, the operation is to be repeated. The residue, consisting chiefly of nickel oxide, is dissolved in aqua regia, and the hydrated nickel oxide precipitated from the solution by caustic potash. It is very difficult, if not impossible, to wash this very voluminous oxide, so the best plan is to wash incompletely, dry, and slightly calcine the oxide; after grinding this in an agate mortar, it is easily freed from the last trace of potash by washing in warm water. The oxide thus obtained is reduced in a platinum crucible in an atmosphere of hydrogen.

This process is in use in the Belgian mint, where copper and nickel alloys are used for coinage.

Separation of Copper from Zinc

The solution of copper and zinc must contain no other metal which forms an insoluble iodide. Add sulphurous acid to the solution, and

then, after gentle heating, potassium iodide, until the supernatant liquid has lost its blue colour and a precipitate is no longer formed. There should be a slight excess of sulphurous acid the whole time. The copper subiodide being very dense, deposits readily, especially on warming, like silver chloride. Heat to the boiling-point and collect on a weighed filter. The precipitate, washed with warm water, is dried at 120° and weighed. All the zinc will be in the solution.

Separation of Copper from Cadmium

(*A*) Cadmium sulphide dissolves with the greatest facility in boiling dilute sulphuric acid, which has no action on copper sulphide. On precipitating by sulphuretted hydrogen a solution containing not more than 1 milligramme of cadmium mixed with 1000 milligrammes of copper, and boiling the black precipitate for a few seconds with dilute sulphuric acid (one part concentrated acid and five parts of water), a colourless filtrate is obtained, in which an aqueous solution of sulphuretted hydrogen produces an unmistakable precipitate of yellow cadmium sulphide. Another solution of the same composition was mixed with an excess of potassium cyanide and treated with sulphuretted hydrogen gas. A distinct yellow colouration was observed : a deposit likewise took place, but so slowly that in delicacy the former experiment appears to have a considerable advantage, especially since a solution of *pure* copper in potassium cyanide also gives rise to a yellow colouration when submitted to the action of sulphuretted hydrogen.

(*B*) Another method for the separation of cadmium from copper, due to Wöhler, is as follows. Well wash the precipitated sulphides, and then dissolve them in hydrochloric acid, to which is added potassium chlorate. Precipitate the solution by an excess of potash, and dissolve the precipitate in hydrocyanic acid. This will form a solution of double cyanides, from which sulphuretted hydrogen precipitates the cadmium, but not the copper.

(*C*) Another plan is to add to the solution of the two metals a considerable excess of tartaric acid, then a solution of caustic soda to alkaline reaction. Now dilute considerably and boil for some hours ; the cadmium will be deposited. The filtrate containing the copper is then oxidised with aqua regia and precipitated with caustic potash.

Copper and cadmium may also be separated by precipitating the former with potassium sulphocyanide, after having first reduced it with sulphurous acid.

(*D*) Mr. G. Vortmann, for the separation of copper and cadmium, mixes the dilute solution (sulphuric or hydrochloric) of the metals with sodium thiosulphate till completely decolourised ; it is then heated to the boiling-point, when the copper is separated as a heavy black sulphide. The boiling is continued till the liquid has become

clear. After filtration and careful washing, the copper sulphide is mixed in the known manner with sulphur, and heated in a current of hydrogen. The cadmium in the filtrate is precipitated by one of the known methods.

(*E*) Dr. Wells finds that cadmium and copper may be easily separated by the following method. To the neutral solution containing these metals (ammonia salts must not be present), add sodium thiosulphate until the solution becomes colourless, then add sodium carbonate and the cadmium will be precipitated as white carbonate; filter, and to the filtrate add hydrochloric acid and boil, when the copper will be precipitated as sulphide. To use this method in the ordinary course of analysis, the solution, after removal of the bismuth, would have to be evaporated to dryness and ignited so as to remove all ammonia salts.

LEAD

Preparation of Pure Lead

As in the case of silver, the most valuable information on the subject of the purification of metallic lead is due to the researches of Professor Stas on the relations existing between atomic weights. The preparation of pure lead offers more difficulties than that of pure silver.

In the following pages are given those processes which yielded the best results.

(*A*) **Preparation of Lead by reducing the Carbonate with Potassium Cyanide.**—Commercial lead acetate is dissolved in warm water, contained in a large leaden digester, and kept at a temperature of 40° to 50° in contact with very thin sheets of lead until all the copper and silver is precipitated. The solution is then filtered and poured into nearly boiling water, strongly acidulated with sulphuric acid. The lead sulphate is washed by decantation until the washing-waters contain no trace of sulphuric acid. The salt is then transformed into carbonate by means of a mixture of ammonium sesquicarbonate and solution of ammonia; for this it is only needful to diffuse it in the water containing the alkaline salt; an effervescence takes place, which lasts as long as there remains lead sulphate undecomposed. At this point the solution of ammonium sulphate and the excess of ammonium carbonate is decanted, and the precipitate washed with pure water as long as the washing-waters contain sulphate in solution.

The lead carbonate thus formed dissolves entirely in dilute nitric acid. It is perfectly free from foreign metals, except traces of iron, which adhere to the lead sulphate in spite of the excess of sulphuric acid employed. To separate the iron, transform a portion of this lead carbonate into oxide, by heating it carefully in a platinum vessel.

Another portion is dissolved in dilute nitric acid, taking the precaution to leave some of the carbonate undissolved. The solution of nitrate is heated to ebullition and the lead oxide then gradually added to it. The oxide in dissolving precipitates traces of iron. The liquid is filtered and an excess of ammonium sesquicarbonate poured into it. In the lead carbonate thus obtained it is impossible to discover the slightest trace of foreign metal. It is this carbonate which is converted into metallic lead. To effect this, after having dried it, project it, by small quantities at a time, into pure fused potassium cyanide. As this reduction ought to be effected in a white, unglazed porcelain crucible, which is very liable to break, recourse may be had to the same plan which was used in the reduction of silver from its chloride, and in the fusion of the pure metal (page 271)—that is to say, fix the porcelain crucible in the centre of another larger one, interposing between them calcined pipeclay, which has been reduced to powder, cementing the whole together by the addition of 5 per cent. of fused and powdered borax.

The lead obtained by the first operation is heated a second time with pure potassium cyanide until it presents at the bottom of the cyanide a surface as convex and brilliant as pure mercury. When it is somewhat cool, cast it in a polished ingot-mould of cast steel.

When the lead contains the slightest trace of oxide or sulphide it does not present a convex surface when it is fused.

Pure lead is much whiter and more soft than the ordinary metal. It appears to tarnish very rapidly when exposed to the air.

(*B*) **Preparation of Lead by reducing the Carbonate by Black Flux.**—Instead of reducing the lead carbonate by potassium cyanide, black flux obtained by carbonising purified Seignette salt may be employed. To entirely deprive this salt of foreign metals, first pass a current of hydrosulphuric acid through its boiling solution ; then pour in a few drops of sodium sulphide solution. The coloured solution, left to itself for fifteen days in a well-stoppered bottle, becomes completely decolourised by depositing the metallic sulphides. The decanted solution is agitated with lead tartrate as long as it contains the slightest trace of sodium sulphide. Before calcining the Seignette salt, it should always be tested to see that it contains neither sulphide, sulphate, nor foreign metals.

The lead carbonate mixed with the pulverised black flux is reduced by the action of heat. The temperature necessary for the fusion of the alkali being tolerably high, there is almost always a certain quantity of alkaline metals reduced which alloy with the lead. To remove these metals, heat the lead for some time in contact with the air, continually stirring the metallic bath with a rod of pipeclay. When a certain quantity of the lead has been thus oxidised, pour on the mass fused potassium cyanide, and heat the whole until a great portion of the cyanide is volatilised. The lead is then allowed to cool

to near its point of solidification, and then run into an ingot-mould of polished steel.

(*C*) **Preparation of Lead by reducing the Chloride.**—Treat with an excess of dilute hydrochloric acid the lead carbonate prepared by the action of ammonium sesquicarbonate upon the lead sulphate. The minute traces of iron contained in the carbonate remain dissolved in the excess of hydrochloric acid. Two different plans may be used to reduce the chloride. One consists in mixing it with two-thirds of its weight of pure sodium carbonate and projecting the intimate mixture into fused potassium cyanide. The metallic lead produced is poured into another crucible with a fresh quantity of pure fused potassium cyanide. It is there kept at a high temperature and continually agitated until the surface, flat and dull as it is at first, becomes strongly convex and brilliant. When sufficiently cool it is poured into an ingot-mould and kept away from moist air.

The other plan for reducing the chloride consists in heating an intimate mixture of it with sodium carbonate and black flux. The resulting lead is fused and agitated for some time in contact with air, and then heated with cyanide to remove the last traces of oxide.

Estimation of Lead as Carbonate

In face of the difficulties to be encountered in estimating lead with great accuracy, it is advisable that it should be estimated in the state of carbonate, and for that purpose ordinary ammonium carbonate, to which is added caustic ammonia, should be used. The object of this addition is to avoid the employment of too large a volume of solution of ammonium carbonate, a salt not very soluble in water. Ammonia forms, with lead nitrate, for instance, a very incomplete precipitate. It would not, then, be prudent to divide the operation into two—that is to say, to employ ammonia first to saturate the liquid—and, consequently, the ammonia should not be poured in until it has been charged with ammonium carbonate, which it dissolves abundantly. The precipitate separates perfectly from the liquid, is easily collected, and is dried on a filter. The deposition of the precipitate is completed in about twenty-four hours, especially under the influence of gentle heat. Two or three parts of lead in a thousand can be estimated by this process.

The precipitate, which is the anhydrous monocarbonate, is deposited on a small double filter, each one of the same weight.

If, as frequently happens in analysing metallic substances, the colour, which should be pure white, is yellowish, it is owing to the presence of iron, which is easily got rid of by washing the filter with water acidulated with sulphuric acid after weighing.

If there is reason to suspect the presence of bismuth, treat a small quantity of the weighed precipitate with a little nitric acid. A few

drops of potassium iodide in the liquid will detect the presence of bismuth by forming a brown precipitate, or yellow-brown if there is bismuth and lead. The latter metal, when present alone, gives a pure yellow precipitate. (See also Separation of Bismuth from Lead.)

Estimation of Lead as Iodate

Sir Charles A. Cameron finds that lead iodate is practically insoluble. Iodic acid and alkaline iodates precipitate lead far more perfectly than sulphuric acid, even when alcohol is added to the latter. The plumbic iodate formed is weighed, or, if a volumetric method be desired, the following is the process:—Precipitate with standard solution of soluble iodate, and filter off the plumbic iodate. The filtrate and washings are to be mixed, and the excess of iodic acid contained in them estimated volumetrically by the hydrochloric acid and thiosulphate method. As it is almost impossible to procure pure iodic acid from potassium iodate, the solution of iodate must be standardised by means of a solution of pure lead nitrate. Owing to the slight solubility of plumbic iodate in alkaline chlorides, iodides, and bromides, none of these salts must be present. Hydrochloric acid rapidly dissolves lead iodate.

Electrolytic Separation of Lead [1]

(*A*) In the electrolysis of a hot solution of lead mixed with an excess of ammonium oxalate with a current of about 0·2 c.c. of detonating gas per minute, Classen obtains the lead with its characteristic metallic properties firmly adhering to the negative electrode, but it becomes partially oxidised on washing with water or alcohol, so that the determinations are always in excess.

(*B*) The separation of lead as amalgam (see Zinc) likewise presents some difficulties, as along with the amalgam there is always formed at the positive electrode some lead peroxide which must be dissolved away. According to G. Vortmann we proceed by adding to the aqueous solution of the lead salt, which contains a quantity of mercuric chloride sufficient for the formation of amalgam, from 3 to 5 grammes of sodium acetate and a few c.c. of a concentrated solution of potassium nitrate. The precipitate caused by the last reagent (which is said to prevent the formation of lead peroxide) is dissolved in acetic acid, and the clear yellow liquid is electrolysed after dilution with water. If during the electrolysis lead peroxide appears at the positive electrode, potassium nitrate is again added. The end of the reaction is ascertained by means of ammonium sulphide. As the lead amalgam in the moist state becomes oxidised with relative ease, it is quickly washed with water, alcohol, and ether, dried first by the heat of the hand and by blowing upon it, and finally in the desiccator.

[1] For details of operation see chapter on Electrolytic Analysis.

(*C*) The separation of the amalgam can be effected also from aqueous solution acidulated with nitric acid. As free nitric acid, however, promotes the formation of lead peroxide, the addition of potassium nitrate is often requisite, whereby the complete precipitation is notably retarded.

(*D*) In a solution containing free nitric acid lead behaves like manganese; it is oxidised and deposited on the positive electrode as a hydrated peroxide. If the solution to be electrolysed contains no other metals besides lead, it must, according to Luckow, contain at least 10 per cent. of nitric acid; in presence of other metals (*e.g.* mercury or copper) a complete oxidation occurs in presence of a smaller proportion of nitric acid.

Small quantities of lead peroxide adhere firmly enough to the positive electrode to be determined as such after previous washing with water and drying at 110°. For larger quantities of lead the platinum capsule is used as a positive electrode, proceeding as above.

For the precipitation, according to Luckow, a current of a few tenths of a c.c. of detonating gas per minute is sufficient. Care must be taken to effect the washing of the peroxide without interrupting the current, as loss otherwise ensues.

(*E*) J. Messinger recommends the addition of 30 c.c. nitric acid (sp. gr. 1·39) to the solution of 175 c.c. in volume, using the platinum capsule as a positive electrode, and applying a current of 0·1 c.c. detonating gas (2 Meidinger elements). The peroxide is washed with alcohol and water and dried at 120° or 130°. It is found advantageous at the beginning of the electrolysis to weaken the current by the insertion of a rheostat, and only to intensify the current to the strength indicated after the formation of a stratum of peroxide. The peroxide adheres very firmly and may be washed without loss when it exceeds 0·2 grm. in quantity. Otherwise compounds must not be present in the liquid to be electrolysed.

Experiments on the quantity of nitric acid (sp. gr. 1·30) have been made, with the result that it must be regulated according to the temperature of the liquid and the density of the current to be employed. The density of the current again depends on the character of the surface of the positive electrode. If it is very smooth, then N.D. 100=0·05 ampère, and in the other case=0·5 ampère must be used to obtain a firmly adhesive deposit. At N.D. 100=0·05 ampère, on heating the liquid, the addition of nitric acid is 2 vols. per cent., but under the same conditions 10 vols. per cent. At N.D. 100=0·5 ampère, if the liquid is heated, we add 7 vols. per cent.; otherwise 20 vols. per cent. nitric acid of the above strength.

Heating the liquid to about 50° accelerates the separation very decidedly. The precipitate can be washed without loss after the current is interrupted.

(*F*) The separation of lead as peroxide requires, according to

Classen, the exact observance of certain conditions. Luckow says that a certain quantity of nitric acid is required for the complete oxidation to peroxide. The quantity is regulated by the temperature of the liquid and the density of the current to be used. Concerning the latter point, it has been ascertained that it depends on the nature of the anode. If its surface is very smooth it must be only 0·05 ampère (for a surface of 100 square cm.), otherwise 0·5 ampère. Even on observing these conditions, the quantity of lead which can be deposited as firmly adherent peroxide is relatively very trifling. The rapid separation of larger quantities of lead peroxide adhering completely like a metal succeeds only if the platinum capsule serving as an anode is roughened internally by means of a sand-blast. On using such capsules it is possible in a few hours to deposit quantities of lead peroxide up to 4 grms. upon a surface of 100 square cm. with a current of 1·5 ampère. In carrying out the determination of lead, we add, after dissolving the lead salt, 20 c.c. of nitric acid (of specific gravity 1·35 to 1·38), dilute with water to about 100 c.c., heat to 50° to 60°, and electrolyse with a current of N.D. 100=1·5 to 1·7 ampère. If the application of heat is continued, the precipitation for quantities of 1·5 grm. lead peroxide is completed in three hours; for larger quantities in four to five hours. To ascertain the completion of the separation, add about 20 c.c. of water, and observe if any blackening takes place on the surface of the electrode when recently moistened. If blackening is not observed in ten to fifteen minutes, the deposit, after interrupting the current, is washed with water and alcohol, and dried at from 180° to 190°. The residue is anhydrous peroxide. The tension of the current does not affect the nature of the lead peroxide. In Classen's experiments it varied from 4 to 8 volts.

Detection and Estimation of Small Quantities of Lead in the Presence of other Metals

The separation of lead from its solutions and from other metals by means of potassium chromate does not appear to have attracted the attention of analytical chemists to the extent which it merits, judging from the published special methods of analysis which include the estimation or detection of that metal.

(*A*) There are frequent instances in which potassium chromate offers considerable advantage as a precipitant of lead over hydrosulphuric or sulphuric acid, the two reagents in general use, more particularly for the detection of minute quantities. The efficiency of this reagent is, moreover, much increased by the circumstance that lead chromate is all but insoluble in acetic acid. It is, indeed, one of the most insoluble of the lead salts, and has, therefore, claim to superiority over the more soluble sulphate; while the scarcity of insoluble chromates renders potassium chromate valuable for effecting

the separation of lead from other metals in cases where the reagents referred to are inapplicable. The precipitation of lead in the presence of copper, for example, is readily affected by the addition of potassium bichromate to an acetic solution; a trace of lead which would otherwise escape detection is rendered evident after a time by the deposition of the characteristic yellow precipitate.

(*B*) Potassium bichromate in the presence of free acetic acid is also applicable as a means of separating small quantities of lead from zinc (*i.e.* in the analysis of the spelters in commerce). The precipitation of lead by hydrosulphuric acid from the hydrochloric solution is at times anything but satisfactory; the solubility of the lead sulphide in the excess of hydrochloric acid which must be employed to prevent the precipitation of the zinc is frequently sufficient to cause the belief that lead is absent when it really exists in the spelter to a very appreciable amount. (It may be observed that this liability to error, in the use of hydrosulphuric acid, is not nearly so great when nitric acid is employed.)

If much bismuth be present in the substance under examination, some bismuth chromate will be precipitated, together with the lead. In such instances the separation of the two metals must be effected by a special method.

The lead chromate, when freshly precipitated from a cold solution, is sometimes difficult to separate perfectly from the liquid by filtration; this is not the case, however, if the precipitate is allowed to stand for some time, or if it is produced in a hot solution.

(*C*) The most accurate way of estimating the weight of minute quantities of lead precipitated as chromate is to convert the metal finally into sulphate. For this purpose the chromate is dissolved in a little hot dilute hydrochloric acid; a small crystal of tartaric acid is added, and the solution, rendered alkaline by ammonia, is treated with hydrosulphuric acid, or mixed with a few drops of ammonium sulphide. The lead sulphide thus obtained is washed and converted into sulphate by the usual method.

Assay of Galena in the Wet Way

(*A*) The reaction with zinc and hydrochloric acid has been employed with advantage by F. H. Storer, Professor of Chemistry in the Massachusetts Institute of Technology, for assaying galena, particularly the common American variety, which contains no other heavy metal besides lead. The details of the process are as follows:—Weigh out 2 or 3 grammes or more of the finely powdered galena. Place the powder in a tall beaker, together with a smooth lump of pure metallic zinc. Pour upon the mixed mineral and metal 100 or 150 c.c. of dilute hydrochloric acid which has been previously warmed to 40° or 50° C.; cover the beaker with a watch-glass or broad funnel, and put in a moderately warm place.

Hydrochloric acid fit for the purpose may be prepared by diluting 1 volume of the ordinary commercial acid with 4 volumes of water. For the quantity of galena above indicated, the lumps of zinc should be about one inch in diameter by a quarter of an inch thick; they may be readily obtained by dropping melted zinc upon a smooth surface of wood or metal.

The zinc and acid should be allowed to act upon the mineral for fifteen or twenty minutes in order to ensure complete decomposition. Any particles of galena which may be thrown up against the cover or sides of the beaker should, of course, be washed back into the liquid. It is well, moreover, to stir the mixture from time to time with a glass rod.

When all the galena has been decomposed, as may be determined by the facts that the liquid has become clear, and that no more sulphuretted hydrogen is evolved, decant the liquid from the beaker into a tolerably large filter of smooth paper, in which a small piece of metallic zinc has been placed. Wash the lead and zinc in the beaker as quickly as possible with hot water, by decantation, until the liquid from the filter ceases to give an acid reaction with litmus-paper; then transfer the lead from the beaker to a weighed porcelain crucible. In order to remove any portions of lead which adhere to the lump of zinc, the latter may be rubbed gently with a glass rod, and afterwards with the finger or a piece of caoutchouc, if need be. Wash out the filter into an evaporating-dish, remove the fragment of zinc, and add the particles of lead thus collected to the contents of the crucible. Finally, dry the lead at a moderate heat in a current of ordinary illuminating gas, and weigh.

The lead may be conveniently dried by placing the crucible which contains it in a small cylindrical air-bath of Rammelsberg's pattern provided with inlet and outlet tubes of glass, reaching almost to the bottom of the bath.

When the process is conducted as above described, the lead undergoes no oxidation; hence there is no occasion for igniting the precipitate in a reducing gas. The precipitate needs only to be dried, out of contact with the air.

If desirable, the sulphur in the galena can be estimated at the same time as the lead, by arresting the sulphuretted hydrogen in the ordinary way.

If the mineral to be analysed is contaminated with a siliceous or other insoluble gangue, the metallic lead may be dissolved in dilute nitric acid after weighing, and the insoluble impurity collected and weighed by itself. In the case of galenas which contain silver, antimony, copper, or other metals, precipitable by zinc, the proportion of each metal must be estimated by assay or analysis in the usual way after the total weight of the precipitated metals has been taken.

Besides galena, almost any of the ordinary lead compounds may

evidently be assayed by the method above described. For example, metallic lead may be precipitated quickly and completely from the sulphate, chromate, nitrate, oxide, and carbonate—and with peculiar ease from the chloride—by means of zinc and hydrochloric acid. The method would also furnish an easy qualitative test for the detection of baryta in white lead. When applied to the analysis of lead nitrate, it would probably be best to decompose the nitrate by means of a solution of sodium chloride before adding the zinc and hydrochloric acid.

(*B*) Dr. F. Mohr estimates lead in galena as follows :—Two grammes finely powdered galena are placed in a small porcelain pan furnished with a handle. It is covered with ordinary pure hydrochloric acid, covered with a convex glass, heated to expel hydrogen sulphide, and boiled. Much lead chloride separates out. When the acid is saturated with lead chloride, a small ball of zinc is added. A brisk escape of hydrogen ensues, and lead is deposited on the zinc. A gentle heat is applied until the liquid becomes clear and colourless, and the escape of hydrogen sulphide ceases. The liquid is poured off, and the lead is well washed with pure water in the capsule. Dilute nitric acid is poured upon the moist lead, and heat is applied till the metal is dissolved. The lead nitrate is dissolved, if needful, by the addition of water and the application of heat; the liquid is filtered and the filter washed with hot water. In the filtrate the lead is thrown down by the addition of dilute sulphuric acid in excess and heated for a time, when lead sulphate is deposited. The whole is filtered, the precipitate is washed with dilute sulphuric acid, and lastly with a little alcohol, dried, and the weight of the lead sulphate is found after incineration of the filter. The filter, when saturated with ammonia, shows scarcely a trace of brown colouration with sulphuretted hydrogen.

(*C*) P. Jannasch and H. Kammerer [1] employ the following process for the quantitative analysis of galena in the wet way :—

0·7 to 0·75 gramme of finely pulverised galena is placed in a porcelain capsule and moistened with dilute nitric acid, allowed to stand in the cold for some minutes, treated there with 10 cubic centimetres of concentrated nitric acid, heated on the water-bath, and suitably evaporated. Nitric acid and water are added afresh, along with 10 to 15 drops of bromine, and heated, with frequent stirring, until all the sulphur is completely oxidised to sulphuric acid.

For the certain destruction of any bromate formed as a subsidiary product, evaporate the saline mass three times with concentrated nitric acid until quite dry. The dry residue is then boiled for a short time in a covered capsule with 60 cubic centimetres of water and 20 cubic centimetres of concentrated hydrochloric acid, so as to dissolve all the lead sulphate. The residual gangue is filtered off (using a tall beaker),

[1] *Chemical News*, Aug. 16, 1895.

the filter and the tube of the funnel are well washed with boiling water, incinerated, and weighed.

For precipitating the lead, the filtrate is heated to ebullition on a free flame until complete solution has been effected, and the liquid is poured into a previously prepared mixture of 25 cubic centimetres of water, 50 cubic centimetres hydrogen peroxide, and 50 cubic centimetres concentrated ammonia. The lead is thus precipitated as a fine yellowish-red, partially crystalline deposit, the composition of which will be determined subsequently. The whole is allowed to stand covered for several hours, with occasional stirring, filtered, washed carefully with cold water, dried, and weighed in a platinum crucible as lead oxide.

For the determination of the sulphuric acid, the filtrate from the lead precipitate is evaporated on the water-bath until the odour of ammonia has disappeared; 5 cubic centimetres of concentrated hydrochloric acid and the same volume of alcohol are added, and the whole is gently heated for some time in order to regenerate certain quantities of persulphuric acid and to destroy with certainty any hydrogen peroxide still present. The sulphuric acid is then precipitated with the calculated quantity of solution of barium chloride. If this precaution is omitted, the results are much too low, in consequence of the solubility of barium persulphate.

Small impurities of a galena, consisting of copper, nickel, zinc, or arsenic, will be found by use of the hydrogen peroxide method in the ammoniacal filtrate, and, after the separation of the sulphuric acid, may be separately determined by barium chloride.

(*D*) When we have to estimate all the elements of a galena or a chalcopyrites, we often experience much difficulty in finding a sufficiently rapid and complete method for dissolving the mineral. We do not propose here to refer to all the well-known methods for the attack of these minerals, as most of them have come to be, in a way, classic. However, they are not always very convenient to carry out, most of these methods requiring a considerable time.

C. Boucher [1] has had recourse to the action of persulphates, salts which easily give up their oxygen, and of which the acid is fairly energetic.

After a certain time, the sulphide of lead of the galena is completely transformed into sulphate—a change which is also brought about, but less quickly, with sulphate of ammonium, as has been shown by Mascazzini.

By adding to the solution a few drops of concentrated nitric acid, the reaction becomes more rapid, and succeeds also with chalcopyrites. In all cases with this latter mineral the formation of spongy sulphur, which takes a long time to get rid of, becomes an annoying obstacle.

It is necessary then to boil for a long time on a sand-bath, to evaporate almost to dryness to melt the sulphur, and then to make

[1] *Chemical News*, Jan. 29, 1904.

certain that the resulting globule of sulphur does not contain any more of the mineral.

A second series of experiments made by the dry way gave excellent results. As reagent Mr. Boucher uses a mixture of three parts of sodium and one part of nitrate of ammonium, more or less approximately. The use of persulphate alone is insufficient.

Operate on 1 or 2 grammes of the well-powdered mineral, mixed more or less intimately, by means of a platinum wire, with four or five times its weight of the above-mentioned reagent; these amounts are only approximate. The operation may be performed either in an iron crucible, if the estimation of the iron is not indispensable, or in a sufficiently large porcelain crucible.

The mass must not occupy more than one-third of the crucible, which must be covered. The whole is then placed on a moderately heated sand-bath. After five or six minutes the crucible is removed, allowed to cool, and examined to see that the attack is complete (in this case no more black grains of galena will be visible). It suffices now to take up with water, and filter. On the filter we find the lead in the form of sulphate, mixed with the gangue, silica, &c., which are separated by the known methods. As for the sulphuric solution, it contains the other metals.

To better follow the progress of the reaction, and also to avoid all loss, we may very advantageously effect the fusion in an Erlenmeyer flask of Jena glass—about 100 cubic centimetres capacity, for example—taking care to shake from time to time, and not to heat too strongly at the commencement.

As for the other sulphurised minerals—at least, the pyrites, blendes, stilbines, mispickel, &c.—they have not furnished satisfactory results. They appear to be much more stable with the persulphates than are the galenas and chalcopyrites.

A curious thing about these latter is that they are much less easily attacked by acids than the former. Pyrites, especially, almost entirely resists the reagent used above.

Blendes are attacked very incompletely, and the reaction is accompanied with little explosions and the burning of the sulphur.

Detection of Lead Peroxide in Litharge

Heat the litharge in a test-tube with sodium chloride and potassium bisulphate, and introduce into the tube a slip of paper coloured with a solution of indigo. If any peroxide be present, chlorine is disengaged, which bleaches the paper.

Estimation of the Value of Lead Peroxide

H. Fleck places a weighed quantity in a small flask fitted with a gas-delivery tube, and decomposes with dilute hydrochloric acid. The

chlorine evolved is passed into a solution of potassium iodide. When the escape of gas has ceased, the solution is titrated with sodium thiosulphate, and the percentage of lead peroxide is calculated from the quantity of iodine. In rich samples the moisture should be estimated specially.

Separation of Lead from Copper[1]

(*A*) According to Classen, in a solution containing free nitric acid the lead is separated as peroxide at the positive electrode. If it is required to determine lead and copper when jointly present, dilute the solution (made up only to 75 c.c., and containing 20 c.c. of nitric acid), electrolyse the hot liquid with a current of 1·1 to 1·2 ampère (corresponding to N.D. 100=1·5 to 1·7 ampère), and interrupt the electrolysis after an hour. The maximum quantity of lead present (98 to 99 per cent. if the lead in solution reaches 0·5 grm.) is then separated as peroxide, while the cathode still shows no trace of copper. Then interrupt the current, transfer the liquid into another tared capsule, wash the lead peroxide with water which is added to the copper solution, and determine its weight after drying. For the electric deposition of copper, we add ammonia to the solution until the well-known deep blue copper solution appears, and then add about 5 c.c. nitric acid. The platinum capsule is then connected to the negative pole of the source of current, and used as an anode to receive the residue of lead peroxide and the perforated electrode of sheet platinum, also rendered mat, the weight of which must be previously ascertained. The liquid diluted to 120 or 150 c.c. is allowed to become completely cold, and electrolysed with a current of N.D. 100=1 to 1·2 ampère. In three or four hours the copper (if not exceeding 0·25 grm.) and the residue of the lead are separated.

On applying this method to the analysis of sulphuretted products, the lead sulphate formed by oxidation makes itself unpleasantly prominent. Its solution in nitric acid, according to its compactness, often consumes more time than the analysis itself.

If lead sulphate has been formed, whether in consequence of oxidation or by the double decomposition of lead nitrate and copper sulphate, first add ammonia in slight excess and heat for a few minutes. Hereby the dense lead sulphate is converted into loose lead hydroxide. This liquid is gradually poured into the platinum capsule which contains about 20 c.c. of hot nitric acid, stirring constantly with the electrode. The residual lead sulphate dissolves either at once or in chief part (according to its quantity), and the remainder dissolves on heating for a short time.

The vessel in which the transformation with ammonia is effected is cleaned first with a little nitric acid and then with water.

[1] For details of operation see chapter on Electrolytic Analysis.

(*B*) Supposing the two metals to be present in a nearly neutral solution, acidulate with acetic acid and add a solution of potassium bichromate. A yellow precipitate of lead chromate falls down which is insoluble in acetic acid. If only a trace of lead be present the precipitation will not take place immediately. Should the original solution contain free mineral acid, an excess of sodium acetate must be added instead of acetic acid. For quantitative purposes the precipitated lead chromate is best converted into sulphate before weighing (see page 332, *C*).

Separation of Lead from Mercury

Rose's method of precipitating mercury protochloride from the solution by the addition of hydrochloric acid and phosphorous acid, is not applicable to the separation of mercury and lead. A portion of the lead is precipitated in the state of chloride with the mercury protochloride. A better plan for analysing a mixture of the salts of these two metals is to add sulphuric acid, and then alcohol forming about $\frac{1}{6}$ of the volume of the liquid. If this does not contain sufficient hydrochloric acid, and if the proportion of sulphuric acid is insufficient, yellow mercury subsulphate may be precipitated, which is avoided by the addition of sulphuric acid. The lead sulphate requires washing with weak alcohol acidulated with sulphuric acid.

Separation of Lead from Silver

(*A*) R. Benedict and L. Gaus have founded a process on the different behaviour of silver and lead iodides with dilute nitric acid. The solution containing silver nitrate and lead nitrate—in all about 0·5 grm. of metal—is diluted with cold water in a capacious glass capsule to from 200 to 300 c.c., and a solution of potassium iodide more than sufficient for the complete precipitation of the silver, but not excessive in quantity, is allowed to flow in. If 0·5 grm. of metal is used, 10 c.c. of a 10-per-cent. solution of potassium iodide will be sufficient in any case. Then add 10 c.c. of nitric acid free from chlorine, previously diluted with from 10 to 20 c.c. of water. The capsule is covered with a watch-glass and heated on the water-bath, when the yellow colour of the precipitate passes at first into orange-red.

As soon as the liquid has become hot, the lead iodide dissolves, the liquid becomes dark brown, and vapours of iodine are given off. The watch-glass is then removed and rinsed into the capsule, boiling water is added, and the capsule is left on the water-bath, adding water from time to time to compensate for the loss by evaporation until the liquid has become colourless or pale yellow, when the iodine is expelled. The silver iodide is then weighed. The authors collect it in a small glass tube filled with glass wool, dry at 110°, and weigh. Wash it first with

hot water containing nitric acid, and then with a few c.c. of hot water, dry at 110°, and weigh.

The presence of other metals of the same group, with the exception of mercury, does not interfere. Cuprous iodide, bismuth, and cadmium iodide behave with nitric acid like lead iodide; on the other hand, mercurous iodide is converted into red iodide, which is not further attacked.

In the examination of alloys of lead and silver proceed in the same manner. Dissolve in nitric acid, dilute, precipitate with potassium iodide, and heat on the water-bath.

For determining silver in impure leads, from 10 to 50 grms. of the same, according to the proportion of silver, is dissolved in dilute nitric acid containing tartaric acid. To 10 grms. of the sample, use 10 c.c. nitric acid free from chlorine, and an equal quantity of a saturated solution of tartaric acid. The presence of the latter effects much more rapid and complete solution. The solution is heated until the oxidation is completed, diluted with boiling water, filtered into a glass capsule, diluted to from 300 to 500 c.c., allowed to cool, 10 c.c. of a 10-per-cent. solution of potassium iodide are added, and it is heated on the water-bath.

The excess of the nitric acid added for solution is generally sufficient for oxidising the lead iodide; if the development of iodine vapours and the brown colour do not appear, a little more dilute nitric acid must be added.

The proportion of silver in galena may be determined in the same manner. It is oxidised with nitric acid with the addition of tartaric acid. It is most convenient to use equal volumes of nitric acid, solution of tartaric acid, and water. After the oxidation is completed, the liquid diluted with hot water, filtered, and well washed with boiling water, the filtrate is allowed to cool. The process is then completed as above.

(*B*) This is, perhaps, the most appropriate place to describe the valuable improvements which the late Mr. D. Forbes made in the separation of silver and lead before the blowpipe. This assay process is in all cases based upon the reduction to a metallic state of all the silver contained in the compound in question along with more or less metallic lead, which latter metal, when not already present in sufficient quantity in the substance itself under examination, is added in the state of granulated lead to the assay previous to its reduction. The globule of silver-lead thus obtained is soft and free from such elements as would interfere with its treatment upon the cupel, and may then be at once cupelled before the blowpipe until the pure silver alone remains upon the bone-ash surface of the cupel; but if not, it is previously submitted to a scorifying or oxidising treatment upon charcoal until all such substances are either slagged off or volatilised, and the resulting silver-lead globule cupelled as before.

As, therefore, the final operation in all silver assays is invariably that of cupelling the silver-lead alloy obtained from the previous reduction of the substance, effected by methods differing according to the nature of the argentiferous ore or compound under examination, it is here considered advisable to introduce the description of the silver assay by an explanation of this process.

In the ordinary process of cupellation in the muffle, bone-ash or other cupels are employed, of a size large enough to absorb the whole of the litharge produced from the oxidation of the lead in the assay.

This, however, should not be the case when using the blowpipe; for, as the heating powers of that instrument are limited, it is found in practice much better to accomplish this result by two distinct operations—the first being a concentration of the silver-lead, in which the greater part of the lead is converted by oxidation into litharge, remaining upon, but not, or only very slightly, absorbed by the bone-ash cupel; the second consisting in cupelling the small concentrated metallic bead so obtained upon a fresh cupel until the remaining lead is totally absorbed by the cupel and the silver left behind in a pure state. By this means a much larger weight of the silver-lead alloy can be submitted to assay, and, for reasons hereafter to be explained, much more exact results are obtained than would be the case when the cupellation is conducted at one operation in the ordinary manner.

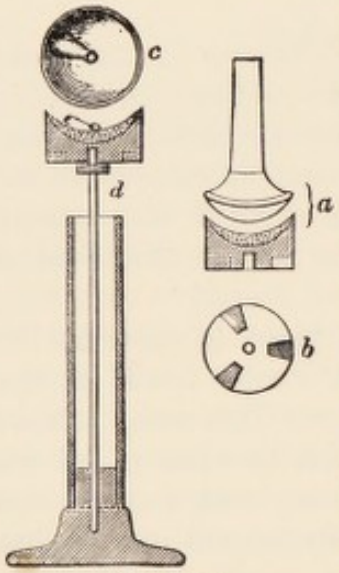


Fig. 19.

The apparatus used by the late Mr. Forbes for these operations are shown to a scale of one-half their real size in the woodcut (fig. 19, *a* to *d*).

In fig. 19, *a*, is represented in section a small cylindrical mould of iron, 0·7 of an inch in diameter and about 0·4 high, in which is turned a cup-shaped, nearly hemispherical depression, 0·2 of an inch deep in centre, the inner surface of which is left rough, or marked with minute ridges and furrows for the purpose of enabling it to retain more firmly the bone-ash lining, which is stamped into it by means of the polished bolt also shown in the figure. This mould rests upon the stand, *d*, having for this purpose a small central socket in its base, into which the central pivot of the stand enters. The socket is seen in the ground-plan, *b*, of the base of the mould, which shows likewise three small grooves or slots made in it to enable a steady hold to be taken of it, when hot, by the forceps. The stand itself is composed of a small turned ivory or wood base, fixed into a short piece of strong glass tubing, which, from its non-conducting powers, serves as an excellent handle. In the centre of the base a slight iron rod rising

above the level of the glass outer tube serves as a support for the cupel mould, into the socket in the base of which it enters.

Bone-ash is best prepared by burning bones which have been previously boiled several times, so as to extract all animal matter. The best bone-ash is made from the core-bone of the horns of cattle well boiled out and burned. The ash from this is more uniform than from the other bones, which have in general a very compact enamel-like exterior surface, while the interior is of a much softer nature.

Concentration of the Silver-Lead.—A cupel is prepared by filling the above-described cupel mould with bone-ash powder not finer than will pass through a sieve containing from 40 to 50 holes in the linear inch ; it should be well dried and kept in an air-tight bottle, and when used, the whole must be pressed down with the bolt, using a few taps of the hammer. It is then heated strongly in the oxidising blowpipe flame, in order to drive off any hygroscopic moisture. The bone-ash surface of the cupel, after heating, should be smooth, and present no cracks ; if the reverse, these may be removed by using the bolt again and re-heating.[1] The silver-lead, beaten on the anvil into the form of a cube, is placed gently upon the surface of the bone-ash, and, directing a moderately strong oxidising flame on to its surface, it is fused, and quickly attains a bright metallic appearance, and commences to oxidise with a rapid rotatory movement. (Occasionally, when the assay is large, and much copper or nickel present, the globule may, under this operation, cover itself with a crust of lead oxide, or solidify ; in such cases direct the blue point of a strong flame steadily on to one spot on the surface of the lead-globule until it commences oxidising and rotating. In some cases, where much nickel is present, an infusible scale, impeding or even preventing this action, may form, but will disappear on adding more lead—say from 3 to 6 grains, according to the thickness of this scale or crust.) When this occurs the cupel is slightly inclined from the lamp, a fine blue point is obtained by placing the blowpipe nozzle deeper into the lamp, and the flame is directed at about an angle of 30° on to the globule—not, however, so near as to touch it with the blue point, but only with the outer flame, so moderating it as to keep the assay at a gentle red heat, and not allowing the rotation to become too violent.

This oxidising fusion should be carried on at the lowest temperature sufficient to keep up the rotatory movement, and to prevent a crust of litharge accumulating upon the surface of the globule, but still sufficiently high to hinder the metallic globule from solidifying. Should this, however, happen, a stronger flame must be employed for a moment until the metal is again in rotation ; such interruptions should, however, be avoided. The proper temperature can only be

[1] These precautions are very important, as the slightest trace of moisture in the substance of the bone-ash would inevitably cause a spirting of the metal during the operation.

learned by practice, a too high temperature is still more injurious, causing the lead to volatilise, and, if rich in silver, to carry some of that metal mechanically along with it. The litharge, also, instead of remaining on the cupel would be absorbed by the bone-ash, and as the surface of the metallic globule is covered by a too thin coating of fused litharge, some silver may be absorbed along with the litharge. In this operation, in order to avoid loss of silver, the fused globule should be always kept in contact with the melted litharge.

By the above treatment the air has free access to the assay, and the oxidation of the lead and associated foreign metals goes on rapidly. The surface of the melted globule, when poor in silver, shows a brilliant play of iridescent colours, which does not take place when very rich in silver. The litharge is driven to the edge of the globule, heaping itself up and solidifying behind and around it. When the globule becomes so hemmed in by the litharge as to present too small a surface for oxidation, the cupel is moved so as to be more horizontal (having been previously kept in an inclined position), thus causing the lead-globule to slide by its own weight on one side and expose a fresh surface to the oxidising action. When the lead is pure, the litharge formed has a reddish-yellow colour, but, if copper is present, is nearly black.

In concentrating silver-lead, it must be remembered that an alloy of lead and silver, if in the proportion of about 86 per cent. silver along with 14 per cent. lead, when cooled slowly in the litharge behaves in a manner analogous to the spitting of pure silver, throwing out a whitish-grey pulverulent excrescence rich in silver. For this reason, therefore, the concentration above described should be stopped when the globule is supposed to contain about 6 parts silver along with 1 part in weight of lead. In case, however, this limit should have been exceeded, it is advisable at once to push the concentration still further until the silver globule contains but very little lead. In practice, with poor ores, it is usual to concentrate the lead until the globule is reduced to the size of a small mustard seed, or in rich ores to some two or three times that size. Upon arriving at this point, the cupel is withdrawn very gradually from the flame, so that the cooling shall take place as slowly as possible until the globule has solidified in its envelope of litharge. If cooled too quickly, the litharge, contracting suddenly, would throw out the globule, or even cause it to spirt; in such case it should be touched by the point of the blue flame so as to re-form it into a round globule, which is cooled slowly as before described. The globule is now reserved for the next operation, for which purpose it is, when quite cold, extracted from the litharge surrounding it.

Cupellation.—The bone-ash required for this process should be of the best quality and in the most impalpable powder, prepared by elutriating finely ground bone-ash and drying the product before use.

The cupel, still hot from the last operation, is placed upon the anvil,

and the crust of litharge, with its enclosed metallic bead, gently removed, leaving the hot coarse bone-ash beneath it in the mould ; upon this a small quantity of the elutriated bone-ash is placed, so as to fill up the cavity, and the whole while hot stamped down by the bolt, previously slightly warmed, with a few taps of the hammer. The cupel thus formed is heated strongly in the oxidising flame, which should leave the surface perfectly smooth, and free from any fissures or scales ; if such appear, the bolt must again be used, and the cupel re-heated. In this process it is very important that the cupel should possess as smooth a surface as possible, while at the same time the substance of the cupel beneath should not be too compact, so as thereby to permit the litharge to filter through and be readily absorbed, leaving the silver bead upon the smooth upper surface.

The bead of silver-lead obtained from the last operation is taken out of the litharge in which it is embedded, and, after removing any trace of adherent bone-ash or litharge, is slightly flattened to prevent its rolling about upon the surface of the cupel.

It is now put into the cupel prepared as before described, placing it on the side farthest from the lamp and a little above the centre of the cupel, which is now inclined slightly towards the lamp, and is heated by the oxidising flame directed downwards upon it, thus causing the globule when fused and oxidising to move of itself into the centre of the cupel. The cupel is now brought into a horizontal position, and the flame, directed on to it at an angle of about 45°, is made to play upon the bone-ash surface immediately surrounding the globule, without, however, touching it; so as to keep this part of the cupel at a red heat sufficiently strong to ensure the globule being in constant oxidising fusion, and at the same time to cause the perfect absorption of the litharge, and prevent any scales of litharge forming upon the surface of the cupel under the globule, which would impede the oxidation, as well as prevent the silver bead being easily detached at the conclusion of the operation. Should the heat at any time be too low and the globule solidify, it must be touched for an instant with the point of the flame and proceeded with as before. Should (in consequence of the bone-ash not having been sufficiently heated to absorb the litharge perfectly) a little litharge adhere pertinaciously to the globule, or a particle of the bone-ash cupel attach itself, the cupel should be slightly inclined, so as to allow the globule to move by its own weight on to another and clean part of the cupel, leaving the litharge or bone-ash behind it ; but, if not sufficiently heavy to do so, a small piece of pure lead may be fused to it in order to increase its weight, and so allow of the same proceeding being adopted.

By slightly inclining the cupel stand, and moving it so as to present in turn all parts of the surface surrounding the globule to the action of the flame, the cupellation proceeds rapidly. If, however the assay contains very little silver, it will be found necessary to move

the globule from one spot to another on the cupel, in order to present a fresh surface for absorbing the litharge formed; this is done by simply inclining the cupel stand, remembering that the bone-ash surrounding the globule must always be kept at a red heat, without ever touching the globule itself by the flame.

In assays rich in silver a play of iridescent colours appears some seconds before the 'brightening,' which disappears the moment the silver becomes pure; as soon as this is observed the cupel should be moved in a circular manner, so that the globule is nearly touched all round by the point of the blue flame, and this is continued until the surface of the melted silver is seen to be quite free from any litharge, upon which it is very gradually withdrawn from the flame, so as to cool the assay by degrees very slowly, in order to prevent 'spitting.'

When the silver-lead is very poor, this play of colours is not apparent, and as soon as the rotatory movement of the globule ceases, the heat must be increased for an instant in order to remove the last thin but pertinacious film or scale of litharge, and subsequently the assay is cooled gradually; when cold it should, while still upon the cupel, be examined by a lens to see whether the bead possesses a pure silver colour, as if not it must be re-heated.

Frequently, when the 'brightening' takes place, the silver globule is found to spread out, and, after cooling, although of a white colour, is found to appear somewhat less spherical or more flattened in shape than a corresponding globule of pure silver would be. This arises from the presence of copper still remaining in the silver, and in such cases a small piece of pure lead (about from 0·5 grain to 1·5 grain in weight, according to size of assay) should be fused on the cupel along with the silver, and the cupellation of the whole conducted as before on another part of the cupel, when the silver globule will be obtained pure and nearly spherical in shape. Sometimes the silver globule in 'brightening' may still remain covered with a thin film of litharge, although otherwise pure; this arises from too little heat having been employed in the last stage of the operation, and consequently the bead should be re-heated in a strong oxidising flame until this litharge is absorbed, and the globule, after slow cooling, appears pure.

If the instructions here given be strictly attended to, it will be found, after some practice, that very accurate results may be obtained in the blowpipe assay for silver, and that no difficulty will be found in detecting the presence and estimating the amount of silver present, even when in as small a quantity as 0·5 ounce to the ton. When substances containing very little silver, or less than that amount, are examined, several assays should be made, and the silver-lead obtained concentrated separately, after which the various globules should be united and cupelled together in one operation.

It is hardly necessary to remark that the lead employed in assaying should be free from silver, or, if not, its actual contents in silver should be estimated, and subtracted from the amount found in the assay.

Assay lead containing less than 0·25 ounce to the ton of lead can readily be obtained, or can be made by precipitating a solution of lead acetate by metallic zinc, rejecting the first portion of lead thrown down. In all cases the lead should be fused and granulated finely—the granulated lead for use in these assays being previously passed through a sieve containing 40 holes to the linear inch. It is also useful to have some lead in the form of wire, as being very convenient for adding in small portions to assays when on the cupel.

Estimation of the Weight of the Silver Globule obtained on Cupellation.—As the amount of lead which can, by the method above described, be conveniently cupelled before the blowpipe is necessarily limited, the silver globule which remains upon the bone-ash surface of the cupel at the end of the operation is, when substances poor in silver have been examined, frequently so very minute that its weight could not be determined with correctness by the most delicate balances in general use.

Globules of silver of far less weight than $\frac{1}{1000}$ of a grain are distinctly visible to the naked eye—a circumstance which induced Harkort to invent a volumetric scale based upon the measurement of the diameters of the globules, which scale in practice has been found of very great utility in the blowpipe assay of silver.

The scale for this purpose consists of a small strip of highly polished ivory about $6\frac{1}{2}$ inches long, $\frac{2}{3}$ inch broad, and $\frac{1}{8}$ inch in thickness, on which are drawn, by an extremely fine point, two very fine and distinct lines emanating from the lower or zero point, and diverging upwards until, at the distance of exactly 6 English standard inches, they are precisely $\frac{1}{25}$ of an inch apart. This distance (6 inches) is divided into 100 equal parts by cross lines numbered in accordance from zero upwards. It is now evident, if a small globule of silver be placed in the space between these two lines, using a magnifying-glass to assist the eye in moving it up or down until the diameter of the globule is exactly contained within the lines themselves, that we have at once a means of estimating the diameter of the globule itself, and therefrom are enabled to calculate its weight.

As the silver globules which cool upon the surface of the bone-ash cupel are not true spheres, but are considerably flattened on the lower surface where they touch and rest upon the cupel, it follows that the weight of globules corresponding in diameter to the extent of divergence at the different degrees of the scale cannot be calculated directly from their diameters as spheres, but require to have their actual weight experimentally estimated in the same manner as employed by Plattner.

The table here appended is an abstract of one calculated by Forbes; in one column it shows the diameter in English inches corresponding to each number or degree of the scale itself, and in the next column the respective weights of the flattened spheres which correspond to each degree or diameter. For ordinary purposes the intermediate weights may safely be obtained by interpolation, but if great accuracy is needed the full table should be consulted. It is given in the *Chemical News* for June 7, 1867, vol. xv. p. 281.

No. on scale	Greatest diameter in inches	Weight of globule in grains
1	0·0004	0·00000005
2	0·0008	0·00000044
3	0·0012	0·00000149
4	0·0016	0·00000355
5	0·0020	0·0000069
6	0·0024	0·0000119
7	0·0028	0·0000190
8	0·0032	0·0000284
9	0·0036	0·0000403
10	0·0040	0·0000554
15	0·0060	0·0001872
20	0·0080	0·0004437
25	0·0100	0·0008667
30	0·0120	0·0014976
40	0·0160	0·0035550
50	0·0200	0·0069335
60	0·0240	0·0119815
70	0·0280	0·0190256
80	0·0320	0·0284000
90	0·0360	0·0404368
100	0·0400	0·0554688

These weights are calculated from the following data, found as the average result of several very careful and closely approximating assays, which showed that globules of silver exactly corresponding to No. 95 on this scale, or 0·038 inch in diameter, possessed a weight of 0·0475573 grain. From this the respective weights of all the other numbers or degrees on this scale were calculated, on the principle that solids were to one another in the ratio of the cubes of their diameters. This mode of calculation is not, however, absolutely correct in principle, for the amount of flattening of the under surface of the globule diminishes in reality with the decreasing volume of the globule. In actual practice this difference may be assumed to be so small that it may be neglected without injury to the correctness of the results.

The smaller the diameter of the globule, the less will be the difference or variation in weight in descending the degrees of this scale, since the globules themselves vary in weight with the cubes of their diameters; for this reason, also, all such globules as come within the scope of the balance employed should be weighed in preference to

being measured, and this scale should be regarded as more specially applicable to the smaller globules beyond the reach of the balance.

Cupellation Loss.—This term is applied to indicate a minute loss of silver, unavoidably sustained in the process of cupellation, which arises from a small portion of that metal being mechanically carried along with the litharge into the body of the cupel. The amount of this loss increases with the quantity of lead present in the assay (whether contained originally in the assay or added subsequently for the purpose of slagging off the copper, &c.); it is relatively greater as the silver globule is larger, but represents a larger percentage of the silver actually contained in the assay in proportion as the silver globule obtained diminishes in size. It has, however, been experimentally proved that in assays of like richness in silver, this loss remains constant when the same temperature has been employed and similar weights of lead have been oxidised in the operation.

In the blowpipe assay this loss is not confined to the ultimate operation of cupellation, but occurs, though in a less degree, in the concentration of the silver-lead, and in the previous scorification of the assay, when such operation precedes the concentration. The total loss in the blowpipe assay is found, however, to be less than in the ordinary muffle assay, since, in the latter case, the whole of the oxidised lead is directly absorbed by the cupel.

In mercantile assays of ore it is not customary to pay attention to the cupellation loss, and the results are usually stated in the weight of silver actually obtained. Where, however, great accuracy is required, especially when the substances are very rich in silver, the cupellation loss is added to the weight of the silver globule obtained in order to arrive at the true percentage.

The amount to be added for this purpose is shown in the annexed table on page 348, which is slightly modified from Plattner's.

The use of the table is best explained by an example, as the following:—An assay to which there had been added, in all, five times its weight of assay lead, gave a globule of silver equivalent to 6 per cent. Upon referring to the table, it will be seen that the cupellation loss for this would be 0·07; consequently, the true percentage of silver contained in the assay would be 6·07. This table is only extended to whole numbers, but fractional parts can easily be calculated from the same.

When the globules of silver are so minute that they cannot be weighed, but must be measured upon the scale, the cupellation loss should not be added, since, as a rule, it would be less than the difference which might arise from errors of observation likely to occur when measuring their diameters upon the scale.

In the case of beginners, it will be found that the cupellation is usually carried on at too high a temperature, and that thereby a greater loss is occasioned than would be accounted for by the following table.

Actual percentage of silver found by assay	Cupellation loss, or percentage of silver to be added to the actual percentage found by assay in order to show the true percentage of silver contained in same, the entire amount of lead in or added to the assay being the following multiples of the original weight of assay :—									
	1	2	3	4	5	6	8	11	13	16
99·75 } 99·50 }	0·25	0·32	0·39	0·45	0·50	—	—	—	—	—
90 ...	0·22	0·29	0·36	0·42	0·47	0·69	0·83	—	—	—
80 ...	0·20	0·26	0·33	0·39	0·44	0·64	0·75	—	—	—
70 ...	0·18	0·23	0·29	0·35	0·40	0·58	0·68	0·82	—	—
60 ...	0·16	0·20	0·26	0·30	0·36	0·52	0·61	0·74	—	—
50 ...	0·14	0·17	0·23	0·26	0·32	0·46	0·54	0·65	—	—
40 ...	0·12	0·15	0·20	0·22	0·27	0·39	0·46	0·55	0·62	—
35 ...	0·11	0·13	0·18	0·18	0·25	0·36	0·42	0·50	0·57	—
30 ...	0·10	0·12	0·16	0·16	0·22	0·32	0·38	0·45	0·51	—
25 ...	0·09	0·10	0·14	0·14	0·20	0·29	0·34	0·40	0·45	—
20 ...	0·08	0·09	0·12	0·12	0·17	0·25	0·29	0·35	0·39	0·45
15 ...	0·07	0·08	0·10	0·11	0·15	0·20	0·23	0·28	0·32	0·37
12 ...	0·06	0·07	0·09	0·10	0·13	0·17	0·19	0·23	0·26	0·32
10 ...	0·05	0·06	0·08	0·09	0·11	0·15	0·17	0·20	0·23	0·27
9 ...	0·04	0·05	0·07	0·08	0·10	0·14	0·16	0·18	0·21	0·25
8 ...	0·03	0·04	0·06	0·07	0·09	0·13	0·15	0·16	0·18	0·22
7 ...	0·02	0·03	0·05	0·06	0·08	0·12	0·13	0·14	0·16	0·20
6 ...	0·01	0·02	0·04	0·05	0·07	0·10	0·11	0·12	0·14	0·17
5 ...	—	0·01	0·03	0·04	0·06	0·09	0·10	0·11	0·12	0·14
4 ...	—	—	0·02	0·03	0·05	0·07	0·08	0·09	0·10	0·11
3 ...	—	—	0·01	0·02	0·04	0·05	0·06	0·07	0·08	0·09
2 ...	—	—	—	0·01	0·03	0·04	0·04	0·05	0·06	0·07
1 ...	—	—	—	—	0·01	0·03	0·03	0·04	0·04	0·05

After some trials, the necessary experience will be acquired in keeping up the proper temperature at which this operation should be effected.

It is not necessary to consider in detail the processes requisite for extracting the silver contents (in combination with lead) from the various silver ores and other argentiferous compounds which are met with in nature or produced in the arts, as this would be to exceed the limits of analysis proper. The following classification of substances will, however, be found convenient :—

I. Metallic Alloys.

A. Capable of direct cupellation.

a. Consisting chiefly of lead or bismuth : silver, lead, and argentiferous bismuth, native bismuthic silver.

b. Consisting chiefly of silver : native silver, bar silver, test silver, precipitated silver, retorted silver amalgam, standard silver, alloys of silver with gold and copper.

c. Consisting chiefly of copper : native copper, copper ingot, sheet or wire, cement copper, copper coins, copper-nickel alloys.

B. Incapable of direct cupellation.

a. Containing much copper or nickel, with more or less sulphur, arsenic, zinc, &c.: unrefined or black copper, brass, german silver.

b. Containing tin: argentiferous tin, bronze, bell-metal, gun-metal, bronze coinage.

c. Containing antimony, tellurium, or zinc.

d. Containing mercury: amalgams.

e. Containing much iron: argentiferous steel, bears from smelting furnaces.

II. Mineralised Compounds.

a. Silver and other ores, furnace products, sweeps, and products of the arts containing sulphides, arsenides, and other compounds of the metals in combination with more or less earthy matters.

b. Argentiferous molybdenum sulphide.

c. Substances nearly free from sulphides or arsenides, but containing chlorine, iodine, or bromine.

d. Argentiferous litharge and other easily reducible oxides.

To give information on the treatment of these substances belongs to the subject of assaying, a branch of analysis of which we have not space now to treat. The reader who wishes to follow out the subject is referred to *A Manual of Practical Assaying*,[1] edited by the author of this work.

Electrolytic Separation of Lead from Silver[2]

As silver is deposited quantitatively as metal in a solution containing free nitric acid, and the lead is separated out as peroxide on the positive electrode, both metals may be determined in the same solution.

Electrolytic Separation of Lead from Mercury[3]

In a nitric solution mercury behaves like silver, and can be separated from lead in the same manner.

Separation of Lead from Zinc

(*A*) The best method of separating small quantities of lead from zinc, as in the analysis of commercial spelter, is to add potassium bichromate and acetic acid to the neutral solution of the metals. A trace of lead causes the formation of a yellow precipitate. For further particulars see page 331, *A*.

(*B*) For the separation of a mixture of lead, zinc, and silver,

[1] London: Longmans & Co. 1888.

[2] For details of operation see chapter on Electrolytic Analysis. [3] Ibid.

F. Maxwell Lyte treats the ore, ground and calcined, with dilute hydrochloric acid in troughs of resinous wood, into which steam is blown to raise the temperature. The zinc, lead, and silver are thus converted into chlorides, the argentic and a part of the plumbic chloride remaining mixed with the gangue. The liquid is then run off, and allowed to cool, when nearly the whole of the plumbic chloride is deposited. The clear mother-liquor, containing zinc chloride and excess of hydrochloric acid, is syphoned back into the first tank, where it takes up a fresh quantity of lead and silver chlorides, the gangue being thus exhausted after three successive decantations. To the entire solution now existing in the second tank, scrap-zinc is added, when all the lead and silver is deposited as a metallic sponge. (It must be remembered that silver chloride is soluble in concentrated solutions of lead chloride.) From the residual liquor the zinc is precipitated as oxide by the addition of milk of lime.

Electrolytic Separation of Lead from Cadmium [1]

Classen proceeds as in separating lead from copper. The lead is deposited as peroxide in a nitric solution, the platinum capsule being connected with the positive pole of the source of current. In order to determine cadmium in the residual liquid, the nitric acid is expelled by evaporation in the water-bath, the cadmium is converted into sulphate, and determined as previously directed.

Separation of Lead from Barium when in the Form of Sulphates

Sodium thiosulphate dissolves lead sulphate, and may be used to separate this salt from the barium sulphate. To effect this separation a concentrated solution of the thiosulphate must be added to the mixture of the two salts, and the whole gently warmed, taking care that the temperature does not exceed 68° C.; at a higher temperature lead sulphite is formed, which is insoluble in the thiosulphate.

The residue of barium sulphate is carefully washed and weighed; to control the results the lead in the thiosulphate may be estimated.

White Lead

Commercial white lead is frequently adulterated with barium sulphate and calcium carbonate. The presence of barium sulphate may be tolerated when its proportion does not exceed 5 per cent.

Gaston Tissandier proposes the following method of analysis:— Weigh 1 gramme of white lead, and calcine it in a small porcelain capsule; treat the residue, while hot, with pure nitric acid diluted with

[1] For details of operation see chapter on Electrolytic Analysis.

water ; this dissolves the lead oxide, while the barium sulphate remains insoluble.

Now filter, and precipitate the filtered liquid with sulphuretted hydrogen ; a formation of lead sulphate will then ensue, and this must be dried at 100° C. and weighed. The liquid, separated from lead sulphide, is treated with ammonia and ammonium sulphydrate, which will betray the presence of zinc oxide, which sometimes occurs in white lead, by precipitating it as zinc sulphide. Filter this latter, and evaporate the filtered liquid to dryness, previously adding hydrochloric acid : take up the residue with water and hydrochloric acid and add ammonia and ammonium oxalate, which will precipitate the lime as insoluble calcium oxalate.

The lead sulphide is converted by calcination into carbonate ; the zinc sulphide is dissolved in hydrochloric acid after calcination, and precipitated as zinc carbonate. The zinc carbonate is collected on a filter, washed with boiling water, dried, calcined, and weighed ; the calcination transforms it into zinc oxide, which is thus extracted directly from the specimen of white lead under examination.

To ascertain whether the white substance which was insoluble in the acid liquid used in the first experiment be really barium sulphate, proceed as follows :—Mix it thoroughly with dry, pure, finely powdered sodium carbonate ; heat it to redness in a platinum crucible, until the liquid mass no longer effervesces, let it cool, and boil it in water, which dissolves the sodium sulphate formed, without acting upon the barium carbonate which is formed during the reaction. The aqueous solution should be precipitated by barium chloride, which determines the formation of insoluble barium sulphate ; the insoluble substance remaining on the filter is treated with pure hydrochloric acid diluted with water, and should yield a precipitate of barium sulphate on the addition of a drop of sulphuric acid.

Separation of Lead from Thallium

(*A*) In analytical operations, these metals may be separated like thallium and bismuth ; or the lead may be precipitated as sulphate, while the thallium sulphate will remain in solution. Sulphuretted hydrogen in an acid solution will also precipitate the lead, and leave the thallium dissolved. If the metals are in the form of insoluble salts, boil the mixture in aqua regia, which will convert the thallium into the perchloride and will leave most of the lead in the insoluble condition. The small quantity of lead which gets into solution is easily separated by the addition of a few drops of sulphuric acid.

(*B*) If a solution of sodium thiosulphate be added to a neutral or alkaline solution of a lead salt, a white precipitate of lead thiosulphate is first formed, which dissolves on adding excess of the precipitant, a complex double salt of lead and sodium thiosulphate being probably

formed, each molecule of lead thiosulphate requiring 10 molecules of sodium thiosulphate before complete solution is effected. From such a solution lead is not precipitated by the majority of the reagents of that metal, such as sulphates, chlorides, iodides, &c. If a solution of sodic thiosulphate be added to a neutral solution of a thallium salt, no precipitate is produced, and in such a solution containing excess of sodium, thiosulphate produces the characteristic yellow precipitate of thallous iodide. By taking advantage of this negative reaction of thallium E. A. Werner effects its separation from lead in a single operation. To the liquid containing both metals in solution (if acid the solution must be carefully neutralised beforehand) sodium thiosulphate is added until the precipitate first formed is entirely redissolved. Potassium iodide is then added until it produces a yellow precipitate. The thallium is thereby wholly removed, and the pure metal can be readily obtained from the washed and dried precipitate by fusion with potassium cyanide.

As a qualitative test for the detection of minute traces of thallium in presence of large quantities of lead this method almost rivals the spectroscope in delicacy. By means of it, 1 part of thallium in 653,600 parts of solution, and mixed with over 5,000 times its weight of lead, can be easily detected.

Separation of Lead from Gallium

This may be effected by six methods:—

(*A*) The hydrochloric solution, slightly acid, is diluted with a little water and submitted to ebullition in presence of an excess of cupric hydrate. The gallium precipitated retains but a feeble trace of lead, which is entirely eliminated by a second similar treatment. The reagents employed must be free from sulphuric acid or sulphates, or otherwise lead sulphate will remain upon the filter along with gallium oxide. The copper and the lead are then separated by known methods. The above process is very exact, and is suitable for removing from gallium sulphate the small quantity of lead which remains in solution after precipitation with sulphuric acid.

(*B*) The separation of lead is also effected accurately if the hydrochloric or sulphuric solution is boiled first with metallic copper and then with cuprous oxide. This method is specially applicable when iron has to be separated at the same time as lead. The first cuprous precipitate contains scarcely a feeble trace of lead, so that two operations are sufficient. If we operate upon a chloride the presence of sulphuric acid must be carefully avoided.

(*C*) The solution—sulphuric, hydrochloric, or nitric—perceptibly though moderately acid, is saturated with hydrogen sulphide, filtered, and evaporated almost to dryness, in order to expel the bulk of the free acid. It is then diluted with water, and again saturated with

hydrogen sulphide. After two or three similar treatments, the gallium salt no longer contains an appreciable trace of lead. The lead sulphides generally retain a trace of gallium, which may be removed by attacking them with concentrated hydrochloric acid, adding alcohol, filtering, evaporating to expel the alcohol and the bulk of the acid, diluting with water, and finally saturating with sulphuretted hydrogen.

(*D*) In a liquid containing from one-fourth to one-third of its volume of strong hydrochloric acid, potassium ferrocyanide precipitates gallium ferrocyanide, generally free from lead. In case of need the gallium salt may be taken up in a small quantity of potash and reprecipitated by adding much hydrochloric acid and a little potassium ferrocyanide.

(*E*) It is often convenient to begin by precipitating almost all the lead by means of sulphuric acid. The liquid is then mixed with double its volume of alcohol at 90°. If properly washed with alcohol, acidulated with sulphuric acid, the lead sulphate does not contain apprcciable traces of gallium. To detect such traces the lead sulphate is suspended in water, acidulated with hydrochloric acid, and treated with a prolonged current of hydrogen sulphide. The filtrate is boiled in order to expel hydrogen sulphide, and treated in heat with cupric hydrate, which precipitates the traces of gallium oxide. The alcoholic solutions derived from the sulphuric precipitation of lead are freed from alcohol by boiling ; the gallium oxide is then separated by means of cupric hydrate.

(*F*) The solution (nitric or other) is mixed with twice its volume of alcohol at 99 per cent., and a small excess of hydrochloric acid. The lead chloride when washed with acidulated alcohol does not retain gallium. The alcoholic liquids are concentrated to a small volume, freed from nitric acid, and treated either with hydrogen sulphide (process *C*), or with cupric hydrate, or metallic copper and cuprous oxide (processes *A* and *B*).

Volumetric Estimation of Small Quantities of Lead in the Presence of Free Hydrochloric Acid

A. P. Laurie has used the direct estimation by titration with bichromate of potash, using silver nitrate as an indicator.

He found that the behaviour of the indicator was affected by the presence of chlorides. On adding a drop of the solution to a drop of silver nitrate on a white plate, before the bichromate is in excess, a white precipitate of chloride is formed. As soon as a little excess of bichromate is present, the white precipitate of chloride is dyed yellow, so that the end of the reaction is indicated, not by the usual pinky colour, but by the yellow tint of the chloride.

The sensitiveness of this indication is affected by the amount of chloride present in the liquid to a certain extent. If very little chloride

is present, the amount of precipitate formed is too small to show the colouration distinctly, and if too much chloride is present the large quantity of the precipitate conceals the effect of the dye.

To obtain the most sensitive reaction, the amount of chloride present should be equivalent to from 0·5 to 0·2 gramme of sodium chloride in 100 c.c.

Under these conditions, 3 parts of bichromate in 1,000,000 parts of water will produce a perceptible change of tint in the silver chloride precipitation. In fact, the reaction is more sensitive than the pink colouration where no chloride is present.

In estimating the lead Laurie made use of a solution of bichromate made up to approximately precipitate 0·0002 gramme lead per 1 c.c. of solution, and standardised it against pure lead.

One serious practical difficulty is the obstinate way in which the lead precipitate remains floating in the liquid. This is fatal to the method, as any lead chromate taken up with the drop of liquid seems at once to stain the silver chloride, and so render the indicator useless. The best way to get over this difficulty is to add most of the bichromate necessary to precipitate the lead, and gradually raise the liquid to boiling with frequent stirring. This will cause most of the lead chromate to settle, merely leaving a little floating on the top. On touching the surface of the liquid this floating precipitate is repelled in all directions, and a little liquid can be withdrawn by means of a capillary pipette (made by drawing out a piece of glass tubing), and blown out into the drop of silver. The fresh precipitate formed on adding more bichromate will usually settle on stirring without much difficulty. The precipitate ceases to form just a little before the yellow reaction appears.

In order to obtain results which agree one with another, certain precautions must be taken. The presence of large quantities of other salts in the liquid should be avoided; the liquid, if acid, must be carefully neutralised; and sodium acetate must be added before titration. In standardising the solution the pure lead is dissolved in as little nitric acid as possible, ammonia is added till a slight permanent precipitate is produced, and then a little sodium chloride and some potassium acetate is added. The amount of potassium acetate added is about twice the weight of the lead present.

On adding the acetate to the neutral solution, basic salts usually separate, and the addition of the chloride causes a slight cloudiness as well. The long heating evidently converts these precipitates completely into chromate, and the result does not seem to be affected by the varying amounts of precipitate that may be formed.

Detection of Lead in Tin Paper

(*A*) A drop of concentrated acetic acid is dropped on the suspected leaf and a drop of a solution of potassium iodide is added. If lead is

present there is formed in two or three minutes a yellowish spot of lead iodide.

(*B*) Kopp moistens the leaf to be examined with sulphuric acid. If the tin is pure, the spot remains white, but if lead is present there is formed a black spot.

Detection of Lead in the Tin Linings of Vessels

Forpoz places, by means of a tube dipped in pure nitric acid, a slight layer of acid upon any part of the tinning, selecting by preference the thickest parts. Both metals are attacked, forming stannic oxide and lead nitrate. After a few minutes, heat slightly to expel the last traces of acid and allow to cool, then touch the pulverulent spot produced by the acid with a rod dipped in a solution of 5 parts of potassium iodide in 100 of water. The iodide has no action upon the tin oxide, but with the lead nitrate it reacts, forming yellow lead iodide, and showing the presence of even a small quantity of this metal. The surface of the tinning must be carefully cleaned before applying the nitric acid, and the acid should not penetrate to the iron or copper which forms the body of the vessel, as the reaction might thus be complicated.

BISMUTH

For the detection of small quantities of bismuth, Pattison Muir recommends Schneider's test liquid prepared as follows :—12 grammes crystalline tartaric acid and 4 grammes stannous chloride are dissolved in caustic potash so as to produce a clear liquid having a distinctly alkaline reaction ; it must remain clear at 60° to 70° C. To the liquid to be tested is added a considerable quantity of tartaric acid. It is warmed and made alkaline with caustic potash. A few c.c. of the test liquid are now added, and the mixture is heated for a few minutes to 60° or 70°. If bismuth is present a brownish-black colour is produced. One part bismuth may thus be detected in 210,000 parts of liquid. Mercury must be absent ; copper and manganese interfere slightly ; lead, arsenic, antimony, iron, cobalt, nickel, and chromium not at all.

Purification of Bismuth

A simple plan to purify bismuth is based on the fact that when a large quantity of water is added to its solution mixed with hydrochloric acid a completely insoluble precipitate of bismuth oxychloride is obtained. Dissolve the metal in nitric acid and evaporate down with excess of hydrochloric acid ; the residue consists of bismuth chloride. Add concentrated hydrochloric acid and heat till the residue is dissolved ; filter if necessary through a sand filter. Now pour the solution in a thin stream, with constant stirring, into a large quantity of cold

distilled water. A white precipitate of oxychloride is produced, which may either be weighed as such or reduced to the metallic state by fusion with potassium cyanide.

W. Muthmann and F. Mawrow[1] use hypophosphorous acid for the estimation of bismuth. With suitable precautions, it may be completely precipitated as metal by hypophosphorous acid.

The solution of the bismuth salt, in a state of moderate concentration, not too strongly acid, is mixed with an excess of hypophosphorous acid, and heated on the water-bath until the supernatant liquid has become perfectly clear, and a further addition of the reagent, heated to ebullition, produces no further colouration. The metal separates out in the form of a reddish-grey spongy mass, which can be easily filtered and washed. It is collected upon a weighed filter or in a Gooch crucible, washed with boiling water and then with absolute alcohol, and dried at 105°.

The results of four determinations on the same hydrochloric solution of bismuth are given below. In four experiments there were used respectively :—

BiOCl.	Obtained.	Bi per cent.
0·1158 gramme.	0·0926 gramme.	79·96
0·1559 ,,	0·1250 ,,	80·17
0·1201 ,,	0·0963 ,,	80·18
0·1068 ,,	0·0857 ,,	80·24

The average percentage being 80·13, and the calculated result 80·15.

The method is doubtless applicable for the separation of bismuth from metals which are not precipitated from their solutions by hypophosphorous acid, especially from zinc and cadmium.

L. Vanino and E. Treubert[2] also estimate bismuth in the metallic state by precipitating it with formaldehyde. A slightly acid solution of the bismuth salt is mixed with formaldehyde and a large excess of a 10-per-cent. solution of caustic soda. The mixture is heated on the water-bath and stirred continuously, until the metallic bismuth is entirely deposited and the supernatant liquid is perfectly clear. Then add an excess of formaldehyde and caustic soda, and heat over a Bunsen for several minutes. The precipitate is washed by decantation with boiling water, then kneaded with a stirring-rod to bring it into a compact mass. It is collected on a tared filter or in a Gooch crucible, washed with absolute alcohol, and dried at 105° C. This reaction can be utilised for the separation of bismuth from certain other metals, such as aluminium, zinc, &c.

Detection of Bismuth by the Blowpipe

(*A*) The mixture of equal parts of potassium iodide and sulphur recommended by Von Kobell for this excellent test has the great dis-

[1] *Chemical News*, Jan. 29, 1897. [2] *Ibid.* April 28, 1899.

advantage of being very deliquescent; even if kept in closely stoppered bottles it sooner or later becomes pasty, and indeed almost liquid, if the bottles are often opened for use. As it is a great advantage to be able to have such mixtures ready for use, and, where possible, to keep them in little wooden boxes in the portable blowpipe apparatus, W. M. Hutchings replaces the potassium iodide by cuprous iodide, and finds that, in addition to the advantage of being non-deliquescent, the mixture so made is in other respects superior for use with the test.

Von Kobell's mixture has another disadvantage, viz. that it itself yields a copious *white* sublimate, the brilliant red sublimate obtained when it is used with a substance containing a good deal of bismuth being caused by the mixture of this white with the dark brownish-red given by bismuth iodide alone. When very little bismuth is present and a good deal of the mixture is used, the white frequently overpowers the red almost completely, and when other metals are present which also give white or light-coloured sublimates, it greatly assists in concealing the bismuth colour. This disadvantage is also got rid of by using cuprous iodide and sulphur.

The precipitated cuprous iodide is washed free from all trace of potassium salts, dried perfectly, and then ground up to an intimate mixture with an equal volume, or rather more, of flowers of sulphur. This proportion is the best; when less sulphur is used, there is more or less white sublimate of cuprous iodide obtained, and also the formation of bismuth iodide is not as copious. For testing pyrites or other sulphides, less sulphur, or even none at all, would be required; but it is best to have a mixture which is equally applicable to *all* bismuth combinations. This mixture can be kept rammed tight into little wooden boxes, and is always ready for use. On an aluminium plate it is decidedly more delicate as a reagent than the potassium iodide mixture, using in each case 2 volumes of reagent to 1 volume of the powdered substance to be tested, intimately mixing to a paste and heating gently on a charcoal slip.

The merest trace of the dark brownish-red bismuth iodide is very conspicuous on the clean aluminium. The plate should be made pretty hot by blowing the flame upon it some distance above the ledge before commencing to heat the test mixture, in order to prevent the settling of a sublimate of *iodine*, or any condensation of moisture, which latter destroys the red bismuth sublimate. This precaution is particularly necessary when very little bismuth is present.

On ordinary charcoal or a blackened porcelain support, the dark-coloured bismuth iodide is not nearly so conspicuous as on aluminium, and does not show so well as the brighter red obtained by using potassium iodide. But a few tests with a substance containing very little bismuth will convince anybody that the aluminium plate, with the cuprous oxide mixture, is very much preferable to charcoal and potassium iodide.

Substances containing mercury, when treated with the iodide mixture on the aluminium plate, give a sublimate of mercuric iodide which is partly red and partly yellow, the relative quantities of the two colours varying much in sublimates from the same substance. The red is much lighter and brighter than that obtained from bismuth from the cuprous iodide mixture. It might possibly be taken for the bismuth sublimate mixed with that of lead; but as the number of minerals containing mercury is so limited, and the presence of that metal is so easily proved by other tests, no mistake is likely to arise from this cause.

The value of this test of Von Kobell's is very great; it deserves to rank as one of the best—in some cases the best—test for bismuth. As little as 0·2 or 0·1 per cent. can be safely detected by it in many cases, and with great rapidity. In pyritic ores which fuse to a regulus, or in smelted regulus, a considerable amount of bismuth might be present and not be detected by the ordinary sublimate of bismuth oxide, which is frequently very difficult to obtain from such combinations. But a fraction of 1 per cent. can be found by this test without resorting to the wet way.

(*B*) Substances containing lead give a copious light yellow sublimate when heated with the iodide and sulphur mixture, and when lead is present beyond certain limits this yellow overpowers the bismuth reaction. According to Cornwall, when lead oxide was mixed with 5 per cent. bismuth oxide, and tested on charcoal by Von Kobell's mixture, the bismuth could only just be detected, and not with distinctness. But when lead oxide containing only 1 per cent. bismuth oxide is tested with the cuprous iodide mixture on an aluminium plate, a fine brownish-red sublimate is always obtained by heating very gently and observing after a few seconds. Later on the yellow covers this up; but the bismuth iodide always comes off first, and can be seen if observed in time. In all cases sublimates must be allowed to get quite cold before judging them; lead iodide is reddish when hot, but pure light yellow when cold.

Cornwall's tests in open glass tubes which will detect bismuth when present in such small quantity with lead and antimony that the above method fails, can be better applied with the cuprous iodide mixture than with potassium iodide, and so much sulphur as he recommends (5 volumes) does not require to be added.

Estimation of Bismuth

(*A*) Pattison Muir estimates the metal by precipitating a nearly neutral solution of the nitrate by potassium chromate or bichromate in a manner similar to that proposed by Pearson, but he ascertains the critical point by testing the clear solution from time to time with argentic nitrate until red argentic chromate is produced; the

chromium solution being previously titrated with a solution of bismuth of known strength. The presence of chlorine, sulphuric acid, calcium, copper, or arsenic interferes seriously with the results obtained by this method.

(*B*) Very accurate results are obtained by another process devised by the same author. The nitric acid solution of bismuth is mixed with an excess of sodium acetate, a measured volume—excess—of standardised sodium phosphate is added, and the liquid boiled and filtered, the precipitate is well washed with hot water, and the excess of phosphoric acid estimated in the filtrate by titration with a standard solution of uranium acetate.

(*C*) Another method also due to Muir is as follows :—An excess of saturated solution of oxalic acid is added to the solution containing bismuth, the precipitate allowed to settle, the supernatant liquid poured off, and the precipitate boiled with water until free from acid. The residue is now dissolved in dilute hydrochloric acid and titrated with permanganate. The absence of free hydrochloric acid must be secured before precipitating. The results are accurate, and the method is generally applicable.

(*D*) Lastly, in a method proposed by Muir and Robbs, the bismuth oxide is dissolved in a minimum quantity of nitric acid, the solution freed from excess of nitric acid by evaporation, and a large excess of acetic acid added. An excess of standard potassium oxalate is added in a measuring-flask, and the double bismuth and potassium oxalate, and allowed to settle. An aliquot portion of the clear solution is drawn off and titrated with permanganate.

Electrolytic Separation of Bismuth[1]

(*A*) According to Classen, the electrolysis of bismuth presents difficulties in so far as it is not practicable to deposit considerable quantities of the metal upon platinum as a dense adhesive mass.

Bismuth is always obtained in the same state whether it is deposited from an acid solution from the double ammonium oxalate, or from a solution mixed with potassium tartrate. If a sufficiently large surface is provided, if the capsule used as a negative electrode is filled to the edge, then, if the quantity of bismuth is not large, the washing out with water and alcohol may be effected without loss. But if the particles of metal are detached from the capsule they must be collected upon a weighed filter and determined separately.

For the execution of the electrolysis the solution is mixed with a large excess of ammonium oxalate and reduced in the cold with a current of about 0·02 c.c. of detonating gas per minute. During the decomposition we observe at the positive electrode a separation of peroxide, which again gradually disappears. In order to protect the

[1] For details of operation see chapter on Electrolytic Analysis.

reduced metal from oxidation, it is necessary to remove the last traces of water by a plentiful washing with absolute alcohol.

(*B*) Good results may be obtained, according to A. Brand, if we mix the acid dilute solution of bismuth with four or five times the quantity of sodium pyrophosphate required for the formation of the double salt, render it exactly alkaline with ammonium carbonate, and dissolve in this liquid from 3 to 5 grammes ammonium oxalate. The solution is diluted to about 200 c.c. and there is then passed a current of from 0·1 to 0·5 c.c., which is gradually intensified until it reaches 2 to 3 c.c. of detonating gas per minute. If we begin with a current of 0·5 c.c. we may, according to Brand's experiments, reduce 0·25 gramme bismuth within twelve hours. If a slight veil of bismuth peroxide is deposited upon the positive electrode, it is removed towards the end of the precipitation with a few drops of oxalic acid. The end of the reaction is recognised by means of sulphuretted hydrogen water. Instead of determining the weight of the deposited metal, which is apt to become slightly oxidised, Brand proposes to convert it into oxide (Bi_2O_3), which is effected by dissolving in nitric acid and igniting the dried nitrate.

(*C*) Rüdorff proposes the following combined method for the determination of bismuth. On the assumption that the quantity of the metal in solution amounts as a maximum to 0·1 gramme he adds to the slightly nitric acid solution so much sodium pyrophosphate that the precipitate is redissolved, and then adds 20 c.c. of a saturated solution of potassium oxalate and an equal quantity of potassium sulphate. The liquid diluted to 120 c.c. is decomposed with the current of 4 Meidinger elements. The reduction requires at least twenty hours. The bismuth obtained is washed and then dried at 60° in the air-bath.

(*D*) G. Vortmann effects the separation of bismuth as an amalgam (see Zinc). The compound of bismuth, dissolved in a minimum of hydrochloric acid, is mixed with a weighed quantity of mercuric chloride, and so much potassium iodide is added that the precipitate produced at first is redissolved. After dilution with water he proceeds as directed for zinc. During the electrolysis the iodine is deposited on the surface of the liquid in the form of a mass of bubbles. When the reduction is completed, which is ascertained by means of ammonia and ammonium sulphide, Vortmann, without interrupting the current, adds a little concentrated soda-lye and accelerates the solution by stirring up the liquid with the positive electrode. If the intensified current is then allowed to act for an additional hour, the separation is complete.

This is ascertained by adding sodium sulphite and ammonium sulphite to a small portion of the liquid.

The amalgam is heated as described under Zinc.

(*E*) The use of potassium iodide may be avoided if the deposition of the amalgam is effected from a hydrochloric solution mixed with

alcohol. For this purpose the bismuth compound and the weighed quantity of mercuric chloride are dissolved in hydrochloric acid, and there are added about 50 c.c. of alcohol at 96 per cent. By degrees the liquid is diluted with so much water that the surface of the solution reaches to 1 cm. from the edge of the capsule, and electrolysed as usual.

Vortmann especially recommends the last method for the separation of larger quantities of bismuth.

Detection of Calcium Phosphate in Bismuth Subnitrate

Calcium phosphate is sometimes met with in bismuth subnitrate as an adulterant. It may easily be detected in the following way :—

To 1 part of the bismuth salt dissolved in weak nitric acid add 2 parts of citric acid ; dissolve with the aid of a little water ; add an excess of solution of ammonia and boil. Any phosphate present will be thrown down by continuous boiling of the solution.

Separation of Bismuth from Thallium

These elements frequently occur together in minerals containing bismuth, and thallium may often be detected in medicinal preparations of bismuth, especially the carbonate. The bismuth compound is to be first obtained in the form of a dilute solution, any convenient acid being used for this purpose. A slight excess of sodium carbonate is now added, and then a little potassium cyanide free from sulphide. The mixture is to be gently warmed and allowed to stand for ten minutes, then filtered, and a few drops of ammonium sulphide added to the clear liquid. If the slightest trace of thallium were originally present in the bismuth compound, it will now be precipitated as a sulphide, which, upon gently heating the liquid (not to the boiling-point), gradually collects together in deep brown, almost black flakes, after the characteristic manner of thallium sulphide.

This process is one of extreme delicacy. By means of it 1 part of thallium can be detected in the presence of more than 10,000 parts of bismuth. In some cases, the thallium is present in so small a quantity as to occasion only a slight darkening of the liquid when the ammonium sulphide is added. Upon allowing this to digest at a gentle heat, it will generally collect in the form of a few flakes at the bottom. These may be collected together on a small filter, washed to the apex, and tested in the spectroscope. When the precipitate is only present in sufficient quantity to produce a faint dark stain on the filter-paper, the latter may be partially dried by pressure between blotting-paper, opened, and the stained surface scraped up with a knife. The dark fibres are now to be twisted up in a platinum wire loop and held in the flame of the spectroscope, when they will give abundant indications of the presence of thallium.

Separation of Bismuth from Gallium

Three methods are to be recommended:—

(*A*) The distinctly acid hydrochloric solution is saturated with hydrogen sulphide. All the bismuth is obtained as sulphide, which retains no gallium. The operation succeeds even when the liquid has been rendered turbid by a previous dilution.

(*B*) The bismuth may be reduced by zinc in a solution which is kept distinctly acid, but it is better to use copper, which does not introduce impurities like zinc, and the ulterior separation of which from gallium is easy. The acid hydrochloric solution is treated for from twelve to eighteen hours with an excess of finely divided copper. The liquid is kept at a gentle heat all the time, which hastens the deposition of the bismuth. We find no bismuth in the liquid or gallium in the deposit. The formation of insoluble cuprous chloride is not an inconvenience.

(*C*) In a solution containing one-third of its volume of concentrated hydrochloric acid, and in presence of bismuth, gallium chloride is precipitated by potassium ferrocyanide, either in the cold or at 60° to 70°. The gallium ferrocyanide, well washed with hydrochloric water, retains no bismuth. It is to be remarked that, contrary to the statements of the chemical text-books, the precipitate formed by ferrocyanide with bismuth chloride is readily soluble in hydrochloric acid, even if dilute.

Boiling potash does not affect the exact separation of gallium from bismuth. The precipitated oxide is free from gallium, but the alkaline liquid retains a notable quantity of bismuth. It is generally, but erroneously, assumed that in analysis bismuth oxide is completely precipitated by potash.

Separation of Bismuth from Lead

(*A*) Add to the concentrated solution just enough hydrochloric acid to precipitate all the lead chloride, but so that a few drops of water do not render the liquid turbid. Then add dilute sulphuric acid, the slow action of which is hastened by occasional agitation; finally, after having added alcohol and well mixed the whole by renewed agitation, allow the lead sulphate to deposit. This precipitate is to be filtered and washed, first with alcohol containing a few drops of hydrochloric acid, and then with pure alcohol. The bismuth may be precipitated in the filtrate by dilution with a large quantity of water.

(*B*) There is no difficulty in volatilising bismuth in presence of lead by merely heating their sulphides in a glass tube in a current of bromiferous air, with a gas flame one and a half inch in height.

The mixed precipitated sulphides are dried at 100°, placed in a porcelain boat which has been previously weighed, and heated in a

current of air and bromine vapour. Bismuth bromide distils over completely, while lead bromide remains in the boat sufficiently pure for weighing. The receivers for the bismuth bromide should contain very dilute nitric acid.

For success the following precautions are absolutely necessary. The sulphides obtained must not be allowed to stand a long time, either in the liquid or in the funnel, &c., but the operation must be proceeded with as soon as possible. A too prolonged action of the air upon the mixed sulphides is decidedly injurious, and sometimes may lead to results which are completely worthless. Such preparations when subsequently heated in the current of bromine vapour do not yield simply pure bromides, but simultaneously basic compounds, a circumstance which more or less interferes with the complete volatilisation of the bismuth. P. Jannasch and P. Etz make the following arrangement. In the evening the solution is placed ready for the introduction of the sulphuretted hydrogen, so that the precipitation may be effected without loss of time the next morning. The filter is carefully lifted out of the funnel and dried, first on a flat porcelain capsule, and then in the funnel, so that in the afternoon, after the commencement of the analysis, they are able to undertake the heating in a current of bromine vapour. The expulsion of the bismuth by bromine succeeds best when a somewhat abundant quantity of sulphur is mixed with the precipitated sulphides. Hence it is advantageous to add to the hydrochloric solution of the metals a few drops of red, fuming nitric acid, prior to the introduction of the current of sulphuretted hydrogen.

The mixed sulphides in the porcelain boat, before their introduction into the glass tube, should be duly comminuted by means of a platinum rod, in order, on the one hand, to admit of a rapid and thorough action of the bromine, and on the other to prevent the projection of particles, which is apt to occur if the mass consists of large fragments.

The current of bromine from the very commencement of the operation should be rather rapid (about 300 gas bubbles per minute from a glass tube of 6 mm. in width), since a deficiency of bromine may interfere with the formation of the volatile bismuth tribromide, and may also allow of sublimation in the wrong direction. At the end of the operation, and while the tube is cooling, the current may be moderated accordingly.

As it is found disadvantageous to leave the mixed sulphides in the drying-closet at 100° too long, it is better to put an end to the desiccation as soon as the loss of weight of the substance does not exceed a few milligrammes in a quarter of an hour. Hence it appears necessary before commencing the bromine treatment to pass first a current of dry air over the substance in the boat at a very gentle heat, so that the moisture still present may be carried over into the receiver.

In the treatment with bromine an unnecessarily strong heat must

be avoided. A Bunsen flame of 8 cm. in height is sufficient. The tube is first heated in front of the boat, waving the flame to and fro, and then the boat itself is gradually heated until the residual lead bromide melts. When all the bismuth has been driven as far forward as possible the flame is brought back to the boat, its contents being again heated to fusion. This is repeated two or three times, and when nothing further passes over, the heat must not be increased, but the contents of the tube are allowed to cool quietly in the current of bromine.

The lead is weighed first as bromide in the boat and finally as sulphate, into which state it is converted by heating the bromide with saturated chlorine water and precipitating the solution of lead chloride with sulphuric acid.

The solution of bismuth nitrate in the receivers is concentrated, precipitated at the temperature of ebullition with ammonium carbonate, and weighed as bismuth oxide. The ignited oxide is covered with solution of ammonium carbonate, evaporated on the water-bath, heated more strongly in an air-bath, and fully ignited to expel any traces of sulphuric acid.

Estimation of Bismuth in Lead Alloys.—The alloys are dissolved in nitric acid, the solution diluted with water, and the bismuth precipitated by a strip of pure lead. The precipitated bismuth, black in colour and in the state of powder, is quickly washed off the lead, and the solution of lead decanted; the bismuth is then washed first with water and then with alcohol, filtered on a weighed filter, dried, and weighed.

Arthur L. Benkert and Edgar F. Smith [1] separate bismuth from lead by precipitation as formate.

Solutions of lead nitrate and bismuth nitrate in nitric acid are made up of such strength that 20 cubic centimetres of the first contain 0·2076 gramme of lead oxide, and 20 cubic centimetres of the second 0·1800 gramme of bismuth trioxide. The lead and bismuth are accurately determined after dilution to a litre. 20 cubic centimetres of these two nitrate solutions are then introduced into a glass beaker, carefully diluted and almost neutralised with sodium carbonate, or until the incipient precipitate dissolves slowly, when much sodium formate solution of specific gravity 1·084 and a few drops of aqueous formic acid are added. The total dilution of the liquid is 250 cubic centimetres. It is gradually heated to boiling, and kept so for five minutes. The precipitate is then allowed to subside, and filtered while hot. The basic formate separates rapidly, and is easily washed if not boiled too long. It is washed with hot water, then dissolved in dilute nitric acid, and precipitated with ammonium carbonate. The ignited bismuth trioxide frequently contains lead. It is dissolved in nitric acid, diluted to 250 cubic centimetres, and after the addition of sodium

[1] *Chemical News*, Jan. 15, 1897.

carbonate to almost complete neutralisation, sodium formate and free formic acid are added as before, and the precipitation of basic formate repeated. This precipitate after solution, and the bismuth thrown out by ammonium carbonate, gives 0·1804 gramme of bismuth oxide, instead of 0·1800 gramme as required by theory.

With a solution containing 0·3600 gramme of bismuth oxide, and 0·2076 gramme of lead oxide, operating in an analogous manner, two results were obtained :—

0·3595 gramme of Bi_2O_3
0·3605 gramme of Bi_2O_3

instead of 0·3600 gramme.

The residual bismuth trioxide was examined for lead, but none was found.

Separation of Bismuth from Cadmium

In the separation of certain metals of the sulphuretted hydrogen group, such as lead, bismuth, cadmium, and tin, according to the customary methods, P. Jannasch and P. Etz not seldom encountered unexpected difficulties which seriously affect the accuracy of the results. Separations in a current of chlorine are evidently more trustworthy, and most of these have already been studied.

The decided advantages which bromine permits in its use, as well as the observation that the temperatures of volatilisation of the metallic bromides differ more widely among themselves than those of the corresponding chlorides, suggested the re-examination of the analyses which were effected some years ago with bromine vapour, and the extension of the method. The first examination of this kind was so favourable that the authors could hope by means of the new process to enrich quantitative analysis with a series of exceedingly simple and accurate metallic separations.

The procedure is as follows :—As initial materials they used cadmium sulphate and metallic bismuth, of the purity of which they were satisfied by special analyses. These substances are dissolved in nitric acid, the solution evaporated down on the water-bath, and the residue taken up with as much hydrochloric acid as is necessary to prevent the deposition of basic bismuth chloride on the addition of about 100 c.c. of water. From the solution in hydrochloric acid, which is heated to ebullition, the metals are thrown down as sulphides by means of a current of sulphuretted hydrogen collected upon a filter, dried and weighed at 100°, washed with hot sulphuretted hydrogen water, and then completely dried in an air-bath and weighed.

The desiccated mixture of sulphides is placed in a porcelain boat in a dried tube of potash glass, and a brisk current of air, which has traversed a cylinder containing bromine, is passed over it from a gasometer. The bromine acts upon the substance even in the cold, but the reaction must be assisted and completed by moderate heating with a

gas flame one and a half inch high, kept in a wavering motion, during which the occasional appearance of a russet-yellow flame may be observed in the tube.

After about half an hour, all the bismuth has been carried into the receivers, which have been charged with weak nitric acid, while all the cadmium remains behind in the boat as a bromide. This bromide is dissolved in a little dilute hydrochloric acid, heated to ebullition, and precipitated with sodium carbonate. The solution of bismuth taken from the receivers is evaporated down, and the bismuth is finally separated by boiling with a mixture of ordinary ammonium carbonate and a little ammonia.

The complete separation of the bismuth is evident on the careful examination of cadmium. No trace of a brown precipitate appears on passing sulphuretted hydrogen into the hydrochloric solution. The precipitate is a pure yellow from the first. Moreover, the solution of cadmium, copiously diluted with water, gives no milky turbidity of bismuth oxychloride.

The mixed sulphides must be perfectly free from water when exposed to the action of the current of vapour of bromine.

Electrolytic Separation of Bismuth from Copper [1]

(*A*) A separation of both metals cannot be effected in the solution of double oxalates ; they are always precipitated together. The separation succeeds, however, in a solution containing free nitric acid. Proceed as directed for the determination of copper, and precipitate the bismuth in the filtrate after the removal of the nitric acid and conversion into sulphate.

(*B*) E. F. Smith adds citric acid for the separation of the two metals (3 grammes to 0·2 gramme of both), renders the solution alkaline with potash-lye, and adds a slight excess of potassium cyanide. The liquid must become clear after this addition, or more citric acid and potash-lye must be added. The solution is diluted to about 200 c.c. and electrolysed with a current giving 1 c.c. of detonating gas per minute.

(*C*) In the reduction of bismuth from its ores, and its subsequent refining, Edward Matthey has frequently found this metal to contain a small proportion of copper, an element most detrimental even in small traces, and hitherto only eliminated by a wet process, costly in practice and tedious in operation, it being necessary by such method to dissolve up the whole of the alloy and precipitate the bismuth in the usual manner ; a bulky operation, and one requiring a considerable amount of time. It became therefore advisable, in order to treat cupreous bismuth rapidly and upon a commercial scale, to effect this separation, if possible, by means of a dry process.

Matthey having observed, in conducting experiments with bismuth

[1] For details of operation see chapter on Electrolytic Analysis.

and its sulphides, that bismuth sulphide is very easily impregnated with copper, made the simple experiment of fusing the cupreous bismuth with bismuth sulphide, and found it possible by this means to remove every trace of copper, the sulphur readily combining with the metallic copper.

In this absorption a proportion of bismuth is reduced equivalent to the amount of copper taken up in the operation.

The residual bismuth and copper sulphides thus produced amount to but a small proportion in comparison with the quantity of alloy treated, and the bismuth readily recovered by subsequent reduction and refusion. Large quantities of alloy can be treated at one operation, and the bismuth so freed from copper is available for commercial purposes. It is better when bismuth is associated with other metals, such as arsenic, antimony, lead, tellurium, &c., as well as with copper, to separate all these metals before attempting to remove the copper by the foregoing method.

The operation has been conducted successfully upon many thousands of pounds of similar alloy, and the whole of the copper and bismuth, within a small fraction, is accounted for, the latter being obtained as commercially pure bismuth and wholly free from copper.

The first separation frees 90 per cent. of the bismuth at once from the copper associated with it.

Matthey has effected complete separation with bismuth containing proportions of copper varying from 0·1 per cent. to 1 per cent. by the above process.

Separation of Bismuth from Mercury

To the solution containing the bismuth and mercury (as persalt) add a large excess of hydrochloric acid to prevent the precipitation of bismuth oxychloride, and then add phosphorous acid. On standing, the mercury will be precipitated in the form of protochloride. After the separation of the mercury add a large quantity of water, which precipitates the bismuth as oxychloride. Reduce this to the metallic state by fusion with potassium cyanide.

Detection of Copper, Bismuth, and Cadmium when simultaneously present

M. Iles adds to the slightly acid solution of the three metals, potassium ferrocyanide in slight excess, when all three are thrown down as ferrocyanides. Potassium cyanide is added in excess and the mixture is gently heated. The copper and cadmium compounds dissolve, while the bismuth remains as a white flocculent hydroxide. The filtrate is divided into two portions; the one is tested for copper with hydrochloric acid, which occasions a brown-red precipitate of copper ferrocyanide, while to the other is added a little ammonia and

ammonium sulphide. On the application of a gentle heat, yellow cadmium sulphide is precipitated.

Separation of Bismuth from Cobalt

P. Jannasch and H. Kammerer [1] have experimented on the separation of bismuth from cobalt by means of hydrogen peroxide.

As initial material they use cobalt-ammonium sulphate and pure metallic bismuth. About 0·5 gramme of the cobalt salt and 0·35 gramme of bismuth are heated in a crucible upon the water-bath with 10 cubic centimetres of concentrated nitric acid and 10 cubic centimetres of water until dissolved. In a second large porcelain capsule have in readiness a mixture of 20 cubic centimetres of water, 50 of hydrogen peroxide, and 50 of concentrated ammonia, into which pour the metallic solution after the addition of 10 cubic centimetres of concentrated nitric acid. After subsidence the bismuth precipitate (still including traces of cobalt) is filtered off, and washed first with a mixture of hydrogen peroxide and ammonia, as above, then with dilute ammonia (1 : 2), and lastly with hot water. When this has been thoroughly done the precipitate is dissolved on the filter with hot dilute nitric acid (1 : 3), noting the quantity thus consumed, and then add to the cold bismuth solution so much concentrated nitric acid that 20 cubic centimetres of it may again be present in the liquid. The bismuth is then precipitated a second time, exactly as before, the precipitate washed precisely as above, dried at 90°, incinerated, and weighed as bismuth oxide in a platinum crucible.

The precipitate, containing all the cobalt, is dried perfectly on the water-bath, and then heated strongly in a large air-bath until all the ammonium salts are expelled. The residual cobalt salt is now taken up with a little hot water, to which a few drops of hydrochloric acid and a little hydrogen peroxide have been added, diluted to at most 100 cubic centimetres, and finally precipitated at a boiling heat with a slight excess of pure soda, with the simultaneous addition of some bromine. The precipitate obtained is well washed, dried, incinerated (the filter separately), and weighed as cobalti-cobaltous oxide. Or the cobalt may be directly precipitated from the original ammoniacal solution with ammonium sulphide. This precipitate must be heated for some time on the water-bath until completely deposited, when it is filtered and washed with hot water containing ammonium sulphide. By the use of warm dilute aqua regia alternately with hydrogen peroxide, it is easily practicable to redissolve the sulphide for the precipitation of the cobalt with soda and bromine.

[1] *Chemical News*, Aug. 23, 1895.

CHAPTER VIII

ANTIMONY, TIN, ARSENIC, TELLURIUM, SELENIUM

ANTIMONY

Electrolytic Deposition of Antimony [1]

(*A*) Classen finds that from a hydrochloric solution antimony is deposited as a metal, but is not firmly adhesive. If potassium oxalate is added to the solution of the antimony, the reduction is very easy, but the metal adheres even less strongly than in the former case. A firmly adherent metallic deposit is obtained by an addition of potassium tartrate, but the deposition then proceeds too slowly.

The precipitation of antimony succeeds very well from the solutions of its sulpho-salts. If ammonium sulphide is used for the formation of the double salt, it must contain neither free ammonia nor poly-sulphides. It is therefore advantageous to use ammonium hydrosulphate, which is preserved in small quantities in well-stoppered bottles.

For the deposition a cold solution and a feeble current must be used, preferably one which gives off at the voltameter from 1·5 to 2 c.c. of detonating gas per minute. In the electrolysis of a solution of antimony mixed with ammonium sulphide, sulphur is deposited on the capsule above the metal, and cannot be removed by rinsing with water. If the metal is subsequently rinsed with ammonia, we may remove the thin film of sulphur by rubbing with the finger, or with a cloth moistened with alcohol, without the risk of losing antimony.

The use of antimony sulphide is open to an objection, since, when several determinations are executed simultaneously, the smell is unbearable. A series of experiments was therefore made with sodium monosulphide, potassium monosulphide, and also sodium and potassium hydrosulphides, which proves that antimony may be successfully separated from their double salts. Among the above-named alkaline sulphides, sodium sulphide (Na_2S) offers the greatest advantage for the separation of antimony from tin and arsenic. Hence the subsequent details refer exclusively to the use of the salt in question.

[1] For details of operation see chapter on Electrolytic Analysis.

The preparation of sodium sulphide is best effected as follows :— Pure sodium hydroxide is dissolved in so much water that the solution has the specific gravity of about 1·25. The liquid is divided into two equal parts, and one half is saturated in the absence of air with the purest hydrogen sulphide procurable, until no further increase of volume can be observed. The hydrogen sulphide is passed for purification through a washing-bottle filled with water, and then through several glass tubes filled with cotton or wadding. After thorough precipitation the solution is filtered to remove the precipitate, and mixed with the other half of the solution. Hydrogen sulphide is again passed into the mixed liquid, in the absence of air, until perfect saturation is obtained, and the filtration is again repeated. The pale-coloured filtrate is evaporated down as rapidly as possible in a capacious basin of platinum or thin porcelain over a brisk, open fire. The liquid boils without bumping if a platinum spiral is inserted. As soon as a thin crystalline film is observed the ebullition is interrupted, and the liquid, while still hot, poured into small bottles fitted with glass stoppers accurately ground. The exclusion of air must be rendered complete by means of melted paraffin. The solution must have a sp. gr. of 1·22 to 1·225 for separating antimony from tin.

In the electrolysis of the antimony sulpho-salt, the reaction is probably as follows :—The current first decomposes the water

$$3H_2O=6H+3O.$$

There is formed at the cathode

$$Sb_2S_3+3Na_2S+6H=2Sb+6NaHS,$$

and at the anode

$$6NaHS+3O=3Na_2S_2+3H_2O.$$

In the precipitation of antimony from its solution in sodium sulphide, it must be remembered that in presence of the sodium polysulphides the separation of antimony is either not quantitative or may be entirely prevented. As the determination of antimony is generally preceded by a separation from the metals of the sulphuretted hydrogen group (which separation is effected either by digestion or fusion with the alkaline polysulphides), the quantitative determination of antimony in the electrolytic way can be applicable only if the antimony sulphide, separated from the sulpho-salts by means of an acid, is first freed from the accompanying sulphur. It does not require special mention that in such cases electrolysis would present no advantages.

Classen has elsewhere pointed out the energetic oxidising action of hydrogen peroxide, and has shown that it converts the alkaline monosulphides into sulphates, without any separation of sulphur. With the alkaline polysulphides its behaviour is analogous.

The method of determining antimony in the solutions of alkaline

polysulphides is very simple. Add to the solution in question an excess of hydrogen peroxide, and apply heat until the liquid is colourless. If a large excess of hydrogen peroxide is used, it may happen that the alkaline sulphide is completely decomposed and antimony sulphide is liberated. If the solution is entirely decolourised, or if a precipitate of antimony sulphide has already been formed, add, after it has become cold, about 10 c.c. of a saturated solution of sodium monosulphide, and electrolyse the *cold* solution, which should amount to 150 to 175 c.c., by means of a current corresponding to 1·5 to 2 c.c. of detonating gas per minute. If the electrolysis is initiated in the evening, we find the antimony quantitatively deposited the next morning (ten to twelve hours). If the quantity of the antimony does not exceed 0·16 gramme, the metal forms a greyish-white deposit, adhering firmly to the capsule.

The capsule with the antimonial deposit is treated in the usual manner with water and perfectly pure, absolute alcohol, dried for a short time in the air-bath at from 80° to 90°, and weighed.

A Meidinger battery of from 4 to 6 elements may serve to yield a constant current of 1·5 to 2 c.c. detonating gas per minute.

(*B*) H. Nissenson adds to a solution of antimony containing not more than 0·18 gramme antimony, 50 c.c. of a saturated solution of sodium sulphide. This solution is obtained by covering the commercial quality with water, and allowing it to stand with the air excluded until the liquid above the undissolved residue is colourless. The hot solution is electrolysed in a platinum capsule with a current of 0·5 to 1 ampère. About 0·15 gramme of antimony is deposited in the course of one hour.

(*C*) F. Rüdorff mixes the solution of antimony with about 30 c.c. of a 10-per-cent. solution of sodium monosulphide, and electrolyses with 2 or 3 Meidinger elements. The conclusion of the reaction is ascertained by means of acetic acid, which liberates orange-red antimony sulphide, if present.

(*D*) For depositing antimony as an amalgam, G. Vortmann mixes the solution containing the antimony as pentoxide (peroxidised if needful with bromine-water) with a weighed quantity of mercuric chloride (to 1 part of antimony at least 2 parts of mercury), and adds the solution proposed by Classen for separating antimony from arsenic (a mixture of sodium sulphide and hydroxide) until the solution appears perfectly clear. It is diluted with water to about 175 c.c., and electrolysed in the manner directed for amalgam. For preparing the mixture 60 c.c. of solution of sodium sulphide (sp. gr. 1·22 to 1·225) are mixed with so much of a concentrated solution of pure sodium hydroxide that the liquid may contain about 1 gramme NaOH.

(*E*) Dr. C. A. Kohn dissolves the precipitated sulphide in potassium sulphide, and the resulting solution, after warming with a little hydrogen peroxide to decolourise any polysulphides that may be present,

is electrolysed with a current of 1·5 to 2 c.c. of electrolytic gas per minute (10·436 c.c. at 0° and 760 mm.=1 ampère), when the antimony is deposited as metal upon the negative electrode. One part of antimony (as metal) in 1,500,000 parts of solution may be thus detected—a reaction thirty times more delicate than the deposition by means of zinc and platinum. The stain on the cathode, which latter is best used in the form of a piece of platinum foil about 1 cm. in diameter, is distinct even with a solution containing $\frac{1}{2^{\frac{1}{8}}}$ mgrm. of antimony, and by carefully evaporating a little ammonium sulphide on the foil, or by dissolving the stain in hot hydrochloric acid and then passing a few bubbles of sulphuretted hydrogen gas into the solution, the orange-coloured sulphide is obtained as a satisfactory confirmatory test. The detection of 0·0001 gramme of metal can be fully relied on under all conditions, and one hour is sufficient to completely precipitate such small quantities.

Estimation of Antimony

(*A*) When antimony is precipitated in the form of sulphide, instead of weighing it as such, Wöhler advises that it be converted into antimoniate of antimony oxide (Sb_2O_3,Sb_2O_5), by complete oxidation with fuming nitric acid in a weighed porcelain crucible. To avoid ignition, the substance must be moistened with a few drops of dilute acid before adding the fuming acid. A prolonged digestion effects the complete solution of the pulverulent precipitate of sulphur. The excess of acid is then evaporated off carefully, and the residue calcined.

(*B*) Sharples employs the following process in the precipitation of antimonious sulphide:—Into the solution, containing, as usual, tartaric and free hydrochloric acids, a current of sulphuretted hydrogen is to be passed, the liquid being, during the passage of the gas, gradually heated to the boiling-point. The boiling is then to be continued for fifteen or twenty minutes, the current of gas passing uninterruptedly until the voluminous sulphide has become a dense granular powder occupying but a small portion of the original volume of the sulphide. The sulphide may then be washed with great facility, and dried upon a sand filter at 200° or 300° C. All the estimations of antimony made in the laboratory of the Lawrence Scientific School for some years have been executed in this manner, the results leaving nothing to be desired. Arsenious sulphide does not become granular and dense under the same circumstances.

Rapid Detection of Antimony in Minerals

(*A*) Minerals which contain antimony, when heated alone before the blowpipe on charcoal, or with the addition of three or four parts of fusion mixture ($K_2CO_3 + Na_2CO_3$), yield dense white fumes

of antimonious oxide,[1] which in great measure escape into the atmosphere, but which also in part become deposited on the charcoal support, forming a well-marked white sublimate, or incrustation of the oxide.

Those results, though certainly in most cases very useful indications, do not furnish to the satisfaction of the mineralogist sound, conclusive evidence of the presence of antimony in the mineral tested, seeing that several other bodies occurring in the mineral world give, when heated before the blowpipe, exactly the same or nearly similar reactions. As a consequence of the hitherto inconclusive blowpipe evidence, mineralogists have usually considered it essential when engaged in correct work to supplement those indications by means of the accurate but tedious method of the ordinary wet way qualitative chemical analysis.

With a view to remove the necessity of consuming so much valuable time over the certain identification of antimony, Alexander Johnstone proposes the following exceedingly simple test, which he discovered and successfully applied while working among the various metallic ores of antimony.

To the white coat which will invariably form on the charcoal if the mineral containing antimony be properly treated and heated before the blowpipe, add, by means of a narrow glass tube, a single drop of ammonium sulphide. If the white sublimate is composed of antimonious oxide, then the portion touched by the drop (or the part touched by the *edge* of the drop) will immediately become converted into the well-known and highly characteristic *reddish* or *orange* antimony sulphide.

As no other white coat producible on charcoal by heating a mineral in the blowpipe flame becomes *reddish* or distinctly *orange* in colour when treated as above with ammonium sulphide, the value of this easily applied test must at once be apparent.

(*B*) In the examination of mineral bodies for antimony, the test substance is often roasted in an open tube for the production of a white sublimate. Dr. E. Chapman, Professor of Mineralogy at Toronto, recommends for the detection of antimony in this substance the following process—a method more especially available when the operator has only a portable blowpipe-case at his command:—The portion of the tube to which the chief part of the sublimate is attached is be cut off by a triangular file, and dropped into a test-tube containing some tartaric acid dissolved in water. This being warmed or gently boiled, a part at least of the sublimate will be dissolved. Some potassium bisulphate—either alone, or mixed with some sodium carbonate and a little borax, the latter to prevent absorption—is then to be fused on

[1] Not altogether *antimonious* oxide (Sb_2O_3), according to Dittmar. That chemical authority asserts that a small portion of the coat is composed of the amorphous antimony tetroxide (Sb_2O_4).

charcoal in a reducing flame; and the alkaline sulphide thus produced is to be removed by the point of the knife-blade and placed in a small porcelain capsule. The hepatic mass is most easily separated from the charcoal by removing it before it has time to solidify. Some of the tartaric acid solution is then to be dropped upon it, when the well-known orange-coloured precipitate of antimony sulphide will at once result.

In performing this test, it is as well to employ a somewhat large fragment of the test substance, so as to obtain a thick deposit in the tube. It is advisable also to hold the tube in not too inclined a position, in order to allow but a moderate current of air to pass through it; and care should be taken not to expose the sublimate to the action of the flame, otherwise it might be converted almost wholly into a compound of antimonious and antimonic acids, the greater part of which would remain undissolved in the tartaric acid. A sublimate of arsenious acid, treated in this manner, would, of course, yield a yellow precipitate, easily distinguishable by its colour, however, from the deep orange antimonial sulphide. The crystalline character, &c., of this sublimate would also effectually prevent any chance of misconception.

(*C*) Dr. A. Weller proceeds as follows for the estimation of antimony:—Antimonic acid and antimonic oxide, and in like manner antimony penta- and tri-chloride, can be most easily distinguished from each other by their different behaviour with potassium iodide. The property of the former, when in hydrochloric solution, of separating two atoms of iodine from potassium iodide for each atom of antimony, can be used for the qualitative estimation of antimony. In order to verify the method, weighed quantities of finely pulverised pure metallic antimony are oxidised in a flask at a gentle heat with potassium chlorate and hydrochloric acid, and the excess of chlorine is expelled by strong heating. The solution of antimony pentachloride thus obtained is introduced into the flask of Bunsen's chlorine distillation apparatus by means of hydrochloric acid, considerably diluted, and mixed with a sufficiency of perfectly pure potassium iodide, avoiding too great an excess. The liberated iodine is distilled into dilute solution of potassium iodide, observing all the precautions laid down by Bunsen, and especially cooling the retort well in flowing water. When cold the distillate is titrated in the usual manner by means of very dilute sulphurous acid and an iodine solution of known strength. The distillation-flask has the capacity of about 120 c.c. The distillation requires from five to ten minutes. Particularly important is the fact that stannic acid and stannic chloride in acid solutions do not decompose potassium iodide. This behaviour renders it possible to estimate antimony in presence of tin, as in alloys, easily and accurately. The tin is calculated as difference.

Estimation of Antimony in Native Antimony Sulphide

The estimation of antimony in this mineral is very easily effected by means of gallic acid, and its complete and accurate analysis is rendered simple by the gallic-acid process.

Twenty grains of the powdered mineral are treated by a slight excess of hydrochloric acid, and the mixture is gently heated until the whole of the sulphuretted hydrogen disengaged is thoroughly evolved. The solution is then filtered, the filter and matrix are washed with dilute hydrochloric acid, and the solution is slowly evaporated in the flask until it is conveniently concentrated and freed from the excess of hydrochloric acid.

In this solution the whole of the antimony exists in the state of terchloride, a slight excess of a recently prepared solution of gallic acid is added, with the precautions already indicated. Hot water is then added, and the precipitate of antimony bi-gallate is washed, dried, and weighed, as has already been stated. Antimony may also be estimated as sulphide after having been separated as bi-gallate.

Twenty grains of this mineral are quite sufficient for the estimation of antimony, but in the complete analysis it would be inconvenient to operate upon more than 50 grains, as the precipitated antimony bi-gallate is very bulky.

Antimony being separated as above, iron, lead, copper, silver, arsenic, and sometimes zinc, cobalt, and other metals remain in solution.

Arsenic exists much less frequently than is generally supposed. Copper is very often present. It can be estimated here with the greatest accuracy, as the whole of it exists, or may be made to exist, in the filtrate.

The analysis of the filtrate is proceeded with as that of an ordinary liquid containing the metals mentioned. The only metal which cannot be properly estimated in this liquor is iron, the presence of gallic acid preventing its precipitation, even by means of ammonium sulphide, but its complete separation from antimony is so simple by the known methods that this fact need only be mentioned.

Estimation of Antimony in the Antimony Sulphide obtained in the Course of Analysis

In the course of a complicated analysis, it is often absolutely necessary to obtain antimony first in the state of a sulphide mixed with a large quantity of sulphur, and contaminated with copper, arsenic, or tin sulphides.

The gallic-acid process affords a simple means of carrying out a careful analysis in this part of the operation, and of estimating antimony by a direct process.

For this purpose the collected mixture of sulphur, antimony sulphide,

&c., wet or dried, is first of all treated by hydrochloric acid, and when the action has ceased a little potassium chlorate is added, to attack any copper or arsenic which might have escaped the action of the acid. The solution thus obtained decanted from the residue of sulphur is evaporated, reduced by potassium iodide, and precipitated by gallic acid.

Separation of Antimony from Mercury

These metals can readily be separated by precipitating the mercury as protochloride by hydrochloric acid and phosphorous acid, according to the plan previously described, the antimony being retained in solution with tartaric acid, which does not prevent the precipitation of the mercury protochloride.

Separation of Antimony from Copper.—*See* Arsenic.

TIN

Electrolytic Separation of Tin[1]

(*A*) Classen finds that tin separates quantitatively both from the solution of the ammonium double oxalate and from ammonium sulphide. Sodium and potassium sulphides cannot be used, as tin is only partially separated from dilute solutions of the corresponding sulphosalts, and not at all from concentrated solutions.

If tin is precipitated from the ammonium double oxalate there easily occurs a deposition of stannic acid, especially if large quantities of tin are present, so that it becomes necessary to dissolve it repeatedly by the addition of oxalic acid. The reduction of the tin proceeds without any irregularity, if instead of the ammonium oxalate we use the acid ammonium oxalate. The results obtained by this procedure are so accurate that the author is able to employ the method for determining the atomic weight of tin.[2]

(*B*) The solution of the tin salt is mixed with a solution of acid ammonium oxalate saturated at the ordinary temperature, so that there may be 20 c.c. of this solution to each 0·1 gramme of tin. The solution is diluted to 150 c.c. and without applying heat it is electrolysed with a current yielding 2·5 to 3 c.c. of detonating gas, the current being intensified towards the end of the reduction to about 5 c.c. of detonating gas. The tin is deposited quantitatively as a silvery metal, firmly adherent even if the quantity amounts to 6 grammes. After interrupting the current the metal is washed as usual with water and alcohol and dried at 80° or 90°.

(*C*) Tin behaves like antimony in the solution of the ammonium

[1] For details of operation see chapter on Electrolytic Analysis.

[2] Bougarta and Classen, *Berichte Chem. Gesellschaft*, xxi. 2900.

sulpho-salt. If the solution of tin is mixed (after neutralisation with ammonia if needful) with ammonium sulphide free from ammonia (adding no more than is required for the formation of the sulpho-salt), diluted with water to 150 to 175 c.c., and electrolysed with a current of the above-mentioned strength, the tin is quantitatively precipitated in the course of five or six hours. On the inner margin of the capsule sulphur is sometimes deposited so firmly above the separated tin, that it cannot be removed by rinsing with water; it may, however, be readily displaced by gentle friction with a linen cloth, after moistening the edge with alcohol. This method of determining tin is, however, less easy and certain than the former.

(*D*) In separating tin from other metals we often use sodium sulphide instead of ammonium sulphide. In order to determine the tin electrolytically in such cases, the sodium sulphide must be converted into ammonium sulphide (sodium sulphide cannot be replaced by potassium sulphide in separations from other metals, as the latter in the transformation to ammonium sulphide yields sparingly soluble potassium sulphate). For this purpose mix the liquid with about 25 grammes of pure ammonium sulphate free from iron, and heat it very carefully in a covered capsule until the evolution of hydrogen sulphide is at an end. The liquid is then kept in moderate ebullition for about fifteen minutes. The complete transformation into ammonium sulphide is easily recognised by the greenish-yellow colour of the liquid. If heated too long, tin sulphide may be separated out and redissolved with ammonium sulphide. When completely cold any deposit of sodium sulphate is dissolved by adding water, and the liquid is electrolysed with a current of 9 to 10 c.c. of detonating gas per minute.

(*E*) The determination of tin is effected much more simply and easily if the tin sulphide dissolved in sodium sulphide is converted into acid oxalate, and the latter solution is electrolysed. For conversion into this compound two methods may be taken:—(1) Either the sulpho-salts are decomposed with dilute sulphuric acid in order to expel a large part of the sulphur in the state of hydrogen sulphide, and the deposited tin sulphide is oxidised with hydrogen peroxide[1] until the stannic acid formed appears of a pure white; or (2) we add at once to the heated alkaline solution of the sulpho-salts hydrogen peroxide, which requires a great consumption of this reagent. Acidify then with sulphuric acid to eliminate the stannic acid, neutralise with ammonia, and add a little more hydrogen peroxide. In either case heat to decompose the excess of the latter, and allow the stannic acid to deposit and filter. The precipitate is rinsed from the filter into a beaker by means of a solution of oxalic acid; the filter is then washed with a hot solution of the same acid, and the stannic acid is dissolved in the beaker with the

[1] See *Berichte*, xvi. 1062: A. Classen and C. Bauer, 'Applications of Hydrogen Peroxide in Analytical Chemistry.'

aid of heat. Sometimes there results a residue of sulphur, which is separated by filtration.

Assay of Tin Ores

(*A*) J. S. C. Wells reduces the powdered tin ore with nascent hydrogen. About 1 gramme of the finely powdered tin ore (cassiterite) is placed in a large test-tube with a few pieces of zinc, a piece of platinum, and some dilute hydrochloric acid. The tube should be heated and well shaken during the reaction, so as to keep the ore in contact with the zinc and platinum. If this is not done, the ore settles to the bottom and the reduction takes place very slowly.

As soon as the decomposition of the ore appears to be complete, the remaining zinc and the reduced tin are dissolved in hydrochloric acid and filtered from any undecomposed ore or gangue. The residue should again be treated in the same way, with fresh zinc, platinum, and hydrochloric acid, to see if all the tin has been extracted by the first operation. After the tin has been obtained as chloride, it can be determined by any of the usual methods.

(*B*) J. W. B. Hallett has found that tin-stone is very easily resolved by fusion in a platinum crucible with three or four times its weight of potassium hydric fluoride. The mineral must be finely pulverised. The fused mass is treated directly in the crucible with sulphuric acid to expel fluorine, after which, by adding water, filtering, and boiling the filtrate, the whole of the tin is thrown down as stannic acid, which is to be separated from traces of iron in the usual manner. This method of resolving the ore of tin is much more convenient than fusion with caustic alkalies, or with sulphur and sodium carbonate.

(*C*) Peter Hart gives the following method for the rapid estimation of tin in tin ore :—Finely powder in the agate mortar some 20 to 25 grains of the perfectly dry ore; place this in a small test-tube and weigh. Fuse about four times its weight of potassium cyanide in a small and rather deep porcelain capsule over a Bunsen burner. When in calm fusion and quite red hot remove the flame and project the ore into the crucible. Now weigh the tube again, and the difference will equal the weight of ore employed. Replace the gas-flame, and keep in quick fusion for fifteen or twenty minutes, by which time the tin and iron oxides will be reduced to the metallic state, and lie as a sponge at the bottom of the capsule; pour the whole contents on to an iron plate, and when cold the mass will leave the iron. Put cake and capsule into a basin, and add water to dissolve the cyanate and excess of cyanide; carefully decant, and when sufficiently washed free from these salts add hydrochloric acid. The metal will dissolve, and after solution pour the whole and wash the capsule into a beaker; add metallic zinc until the last piece ceases to show a tin precipitate. Break up the sponge with a rod, dilute, and when settled carefully pour off the zinc chloride and wash until the tin is pure; again dissolve in hydrochloric acid, dilute,

and estimate the tin by a standard solution of potassium bichromate, using potassium iodide and starch-water. The metals may be reduced by a stream of dry hydrogen, but with comparatively little advantage. Not much more than an hour is required for an estimation.

Separation of Tin from Antimony

(*A*) F. Wigglesworth Clarke has found that both tin sulphides, if moist and freshly precipitated, are readily decomposed by moderately long boiling with an excess of oxalic acid, sulphuretted hydrogen being given off. The monosulphide is converted into the insoluble, crystalline stannous oxalate, while the yellow disulphide is completely dissolved. The commercial 'Mosaic gold,' however, seems to be unacted upon by the reagent. In presence of an excess of oxalic acid, tin cannot be precipitated by sulphuretted hydrogen.

The antimony sulphide behaves in a somewhat different manner. Although upon long boiling with oxalic acid considerable quantities of the metal are taken into solution, yet every trace of it may be reprecipitated by sulphuretted hydrogen.

By taking advantage of the solubility of the tin sulphides in oxalic acid, this metal may be separated almost perfectly from antimony. To the solution containing the metals (this solution being prepared in the usual manner for the precipitation of the sulphides) add oxalic acid, in the proportion of about 20 grammes of the reagent for every gramme of tin, taking care to have the whole so concentrated that the acid will crystallise out in the cold. Then heat to boiling, and pass in sulphuretted hydrogen for about twenty minutes. No precipitate appears at first; but as soon as the liquid is saturated with the gas the antimony sulphide begins to fall, and in a very few moments is completely thrown down. Then, as usual, the whole should be allowed to stand about half an hour in a warm place before filtering. Every trace of antimony is precipitated, so that in the filtrate from the sulphide nothing can be discovered by Marsh's test, nor can any antimony-stain be produced with zinc upon platinum.

The antimony always carries down a minute trace of tin with it; this trace, however, if the operation has been carefully performed, can scarcely be detected, and generally may be ignored with safety. If, however, the greatest accuracy is desired, it may be well to redissolve the antimony sulphide in an alkaline sulphide, decompose the solution with an excess of oxalic acid, boil with a little strong sulphuretted hydrogen water, filter, and add the filtrate to the tin solution previously obtained.

Since the presence of oxalic acid interferes somewhat with the complete precipitation of tin by ordinary methods, some precautions are needed in the estimation of that metal after the separation. It can be thrown down as follows:—The solution, after being rendered slightly

alkaline with ammonia, is mixed with enough ammonium sulphide to redissolve the precipitate at first formed; an excess of acetic acid is added, and the whole allowed to rest several hours in a warm place. Acetic acid must be used, for stronger acids would be liable to set free some of the oxalic acid to redissolve the tin. The precipitate, which at first varies from white to pale yellow, rapidly darkens in colour, and seemingly consists of a mixture of tin oxide and sulphide. It should be washed with a solution of ammonium nitrate, and, after ignition, is weighed as tin binoxide.

The separation of antimony and tin presents considerable difficulties when the two substances are alloyed with other metals precipitable by sulphuretted hydrogen, such, *e.g.*, as anti-friction metal, for in this case it is scarcely practicable to transform the two metals into sulphides, their complete solution in alkaline sulphides for their separation from other metals being long and troublesome.

With an alloy of this sort Mr. Mangin[1] considers it is best to attack it with nitric acid, which dissolves the other metals and converts the tin and the antimony into insoluble oxides. Collect these oxides, wash, ignite, and weigh. Here arises the difficulty, for if we have succeeded in separating the antimony and tin from the other metals, it is not easy to determine them in this state. A number of methods have been proposed, all of which leave something to be desired, because they present causes of error or because they are tedious and difficult in execution. The following is a satisfactory method of operation :—

After having ignited the two oxides and taken their weight, they are placed in a beaker of Bohemian glass along with a plate or a ball of pure tin, some water, and hydrochloric acid. The beaker is set on the sand-bath (for 1·5 to 2 grammes of oxides three hours are required in a very acid liquid). The antimony begins to be reduced, and the tin oxide is converted into chloride. It is well to stir from time to time to renew the contact. We know that the reaction is at an end when we no longer perceive a trace of oxides. At this moment the liquid is perfectly clear, and the reduced metal, very black, is precipitated rapidly to the bottom of the vessel on withdrawing the source of heat.

The liquid is decanted, and the precipitate is washed in the glass with water which has been boiled and allowed to cool, with exclusion of air.

The precipitate is collected on a filter, washed with water and then with alcohol, dried in the stove, and weighed. We thus obtain the exact weight of the antimony. There is no appreciable oxidation of the antimony.

Knowing the weight of the ignited oxides and that of the antimony, we find the weight of the tin by a very simple calculation.

Let A be the weight of the antimony; multiply this number by

[1] *Chemical News*, Aug. 24, 1894.

1·262 to find the corresponding weight of antimony oxide, which is deducted from the weight M of the mixture of the two oxides.

M—A 1·262=the weight of tin oxide; this latter multiplied by 0·78667 gives the weight of tin contained in the alloy.

(*B*) The following process of separating tin from antimony has given very accurate results :—Thoroughly oxidise the metallic alloy by means of strong nitric acid, evaporate the mass to dryness, and gently heat it. Then fuse it in a silver dish with a large excess of caustic soda. After cooling dissolve in a minimum quantity of water, and then add one-third of its volume of strong alcohol. This precipitates sodium antimoniate, while sodium stannate remains in solution. Filter and wash, first with dilute, then with strong alcohol. Next dry the precipitated sodium antimoniate, and fuse it in a porcelain crucible with an excess of potassium cyanide. The antimony is reduced, and collects in a metallic button at the bottom of the crucible. The solution containing sodium stannate is boiled to expel alcohol, diluted, acidulated with dilute sulphuric acid, and saturated with sulphuretted hydrogen gas. The precipitated tin sulphide is then oxidised to tin binoxide, and this is reduced to the metallic state by fusion with potassium cyanide, as described on page 378, *C*.

(*C*) Ad. Carnot advises the following procedure for the rapid and exact separation of tin and antimony.

The hydrochloric solution of tin and antimony is mixed with ammonia or ammonium chloride; about 2 grammes of oxalic acid, previously dissolved, are added, and then ammonia almost to saturation. The liquid is diluted to 250 or 300 c.c., and a solution of thiosulphate is added containing at least 10 parts of this crystalline salt to 1 part of the antimony to be determined. The liquid, which is clear at first, becomes turbid on heating, and passes successively to yellow and red. A few c.c. of dilute hydrochloric acid are added, and the boiling is kept up for some minutes. On removing the heat, the red precipitate is deposited and the liquid quickly becomes clear. On adding, further, a few drops of hydrochloric acid and boiling for some moments, we observe the aspect of the liquid. If it remains clear, a little thiosulphate must be added. If it is milky and entirely white, the precipitation of the metal is complete. But if it takes a yellow or reddish colouration, antimony remains in solution, and the addition of acid (and sometimes of thiosulphate also) must be repeated until the turbidity is white. The oxysulphide, mixed with sulphur, is collected on a tared filter, where its consistence allows it to be easily washed. If a red coating of oxysulphide adheres to the glass, it is taken up with a minimum amount of hydrochloric acid, the hydrogen sulphide is expelled, the liquid is diluted again and precipitated with thiosulphate at a boil; or it may be dissolved with 3 or 4 drops of ammonium hydrosulphate, and after dilution it is decomposed with hydrochloric acid. In either case this precipitate is added to the former

upon the filter. The filtrate contains all the tin ; it is saturated with ammonia while still hot ; the precipitate is redissolved in hydrosulphate and the sulpho-salt is decomposed with acetic acid. Hydrochloric acid is not applicable. In a short time the precipitate subsides and is received on a filter, washed with water and a little ammonium nitrate, dried, and ignited in a porcelain crucible, and weighed as stannic oxide. As for the antimony oxysulphide, it is always mixed with an excess of sulphur, and may be converted into antimony tersulphide by simple calcination in a current of dry carbonic dioxide. Or, after having separated the two metals as above, the red oxysulphide may be dissolved in hydrochloric acid while still moist, and the antimony may be determined volumetrically.

Electrolytic Separation of Tin from Antimony [1]

(*A*) Classen finds that the quantitative separation of antimony from tin, which by ordinary gravimetric methods presents many difficulties and yields uncertain results, can be easily and accurately effected by electrolysis. The quantitative precipitation of antimony in presence of tin can be effected in a concentrated solution of sodium sulphide to which a certain quantity of pure sodium hydroxide has been added. The strength of the current should correspond to 1·5 or 2 c.c. detonating gas per minute.

(*B*) The crystalline sodium monosulphide of commerce can not only make no claim to purity, but is by no means a monosulphide, but a mixture with varying quantities of sodium hydroxide.

This explains the large proportion of alumina always found in the preparation. If the commercial product is to be used for this purpose, it should be completely saturated with pure sulphuretted hydrogen, in the absence of air.

The precipitate formed is filtered off, and the filtrate evaporated down in a capacious porcelain or platinum capsule. As the nature of the solution of sodium sulphide has an essential influence on the execution of the process, it is thought preferable for the analyst to prepare the solution as follows :—Pure sodium hydroxide is dissolved in water so as to form a solution of about 1·25 sp. gr. The liquid is divided into two equal portions, and one half is saturated with pure sulphuretted hydrogen, in the absence of air, until an increase of volume is no longer perceptible. The sulphuretted hydrogen is passed for purification through a washing-bottle filled with water, and then through several glass tubes filled with cotton or wadding. After complete saturation the precipitate is filtered off, and the filtrate mixed with the other half of the soda-lye. Into this mixture sulphuretted hydrogen gas is again passed, in the absence of air, to complete saturation, and the filtration is repeated. The faintly coloured filtrate is concentrated

[1] For details of operation see chapter on Electrolytic Analysis.

as rapidly as possible in a capacious capsule of platinum or thin porcelain, over a brisk flame. The liquid boils without bumping if a coil of platinum wire is introduced. As soon as a light crystalline film appears on the surface of the liquid the ebullition is arrested, and the liquid, while still hot, is poured into small bottles fitted with ground-glass stoppers, which may be coated at the top with melted paraffin for the better exclusion of air.

(*C*) For effecting the separation, the pure metallic sulphides, or the residue obtained on the evaporation of a solution of both metals in a platinum capsule, are covered with about 60 c.c. of solution of sodium sulphide (sp. gr. 1·22 to 1·225), and so much of pure concentrated soda-lye is added that 1 gramme sodium hydrate may be contained in the liquid. If the solution of the metals is not effected at once, the liquid is heated over a small flame, the covering glass is rinsed with 10 to 15 c.c. of water, and the liquid is allowed to become completely cold. It is then submitted to electrolysis, with a current producing 1·5 or 2 c.c. of detonating gas per minute, obtained from a battery of Meidinger elements, or from two Bunsen elements, or from accumulators, or from a dynamo. The separation of the antimony is best effected overnight. The action of the current is completed in about twelve hours, and yields the antimony as a shining deposit which adheres firmly to the capsule.

In order to avoid loss, the capsule is kept covered with a watch-glass, which is from time to time rinsed with a drop of water, the rinsings being finally allowed to flow down the positive electrode. After twelve hours the current is interrupted, the liquid transferred into a second clean, tared, platinum capsule into which the first capsule is rinsed two or three times with about 10 c.c. of water. The antimony is then treated as previously directed, and weighed.

(*D*) Tin cannot be reduced from a solution of sodium sulphide, but it is completely deposited from the solution in ammonium sulphide. Hence it is determined in the liquid after the elimination of antimony. (See section on Tin.)

(*E*) If it is required to separate both metals in the yellow solution of the alkaline polysulphides, the liquid is decolourised by means of ammoniacal hydrogen peroxide, evaporated nearly to dryness, about 60 c.c. of sodium sulphide solution and the requisite quantity of pure soda-lye are added, and the process is completed as above.

Detection of Tin in Presence of Antimony

Pattison Muir warms the precipitated sulphides of the arsenic group with concentrated hydrochloric acid; the insoluble portion is washed and tested for arsenic by Bunsen's film test. The solution is somewhat diluted; about three-fourths of it is boiled for at least ten minutes with copper turnings (which must of course be free from tin),

poured off from the copper, and tested for stannous chloride by adding mercuric chloride. The remaining smaller portion of the solution is poured on to a piece of platinum surrounded by a piece of zinc-foil. If the platinum become covered with a black deposit it is removed and examined in the ordinary way.

Separation of Tin from Bismuth

To the strong hydrochloric solution of the two metals add a large excess of water. This produces an insoluble precipitate of bismuth oxychloride, which may either be dried, and weighed in that state, or fused to a metallic button under potassium cyanide. The tin will remain in solution.

Separation of Tin from Thallium

When these two metals occur together in a liquid, they may be separated by adding an excess of ammonium sulphide to the alkaline solution. Thallium sulphide will be precipitated, while the tin will remain in solution.

Sulphuretted hydrogen passed through an acid solution containing tin and thallium precipitates the tin, but a little thallium is carried down by the tin sulphide.

Separation of Tin from Lead

To detect and separate small quantities of lead in the presence of a great excess of tin, treat a small quantity of the metal with an excess of nitric acid, diluted with three times its weight of water, boil the mixture, filter, and then drop into the solution a crystal of potassium iodide. If only $\frac{1}{10000}$ part of lead is present, a yellow precipitate is formed, which does not disappear on adding an excess of ammonia.

Separation of Tin from Copper

On digesting a solution of these metals with sodium sulphide, there is formed soluble sodium-tin-sulphide and insoluble copper sulphide. They are separated by filtration, and determined by methods already given.

Separation of Tin from Copper (Analysis of Gun and Bell Metals, containing besides traces of Lead, Zinc, and Iron)

(*A*) The following process has been employed for some years at the Ecole Normale:—Dissolve about 5 grammes of the alloy in strong nitric acid contained in a flask provided with a funnel in the neck to prevent loss by spirting. When quite dissolved boil the strong solution for about twenty minutes; dilute with two or three times its bulk of

water and boil again for the same time. Separate the insoluble tin oxide by decantation or filtration, and weigh after calcining it. (The tin oxide is sometimes rose-coloured, owing to the presence of minute traces of gold; this may be disregarded.) The nitric acid solution freed from the tin is evaporated on a small platinum or porcelain dish, and the residue is calcined at a dull-red heat. In this manner a mixture of oxides is obtained in sufficient quantity to suffice for at least two analyses.

About 2 grammes of the finely pulverised oxides are placed in a small platinum or porcelain boat, and thence introduced into a small glass tube closed with a good cork suitable for weighing. The boat, the tube, and the cork having been previously weighed, the weight of the oxides is obtained after they have been heated to dull redness in the apparatus, through which a current of dry air circulates. After having weighed the whole, the current of air is replaced by dry hydrogen, and the tube is heated over a lamp until the contents cease to lose weight. It then contains unreduced zinc oxide, together with copper, lead, and iron in the metallic state; the colour of the product shows when the experiment is concluded. On weighing again, the loss of weight indicates with great accuracy the amount of oxygen contained in the oxides of these three metals.

If the iron and lead are present in inappreciable quantities, by multiplying this loss by 5 very nearly the weight of copper present will be given, and, in consequence, the composition of the alloy itself. In an approximate analysis of gun-metal the operation will, therefore, be terminated. If, however, a complete analysis is required, proceed as follows:—

(*B*) Prepare a standard solution of sulphuric acid (which has been distilled from ammonium sulphate). Of this solution, in 200 or 300 c.c. of water, take a sufficient quantity to dissolve about double the amount of the mixed iron and zinc which are supposed to be present.[1] Boil the acid liquid to completely expel the air, and cool it in a flask, which should be almost full and well corked. Then introduce into it the platinum or porcelain boat containing the zinc oxide and the reduced metals. The zinc oxide quickly dissolves, together with the iron, the solution of which is facilitated by the presence of the metallic copper. The copper and lead remain. The flask must be frequently shaken, so as to diffuse these metals throughout the liquid, and the whole is allowed to stand for some hours; the clear liquid is then carefully decanted and the metals washed with boiling water. During this operation a trace of copper or lead may, perhaps, get into solution in the form of sulphate, through the action of the air, or be carried over mechanically. This may be ascertained by adding to the solution a few drops of a clear solution of sulphuretted hydrogen, and heating.

[1] It is a good plan always to weigh the reagents used in analysis, or, at all events, to ascertain approximately the quantities taken.

If brown flocks are deposited, separate them by decantation and add them to the metals.

The solution contains only the zinc and iron sulphates ; evaporate to dryness, heat the sulphates to a temperature of about 400° C., and weigh. If no iron is present, the amount of zinc present may be calculated at once. This method of estimating zinc is very accurate.

Separation of Tin from Tungsten

(*A*) The ignited and weighed mixture of stannic and tungstic acids, as resulting in the analysis of the alloys by decomposition with nitric acid, is ground in an agate mortar with twice its bulk of zinc powder or zinc filings, and ignited for fifteen minutes in a covered crucible. The spongy mass is treated with dilute hydrochloric acid (1 part acid and 2 parts water) in a covered beaker, until there is no further escape of hydrogen. When it is cold, potassium chlorate is added until the tungstic oxide is oxidised to yellow tungstic acid, diluted with 1½ volume of water, and allowed to stand for twenty-four hours. The tungstic acid is washed first with water containing nitric acid, and finally with a dilute solution of nitric acid, and weighed. The tin may be either determined as difference, or directly by precipitating the filtrate with sulphuretted hydrogen.

(*B*) Another satisfactory method of separating tin from tungsten has been described by J. H. Talbott.

The method is based on the fact that tin oxide is reduced by potassium cyanide with great facility; while tungstic acid undergoes no reduction, even when heated with the cyanide at a high temperature. The tin and tungsten oxides are to be heated in a porcelain crucible with three or four times their weight of commercial potassium cyanide previously fused, pulverised, and thoroughly mixed with the two oxides. The mass is kept fused for a short time, when the tin separates in the form of metallic globules, while the tungstic acid unites with the alkali of the potassium cyanate and carbonate present. After cooling, the mass is to be treated with hot water, which dissolves the alkaline tungstate and other salts and leaves the tin as metal; this is to be separated by filtration, washed, dried, and weighed as tin oxide, after oxidation in the crucible with nitric acid. The tungstic acid may be estimated by difference, or be precipitated by mercury protonitrate, after boiling the solution with nitric acid to decompose the excess of potassium cyanide present, and then redissolving the precipitated tungstic acid by means of an alkali.

Separation of Tin from Titanium

In the separation of tin oxide from titanic acid H. Haas proceeds as follows :—The mixture of tin oxide and titanic acid is placed

directly in a dry tube of the most infusible glass, and ignited for about fifteen minutes in a current of hydrogen over a common Bunsen burner. After being allowed to cool thoroughly in a current of hydrogen the grey mass is rinsed with water into a beaker, and if a small portion adheres to the side of the tube it is dissolved away by touching with dilute hydrochloric acid, and subsequent rinsing with water. About 30 c.c. of hydrochloric acid at 20 per cent. are then added, and the liquid is kept for half an hour at a gentle boil. When cold it is filtered, and the residue is washed with hot water.

The filtrate is neutralised, slightly acidified, and treated with a current of sulphuretted hydrogen. After standing for some time in a warm place the precipitated tin sulphide is collected on a filter, washed with water to which a little ammonium acetate has been added, and dried. After the precipitate has been cautiously separated from the filter and the latter incinerated, the tin sulphide and the ash of the filter are again reduced by gentle ignition in a glass tube in a current of hydrogen.

The reduced tin is washed with water into a capacious porcelain crucible, mixed with about 10 c.c. dilute nitric acid; evaporated to dryness on the water-bath; the residue is again taken up with nitric acid and hot water, and the tin oxide is determined in the ordinary manner.

In treating the residue of the reduced mass (titanic acid) with hydrochloric acid, it is burnt along with the filter and melted in a platinum crucible with 10 parts of potassium carbonate. The melt is moistened with about 200 c.c. of water, and strong sulphuric acid is added drop by drop until the acid potassium titanate dissolves. The clear or perhaps slightly opalescent solution is neutralised with sodium carbonate, 2 grammes of concentrated sulphuric acid are added, the solution is made up to 400 c.c. with water, and boiled for six hours, replacing the water as it evaporates. On account of the unavoidable bumping it is boiled in a capacious well-glazed porcelain pan, which may be conveniently covered with a large clock-glass or an inverted funnel.

After the titanic acid which separates out has been filtered off and washed with hot water, the filtrate is measured, mixed with so much concentrated sulphuric acid that the liquid may contain $\frac{1}{2}$ per cent. of the acid, and again heated to a boil; a separation rarely takes place. The titanic acid collected upon the filter is weighed as such after drying and ignition.

In determining tin and titanium in a mineral, 5 to 10 grammes of the substance, finely ground and sifted, are placed in a platinum capsule or a roomy platinum crucible upon the water-bath, and opened up with dilute sulphuric acid (1 : 10) and hydrofluoric acid, so that the silica is completely volatilised and the residual compounds are converted into sulphates. The absence of hydrofluoric acid is ascertained

by a further addition of sulphuric acid, evaporation on the water-bath, and heating the residue over the open flame. Neither hydrofluoric nor silicic acid must be present in the residue. Water is then added, the whole is heated for some time, and the contents of the vessel in which the sample was opened up (without filtering off the residues) are rinsed into a spacious porcelain pan, and, as indicated above, boiled in presence of ½ per cent. of concentrated sulphuric acid for six hours after dilution to 400 c.c. It is then cooled, filtered, washed out with hot water, examining if a further deposit is produced in the filtrate on boiling again in presence of ½ per cent. sulphuric acid. If a precipitate appears, it is collected like the former. The precipitates which contain all the tin and the titanium are placed in a porcelain crucible, the filters are burnt cautiously, the whole ignited gently for some time with excess of air ; the contents of the crucible are rinsed upon a filter, and washed with hot water.

After the residue has been dried and again gently ignited in a porcelain crucible, it is placed in a dry tube of hard glass, and ignited in a current of hydrogen for a quarter to half an hour.

The reduced mass is then, as above directed, treated with hydrochloric acid ; the undissolved residue is again submitted to reduction and treated as before. The tin is determined in the combined filtrates in the manner above described.

The residue left after the second treatment with hydrochloric acid is fused in a platinum crucible with 6 to 10 parts of potassium carbonate until everything is dissolved, proceeding exactly as above described.

If the titanic acid seems to contain a trace of iron, it is again reduced in a current of hydrogen, and the iron is dissolved out with hydrochloric acid.

Commercial Analysis of Tinware

The chief drawback to the analytical processes used in investigating the composition either of utensils of block tin or of thin layers of tin covering other metals, such as copper and iron, is the excessive weight of the metal to be operated on, recommended in special treatises on the subject.

The following process of analysis, devised by Millon and Morin, has been found to be free from the objections attached to the ordinary method of analysis with nitric acid.

In a small flask of from 80 to 100 c.c. capacity, furnished with a disengaging-tube, put about 1½ gramme of the tin, taking care to reduce the metal to fine grains, if it be not already divided by scraping ; nearly fill the flask with pure fuming hydrochloric acid ; adapt to the disengaging-tube a bulb tube containing a solution of gold chloride, and supplement this apparatus with another bent tube plunged into mercury.

The reaction commences in the cold, with a slight effervescence, goes on spontaneously, and ceases in about twenty-four hours. The presence of antimony or arsenic greatly favours the gaseous disengagement; scraped tin is usually more easily attacked than granulated tin.

The evolved gas traversing the bulb tube is composed of a mixture of hydrogen and arseniuretted hydrogen; all the arsenic escapes in the latter form, unmixed with antimoniuretted hydrogen; it remains in the gold chloride, where the arsenic acid is to be sought for and estimated in the usual manner.

When the proportion of arsenic is considerable, the gaseous disengagement becomes so rapid that one bulb tube is insufficient to arrest the arseniuretted hydrogen; but this never happens in the analysis of tinware used for domestic purposes; traces only of arsenic are found in this tin, at the most a few thousandths. However, if in an exceptional instance the amount of arsenic exceeds these limits, the difficulty is overcome by operating on a much less weight of alloy, and using hydrochloric acid diluted with about a fourth of its volume of water.

Antimony and tin alloy resists fuming hydrochloric acid when the antimony is in the proportion of 25 to 30 per cent. The alloy must then be melted with a given quantity of fine tin. To facilitate the action of the hydrochloric acid, nitric acid is added to it drop by drop; the antimony is then precipitated by tin, in presence of a large excess of hydrochloric acid.

When the action of the hydrochloric acid ceases, and no more gaseous bubbles are given off, a more or less abundant black powder is seen at the bottom of the flask, containing all the antimony existing in the tin. This antimony is free from arsenic, but retains the copper. There should also be found the bismuth, which is frequently mentioned by analysts, but which the authors have never once been able to detect.

The copper remains in the black powder, except when it exists in larger proportion than 20 per cent. in the alloy.

The black powder also occasionally contains traces of iron, but this is so slight in quantity that its presence may pass unnoticed.

The supernatant acid liquid is decanted, the black powder washed with distilled water, and the acid liquids mixed. After being well washed the powder is attacked by weak nitric acid (with concentrated acid the reaction is so energetic as sometimes to ignite the powder). The excess of nitric acid is got rid of by boiling, and the residue, containing antimony and copper, is evaporated to dryness and slightly calcined over a lamp.

The residue is dissolved in water acidulated with nitric acid, which dissolves the copper oxide, but takes with it a little antimony. If calcined in too hot a flame, the copper oxide cannot be separated from the antimonic acid. Any bismuth existing in the alloy would be found with the copper in the nitric solution.

Analysis of White Metal

White metal is an alloy of lead, antimony, tin, and a small quantity of copper. For the estimation of these metals, proceed in the following manner :—

One gramme of alloy is treated with 2 to 4 grammes of tartaric acid and 12 cubic centimetres of water; 4 cubic centimetres of nitric acid, of 1·4 density, are added to the solution obtained. This is heated moderately, to assist complete solution. The lead is then precipitated with 4 cubic centimetres of concentrated sulphuric acid. It is necessary to drive off the whole of the nitric acid ; a little cold water is then added, the sulphate of lead allowed to settle, and weighed in the usual manner. The solution, free from lead, is made alkaline by means of caustic soda, and then treated with 50 cubic centimetres of a cold saturated solution of sulphide of sodium. The precipitate of sulphide of copper formed is thrown on a filter, the filtrate is collected in a platinum crucible, heated to about 80°, and subjected to the action of an electric current of about 3 volts and 1·5 ampères. When the antimony is thus entirely deposited, the liquid is quickly poured into a beaker and the precipitated antimony dried. The solution is treated with 25 grammes of pure sulphate of ammonium, to transform the sulphide of sodium into sulphide of ammonium. There then only remains to electrolyse the warm liquid with the same strength of current, to estimate the tin.

Separation of Tin from Phosphoric Acid

For determining metals in the presence of phosphoric acid, Classen precipitates the acid as tin phosphate. If the precipitate, consisting of tin phosphate and tin oxide, is dissolved by digestion in ammonium sulphide and diluted with water, the tin may be deposited electrolytically, and the phosphoric acid determined in the filtrate in the ordinary manner.[1]

ARSENIC

Purification of Metallic Arsenic

In order to restore to this metal its bright aspect, and to remove any slight coat of suboxide which may adhere to it, the metallic arsenic should be boiled for a few minutes in a moderately strong solution of potassium bichromate, slightly acidified with sulphuric acid. The metal is next washed with water, and then with alcohol or ether, and lastly placed in a small tube closed at one end, and sealed immediately after.

[1] For details of operation see chapter on Electrolytic Analysis.

Detection of Arsenic by Marsh's Test

(*A*) When distilled magnesium, as now commonly met with in commerce, is introduced into a solution containing arsenic acidulated with sulphuric or hydrochloric acid, the arsenic is entirely separated in the form of arseniuretted hydrogen. Magnesium possesses great advantages over zinc for toxicological purposes. It is now met with in commerce almost absolutely pure, and the original materials and processes of its manufacture quite remove the poisonous metals most dreaded by chemists—copper, lead, mercury, arsenic, antimony, &c. It is met with in the form of long slight ribbons, well fitted for delicate laboratory experiments. It keeps well in dry air. Its low equivalent displaces the ordinary poisonous metals by relatively small proportions of the precipitating metal, and the perfectly harmless character of its salts, added to the fact that magnesium is a normal constituent of the animal body, renders its introduction into suspected liquids a matter of no consequence.

There is one precaution which must be taken in using magnesium in Marsh's apparatus. Magnesium which contains silicium gives off on contact with acids siliciuretted hydrogen, which decomposes at a dull-red heat like arseniuretted and antimoniuretted hydrogen, leaving a dark brown deposit. The formation of this deposit might give rise to an error. A few words will answer this objection.

1. The magnesium which is now manufactured gives no foreign deposit in Marsh's apparatus; no sample of magnesium ribbon (as made for burning) yet tested has given either rings or spots. The hydrogen it gives off has always appeared remarkably pure and inodorous; its flame is hardly visible.

2. Marsh's apparatus fed by magnesium is tested under precisely the same conditions as when fed by zinc. The suspected liquids are only introduced into the apparatus after the preliminary verification of the gas-producing agents.

3. The deposit of silicium left in the red-hot tube by the passage of the hydrogen accidentally charged with siliciuretted hydrogen is, moreover, clearly distinguishable from the deposits of arsenic and antimony. These last two disappear immediately on contact with a drop of nitric acid or aqua regia; the ring and spot of arsenic disappear suddenly when touched with a dilute solution of a hypochlorite. These three tests have no effect on the deposits of silicium produced in the tube of the apparatus.

If the suspected liquids contain no trace of arsenic or antimony, they may contain other poisonous metals, such as copper, lead, mercury, zinc, &c. In this case the metals are found as flakes, powder, or sponge, either at the bottom of the flask of the apparatus or on the surface of the plates of magnesium. To render the precipitation complete, the liquids must be kept in a proper state of acidity, and

the experiment prolonged till the new plates of magnesium introduced into the liquid dissolve, while retaining their metallic brilliancy. To ascertain the end of the operation, it is well to take out at first a small portion of the liquid of the flask, to put it into a small test-tube, and to introduce a well-cleaned ribbon of magnesium. However it may be, it is always necessary to leave in the flask a small excess of magnesium before pouring the liquid on a filter. All that is in suspension—corroded plates of magnesium, powder, flakes, or metallic sponge—is washed on the filter until the washings show no acid reaction; the filtered liquids should not precipitate on the addition of hydrosulphuric acid. The filter being dried, collect the deposit it contains, and analyse it in the ordinary way, to ascertain the metals precipitated by the magnesium.

(*B*) As an improvement on this process the matter containing the arsenious or arsenic acid is introduced into a Marsh's apparatus and mixed with a concentrated solution of caustic potash and a little aluminium foil. Arseniuretted hydrogen is disengaged on applying heat. Antimoniuretted hydrogen is not formed.

(*C*) Another modification of the Marsh process is as follows:—The substance in question is mixed with a little water, or its solution is poured into a small beaker, and a piece of sodium amalgam as large as a grain of wheat is introduced. The beaker is then covered as rapidly as possible with a piece of white filter-paper or a porcelain lid, previously moistened with a weak feebly acid solution of silver nitrate. The presence of arsenic is indicated by a blackening of the paper or of the porcelain. As antimony hydride is not given off, or only in mere traces from strongly alkaline liquids, the solution should be rendered distinctly alkaline. In this manner the confusion of antimony and arsenic is rendered improbable, though not quite excluded. Organic matter does not interfere.

(*D*) **Improvement in Marsh's Apparatus.**—Everyone who has experimented with an extemporised Marsh's apparatus has found that, after the gas has burned a short time, the glass tube has become fused and the aperture closed. This may be prevented by platinising the extremity of the tube. Draw up the tube, file it to make it a little rough, and then dip it into a strong solution of platinum bichloride, so as to take up a drop or so. Then carefully heat the point until it acquires a beautiful metallic lustre. By repeating this four or five times a good coating of platinum is obtained both outside and inside.

Detection of Arsenic in Beer and Foodstuffs

After an exhaustive trial of the various methods that have been suggested, W. Thomson has found that the Marsh-Berzelius test gives the most satisfactory results.

Materials Required

Hydrochloric Acid.—The acid sold as pure, nearly always contains arsenic. To purify it, dilute strong acid of any kind with about one-third its volume of water, although the dilution is not necessary. (If the acid be not diluted, some water must be put in the receiver to condense or dissolve the HCl liberated as a gas at first.) Put it in a retort, add to it about 1 gramme per litre of chromic acid, and distil. By preference, use a large stoppered glass flask placed on a sand-bath, a tube from the neck of which enters a Liebig's condenser, glass touching glass, and the distillate is collected. It is, however, saturated with chlorine.

Pass a current of filtered air through the distillate—say about half a gallon—for about two hours by means of a water vacuum pump, when every trace of chlorine is removed, and no trace of arsenic will be found in the distillate.

On standing in most glass bottles, hydrochloric acid becomes faintly contaminated with arsenic, but the amount does not exceed $\frac{1}{1000}$ of a grain per gallon dissolved during one month.

Sulphuric Acid is purified in the following manner :—

Into a non-tubulated retort put the sulphuric acid previously mixed with about a gramme to the litre of chromic acid or potassium permanganate. Distil, and collect the distillate, which is free from any trace of arsenic or from sulphuric acid. If the tube of the retort has been contaminated with the crude acid during the process of filling, throw away the first portion of the distillate. The retort is set in a sand-bath standing on a ring burner, with an iron tray underneath, contained in a wooden box; and the neck of the retort passes through a hole in the end of the box; the top of the retort is covered with asbestos cloth, but not the tube. If the tube be covered all the way down, it is liable to break suddenly from the end, the breakage running up towards the retort, and this produces an objectionable evolution of acid vapour into the laboratory. If the retort should break, the gas can be turned off from the outside, the lid placed quickly on the box, and a wet cloth thrown completely over it, thus avoiding any nuisance.

The whole of the distillate, even if the distillation be carried nearly to dryness, is free from any trace of arsenic.

Nitric Acid scarcely ever contains arsenic; still it is advisable to make blank tests to prove that it is free.

Zinc.—The zinc employed should be so pure that when placed in dilute sulphuric or hydrochloric acid very little hydrogen is liberated.

It is necessary to add a little sulphate of copper to start and carry on the reaction. If the reaction commences at once vigorously, the zinc contains some foreign metal, such as iron, in sufficient quantity to hold back considerable quantities of arsenic; so that, although

it may give hydrogen free from arseniuretted hydrogen, it is yet quite unsuitable for the Marsh test.

Apparatus.—Soften by the blowpipe and draw out a piece of tube 200 millimetres long, $4\frac{1}{2}$ millimetres internal and $6\frac{1}{2}$ millimetres external diameter, from the middle, thus producing two tubes, each 100 millimetres in length, with 140 millimetres of drawn-out portion between them. The drawn-out portion is cut in the middle, leaving two tubes with 70 millimetres drawn out from each; the drawn-out portion for receiving the mirror being about 2 millimetres internal diameter.

At 70 millimetres from the drawn-out end the glass is again softened and drawn out for 30 millimetres; and in the remaining 30-millimetre portion of the tube, at the end is inserted a roll of filter-paper previously soaked in a strong solution of lead acetate and dried.

When the test has been completed the point of the drawn-out portion is sealed, and the drawn-out portion at the other end is also sealed by the blowpipe. Mirrors which have been thus sealed in hydrogen have been examined in comparison with others left unsealed, and no difference has been observed between them after many months. But it is desirable to seal up the tube and preserve the mirrors in an atmosphere of hydrogen.

To prepare the device for introducing the solution to be tested, grind the end of a glass rod into the end of the thistle tube entering the Marsh-Berzelius flask, which has previously been rounded in slightly, by softening the end in a Bunsen flame; on raising the rod the liquid flows in, and on letting it down the flow stops. By this means no column of liquid is left in the tube, as is the case when a glass tap is used, and no gas can rise through this simple stopper.

Process for Estimation of Arsenic in Beer and Stout, Malt, Caramel, &c.

Beer.—Take of the sample 50 cubic centimetres, and evaporate to a syrup on a sand-bath or iron plate in a 200 cubic centimetre Jena glass flask. Add 25 cubic centimetres strong nitric acid and 5 cubic centimetres strong sulphuric acid; place on a hot sand-bath, having taken away the flame; allow the first violent action to subside, the acid fumes from which may be drawn away through a glass tube in the mouth of the flask by a water Sprengel pump through a solution of caustic soda in a Wolff's bottle. Then apply a Bunsen flame to the sand-bath, and evaporate till the liquid begins to darken. When this occurs add strong nitric acid in quantities of 3 cubic centimetres at a time (the total quantity of nitric acid required varies from 30 to 50 cubic centimetres, depending on the quantities of organic matter present), until on further heating it continues colourless, and fumes strongly of sulphuric acid; cool, dilute with 10 cubic centimetres of water, and boil to break up

the nitro-sulphuric acid formed. When cold, dilute with 10 cubic centimetres of water, and deliver into the Marsh-Berzelius apparatus, the capacity of which should not exceed 50 cubic centimetres. The gas evolved should be dried over calcium chloride contained in one tube 70 millimetres long by 8 millimetres diameter.

Testing Reagents.—A blank on the reagents and apparatus used should be made by boiling down 100 cubic centimetres HNO_3 and 5 cubic centimetres H_2SO_4 till all nitric acid is expelled, diluting and boiling down (this procedure removes every trace of nitric or nitrous acid), again diluting, and testing in the Marsh-Berzelius apparatus as above described.

Process for Malt, Sugar, Caramel, Hops, Yeast, &c.—Take 5 grammes of malt or other solid organic substance, add 25 cubic centimetres HNO_3, and heat gently till the first violent action is over; then add 5 cubic centimetres sulphuric acid, and proceed as for beer (a total of from 50 to 75 cubic centimetres of nitric acid will be required).

The Marsh-Berzelius Apparatus (50 cubic centimetres flask) should contain about 20 to 25 grammes zinc. The $CaCl_2$ in the drying tube should be renewed as soon as the first few pieces become wet.

Action is started by adding 5 cubic centimetres of dilute sulphuric acid (10 parts concentrated sulphuric acid, 20 of water, and 1 part of a 10-per-cent. solution of pure crystallised copper sulphate). Allow the evolution of gas to go on (the exit tube for the hydrogen being heated in the usual manner by means of a small Bunsen flame) until the hydrogen nearly ceases to be evolved (there is no advantage in removing the air from the apparatus by means of hydrogen generated in another apparatus); then fill up the tube and funnel of the Marsh-Berzelius apparatus with the solution previously treated as above, and allow the whole to run in if only a very minute quantity of arsenic is supposed to be present; or run in an aliquot part if a larger quantity is supposed to exist. In about fifteen minutes the flask is washed with 5 cubic centimetres more of the above acid, which is added to the hydrogen flask in small quantities at a time, to keep up the evolution of gas for a total of from thirty to thirty-five minutes after the first introduction of the previously treated beer; by which time, with an apparatus of this size, all the arsenic will have passed off.

The hydrogen flame at the end of the drawn-out portion should be about 2 millimetres long, and maintained as constant as possible: too slow a flow almost invariably gives double mirrors; too fast a flow gives irregular ones, difficult to compare with the standards.

Zinc.—Twenty grammes of zinc should be tested by the action of 30 cubic centimetres of dilute H_2SO_4—1 of acid to 2 of water—containing a little copper sulphate to start the reaction as above described; there should be absolutely no trace of arsenic mirror on the drawn-out portion of the glass tube.

Another experiment should then be made, adding a minute quantity

of arsenic—say equal to $\frac{1}{500}$ of a grain per gallon (when working on 50 cubic centimetres), equal to 0·029 part per 1,000,000, or an actual weight of 0·00143 milligramme—and compared with a standard tube to make sure that the zinc contains nothing which will hold back minute quantities of arsenic.

The glass tube should be about 4½ millimetres internal diameter, and about 6½ millimetres external. It should be drawn out in the middle and at the end, the length of the drawn-out portions respectively being 30 millimetres and 70 millimetres, and that part of the tube between the drawn-out portions being 60 millimetres. The internal diameter at the beginning of the drawn-out portion for receiving the mirror is about 2 millimetres.

A piece of fine iron gauze 20 millimetres wide is wrapped round the tube and heated by a Bunsen flame. This is a more satisfactory plan than applying the flame directly to the tube, and conduces to the formation of more uniform mirrors.

A roll of lead-acetate paper is introduced to absorb any traces of sulphuretted hydrogen which may be formed.

Bunsen Flame.—This should be about 4 inches long, and protected till near the point by a conical iron or copper chimney about 2½ inches high, by 2¼ inches at the lower and 1½ inch diameter at the higher part of the cone.

Heating the Tube.—This should be heated from the shoulder, or drawn-out portion, for about half an inch.

Standard Mirrors for comparison are made by introducing into the apparatus known quantities of arsenic—say, commencing with $\frac{1}{50}$ of a grain per gallon when working on 50 cubic centimetres. A convenient method of preparing the standard mirrors is to employ a solution of arsenious acid containing 0·007145 of a milligramme of As_2O_3 per cubic centimetre. One cubic centimetre of this solution is equal to $\frac{1}{100}$ of a grain of As_2O_3 per gallon when using 50 cubic centimetres, or $\frac{1}{100}$ of a grain per pound when using 5 grammes of material. This solution is suitable for standards between $\frac{1}{50}$ and $\frac{1}{100}$ of a grain per gallon, and a solution of one-tenth this strength may be employed for the standard mirrors between $\frac{1}{100}$ and $\frac{1}{1000}$ of a grain per gallon.

The mirrors I have found most useful are $\frac{1}{50}$, $\frac{1}{66}$, $\frac{1}{88}$, and $\frac{1}{100}$ of a grain per gallon, corresponding to 2·0, 1·5, 1·25, and 1·0 cubic centimetres of the stronger solution; and $\frac{1}{111}$, $\frac{1}{125}$, $\frac{1}{143}$, $\frac{1}{166}$, $\frac{1}{200}$, $\frac{1}{250}$, $\frac{1}{333}$, $\frac{1}{500}$, $\frac{1}{666}$, and $\frac{1}{1000}$ of a grain per gallon, corresponding to 9·0, 8·0, 7·0, 6·0, 5·0, 4·0, 3·0, 2·0, 1·5, and 1·0 cubic centimetres respectively of the weaker solution.

Estimation of Arsenic in Cacodylic Acid

Professor Thomson has made experiments with a view of finding whether the arsenic contained in this compound could be estimated by his process, with the following result:—

Fifty cubic centimetres of the solution containing cacodylic acid equivalent to $\frac{1}{100}$ of a grain of As_2O_3 per gallon are treated with nitric and sulphuric acids in the ordinary way, along with potassium permanganate (suggested by Villiers for breaking up organic compounds), by using 10 cubic centimetres of a $\frac{1}{2}$-per-cent. solution of potassium permanganate in addition to the sulphuric and nitric acids; the cacodylic acid is thus destroyed, and its equivalent arsenic mirror obtained.

Detection and Determination of Minute Traces of Arsenic

The accompanying sketch (half actual size) is that of an apparatus devised by E. Douzard[1] for the detection of minute quantities of arsenic.

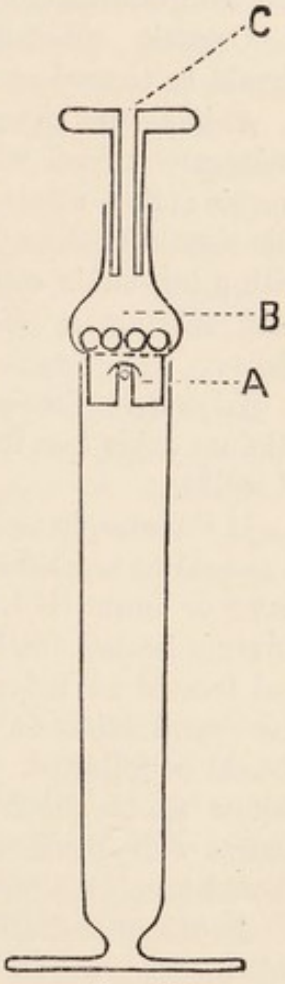


FIG. 20.

A, Trap.
B, Scrubbing chamber containing beads.
C, Orifice, 3 mm. in diameter.

Using this apparatus $\frac{1}{10000000}$ gramme can be detected, and $\frac{1}{15000000}$ to $\frac{1}{20000000}$ gramme can just be recognised. For all practical purposes $\frac{1}{4000000}$ gramme may be taken as the limit. The apparatus is used as follows:—A rod of pure zinc, 2 centimetres long and 5 millimetres in diameter, is placed for about half to one minute in boiling water containing about 5 per cent. pure HCl (sp. gr. 1·124); this to remove any surface impurities. The rod is then washed in distilled water, and placed in the apparatus. Two cubic centimetres of HCl (sp. gr. 1·124), free from arsenic, and containing 6 drops of a 15-per-cent. solution of cuprous chloride in 100 cubic centimetres, is mixed with the substance to be tested, which must be in solution, and the liquid made up to 8 cubic centimetres. Before introducing the liquid a piece of Swedish filter-paper, 3 centimetres square, is prepared as follows:—A ring about 12 millimetres in diameter is drawn with a graphite pencil in the centre of the paper, which is then moistened inside the ring with 5 per cent. mercuric chloride solution, and dried. The ring is drawn merely to show the position of the mercuric spot. The glass beads in the scrubbing chamber may be moistened with a solution of lead acetate or cuprous chloride; the trap underneath is to prevent any washing liquid from entering the apparatus, or the scrubbing chamber may be filled with cotton-wool which has been saturated with a 5-per-cent. solution of lead acetate, and dried.

[1] *Chemical News*, July 4, 1902.

The mercuric chloride paper is now attached to the top of the apparatus with a clip, so that the orifice is under the centre of the ring. The liquid to be tested is introduced into the apparatus, which is placed in water at 60° C. (the water should be on the same level as the liquid inside the apparatus). After thirty minutes the paper is removed and examined in full daylight: a minute trace is indicated by a lemon-yellow spot, and a trace by a deep orange-brown spot.

A blank test with the reagents must precede the examination. It is only necessary to test the same batch of acid and zinc occasionally.

In the absence of organic matter this test is of extraordinary delicacy; for instance, if the sample is a liquid and 4 cubic centimetres is used, 1 part in 16,000,000 can be detected. If the sample is a solid and 0·5 gramme is used, 1 part in 2,000,000 can be detected.

Organic substances, and liquids containing organic substances, should be treated as follows:—

Solids.—0·5 gramme is made into a paste or strong solution with water, and mixed with 0·2 gramme of pure calcium oxide free from arsenic: the mixture is then dried on asbestos felt and ignited; this should be done in a small porcelain dish. The residue is mixed with a few cubic centimetres of water, and HCl added drop by drop until solution is effected; this solution is then examined as described above.

Liquids.—Two cubic centimetres are mixed with 0·1 gramme of pure calcium oxide free from arsenic, and the mixture treated as in the case of solids.

If the sample to be examined contains sulphites or hypophosphites, it should be treated as follows:—The substance should be dissolved in water or dilute HCl, a slight excess of bromine water added, and the mixture heated until free from bromine; the solution is then cooled, and treated as before described. This apparatus is recommended for the examination of beer and glucose for arsenic; the lime treatment should be followed. To facilitate comparisons with the standards, the yellow spots should be encircled with a black band about 2 millimetres wide, made with a graphite pencil—the inner edge of the band should touch the outer edge of the spot.

In the quantitative determination of the minute traces of arsenic by this method, the following points should be observed:—

1. The amount of HCl used, the final bulk of the liquid, and the size of the zinc rod should always be the same. The starting temperature should be 60° C.

2. The reaction should always occupy thirty minutes.

3. When comparing the sample with known amounts of arsenious acid, the standard test must contain the same weight or volume of the same substance as sample, but free from arsenic. A standard set of spots may be prepared for each substance; they should be kept in a tightly stoppered bottle in a dark dry place.

The cuprous chloride solution is prepared as follows:—Sixteen grammes of pure CuO are dissolved in 110 cubic centimetres of HCl, 13 grammes of thin copper-foil are cut into small pieces, and boiled with the above solution for twenty-five minutes; the resulting solution of cuprous chloride is poured into 1000 cubic centimetres of distilled water, and the white precipitate washed by decantation. The chloride is then dissolved in HCl free from arsenic, and the solution standardised to contain about 15 grammes of cuprous chloride in 100 cubic centimetres.

Detection of Arsenic in the Colours of Paper Hangings

Professor Hager recommends the following method:—A little of the paper is steeped in a concentrated solution of sodium nitrate obtained by dissolving this salt in a mixture of equal parts of alcohol and water, and letting it dry. Then the paper is burnt upon a porcelain saucer. The combustion generally takes place quietly and without a flame. Water is poured upon the ashes, potash in excess is added, and the whole boiled and filtered. Dilute sulphuric acid is next added, and then potassium permanganate gently as long as the red colour disappears, and gives place to a yellow under the influence of heat. If the liquid becomes turbid it is filtered anew. It is allowed to cool, and more dilute sulphuric acid added, and a small plate of pure zinc. This should be done in a flask, which is then stoppered with a cork having two slits. In one of these is placed a slip of paper steeped in a solution of silver nitrate; in the other, a piece of parchment moistened with lead acetate. If arsenic is present, the silver paper blackens. The lead paper only serves to detect sulphuretted hydrogen.

Reinsch's Test for Arsenic

To distinguish the arsenical deposit obtained in Reinsch's process from one formed by a mercury salt, J. St. Clair Gray first washes one of the copper slips, coated in the ordinary manner by Reinsch's process, in pure distilled water, and then thoroughly dries it; when thus prepared it is rubbed with a flattened bead of pure gold, or, should this not be at hand, a flat signet-ring will suffice. The result, if the coating be mercurial, is that a portion of the mercury, whose affinity for gold is greater than for copper, is transferred from the copper to the gold, appearing on its surface as a clear white, shining, metallic coat, this being more conspicuous the more highly coloured the surrounding gold is. This stain is at once removed by pure strong nitric acid. This is of itself perfectly conclusive of the presence of mercury in the metallic coating or deposit on the copper, and is equally applicable should there exist in that deposit a combination of mercury with any or all of the other three metals which yield by Reinsch's process a metallic deposit on copper-foil.

Identification of Arsenious Acid by Crystallisation

By allowing the crystals of arsenious acid to form gradually by slow cooling, they can be obtained very large and perfect. The following mode of forming them is the one recommended by F. W. Griffin:—Drive the substance entirely off the lower half of the tube, which is made very hot by waving it about in the flame. Then re-vaporise the sublimate, holding the tube (which should be closed by a loosely fitting cork) as upright as possible. The dense vapour sinks to the bottom, and will give large and regular crystals as the glass slowly cools. These crystals glitter in the sun like diamonds, and exhibit the same play of colours; they are from the $\frac{1}{150}$ to the $\frac{1}{200}$ of an inch in diameter, and under a 1-inch objective, form specimens for the micro-crystallographer. Here and there we find octahedra absolutely perfect, but they are more frequently truncated, all the angles, however, being beautifully sharp. The majority are transparent, but some are only translucent, or even opaque. By reflected light (using a bull's-eye condenser) they appear, in consequence of their adamantine lustre, like diamonds lying in high relief on a black ground; but their complete shape is most strikingly displayed by a combination of strong reflected and feebler transmitted rays of various degrees of obliquity. A tube of $\frac{1}{2}$ inch in diameter, under a 1-inch objective, presents nearly the entire field in focus, and the perfect crystals appear from $\frac{1}{2}$ to $\frac{3}{4}$ of an inch in diameter.

Estimation of Arsenious Acid in Presence of Arsenic Acid

L. Mayer takes as a point of departure the known property of arsenious acid to reduce ammoniacal solution of silver at a boiling heat, and bases upon it a convenient gravimetric method for the estimation of arsenious acid along with arsenic acid. The common method of precipitating arsenic with magnesia solution as ammonio-magnesium arseniate is not free from sources of error, due to the solubility of the latter compound. The methods of H. Rose and Vohl are tedious and elaborate. Mayer's method depends upon the following decomposition. If a solution contains in addition to arsenious acid no other substance which reduces the ammoniacal solution of silver at a boiling heat, reduction takes place, and, after boiling for half an hour, the reduced silver separates out as a fine powder and is filtered off and weighed. The quantities of silver thus obtained agree exactly with the arsenious acid employed. The reduced silver must be washed with warm ammonia and water containing sal-ammoniac. If a portion of the silver is reduced in the form of a mirror on the sides of the glass, it is dissolved off in nitric acid, precipitated as silver chloride, which is added to the main quantity of the silver; for such small traces of silver chloride are reduced on ignition by the carbon of

the filter. In applying this method for the estimation of arsenious acid in the presence of arsenic acid, the arsenious acid is estimated by boiling with ammoniacal solution of silver. On the reduction of the silver the arsenious acid passes into arsenic acid, which is estimated along with the original arsenic acid. The quantity of the latter is found as difference.

Silver Nitrate Test for Arsenic Acid

Silver arseniate is slightly soluble in an aqueous solution of ammonium nitrate, and readily soluble in both ammonia and dilute nitric acid; it is, therefore, not easy to detect small quantities of arsenic by means of silver nitrate as usually employed, unless the test be applied with extreme care.

(*A*) Mr. Every has found that the addition either of sodium acetate, ammonium acetate, or Rochelle salt, to a mixed solution of arsenic and nitric acids, is sufficient to ensure the immediate precipitation of silver arseniate when silver ammonio-nitrate is introduced. Instead of the acetates or tartrates, recently precipitated silver carbonate may be employed to neutralise free nitric acid. When present in relatively large quantity, arsenic acid readily precipitates silver from a solution of ammonium nitrate and silver ammonio-nitrate, but the colour of the precipitate is uncertain.

(*B*) For the recognition of arsenic acid, E. Salkowski dissolves arsenic sulphide in fuming nitric acid, expels the greater part of the acid by evaporation, heats the residue with water holding in suspension calcium or barium carbonate, and filters. The calcium and barium arseniates are sufficiently soluble for the filtrate to give a red precipitate on adding silver nitrate.

Detection of Arsenic in Commercial Hydrochloric Acid

When arsenious or arsenic acid is dissolved in fuming hydrochloric acid, and a solution of tin protochloride dissolved in hydrochloric acid is added thereto, a brown-coloured, very bulky precipitate is formed which rapidly settles down. After having been collected on a filter and washed, first with hydrochloric acid and then with water, to remove the acid, and then dried over sulphuric acid *in vacuo*, the precipitate forms a greyish-coloured powder of metallic aspect; this, on being rubbed in an agate mortar, exhibits metallic lustre, and partially volatilises on being heated, while oxide of tin, in the shape of a very light powder, is left. The precipitate consists of from 95·86 to 98·46 per cent. of metallic arsenic, according as arsenious acid, arsenic acid, or ammonium arseniate and magnesium has been employed. The precipitate is never obtained quite free from tin. When the hydrochloric acid employed has a sp. gr. of 1·115, the arsenious or arsenic acid dissolved therein becomes for the most part converted into arsenic

chloride; and the reaction, therefore, takes place between that chloride and tin protochloride. When the hydrochloric acid has a sp. gr. of 1·1, the arsenious acid is not converted into arsenic chloride, but is dissolved as arsenious acid. Tin chloride does not act upon compounds of antimony under the same conditions.

In order to eliminate all arsenic from it, crude hydrochloric acid, sp. gr. 1·104, should be treated with a strong solution of tin protochloride in pure hydrochloric acid, left standing for twenty-four hours, and the precipitate removed by filtration. The acid is next placed in a retort, the first $\frac{1}{10}$th of the distillate kept separately, and the remainder distilled off to dryness, when that portion will be found absolutely free from arsenic; the first $\frac{1}{10}$th may in some cases retain as much as 0·02 per cent. of arsenic.

Separation of Arsenic from other Metals

Emil Fischer finds that arsenic may be very conveniently separated from a given mixture with other metals by distillation with ferrous chloride, and its subsequent estimation effected with solution of iodine. This offers such great advantages that scarcely any of the older methods will be used when the estimation of this element alone is required. If the substance in question is already dissolved, the whole operation may be completed in four hours. The process is especially adapted for chemico-legal cases.

Estimation of Arsenic as Magnesium Pyro-arseniate

(*A*) Dr. F. Reichel places the well-dried precipitate as completely as possible in a watch-glass, moistens the filter with a solution of ammonium nitrate, dries, and burns it, previously cut up into pieces, in a porcelain crucible. When the crucible is cold the contents of the watch-glass are introduced into it, a few drops of nitric acid added so as to saturate the whole precipitate, and the crucible is dried at 100° or heated carefully over a small gas-flame, to prevent spirting. As soon as the watery vapours no longer escape, the crucible is closed, and ignited strongly for ten minutes.

(*B*) C. Rammelsberg remarks that if magnesium ammonio-arseniate is dried at 100° to 110°, as commonly recommended, a part of the ammonia escapes. It is best to dry at 120°, and ignite with proper precautions. There is no reduction of arsenic. The volumetric estimation of the arsenic acids—arsenic acid being previously reduced by means of sulphurous acid—by supersaturating with potassium bicarbonate, adding starch paste, and titrating with solution of iodine, is very useful.

Separation of Arsenic from Gallium

In a strong hydrochloric solution hydrogen sulphide entirely precipitates the arsenic, while the gallium remains in solution. The

arsenic sulphide is washed with water acidified with hydrochloric acid, and not with pure water, to prevent the precipitate from passing through the filter.

Volumetric Estimation of Small Quantities of Arsenic and Antimony

A. Houzeau has observed that the hydrogen compounds of arsenic and antimony are almost entirely and instantaneously absorbed by slightly acidulated silver nitrate.

On this reaction, an accurate and sensitive process for the indirect estimation of arsenic and antimony according to the quantity of silver precipitated can be based, and also a direct process for the estimation of arsenic according to the proportion of arsenious acid formed.

Indirect Process.—This process is carried on in the following manner:—The substance containing arsenic or antimony, so prepared that it can be reduced by hydrogen, is placed in a Marsh apparatus in which hydrogen is evolved from pure zinc and pure hydrochloric acid. The gas is first conducted through a column of chalk (lumps of chalk put into a tube placed vertically), and next into a titrated solution of neutral silver nitrate, which is then diluted with its own bulk of water, and acidulated with 2 or 3 drops of nitric acid, or, still better, by 0·5 c.c. of acetic acid, so as to prevent the precipitate of a certain quantity of silver arsenite. The silver which remains in solution is estimated by means of a standard solution of common salt.

The estimation of the arsenic may be performed by the direct method, consisting of a chlorometric process with the silver solution which has been used for absorbing the arseniuretted hydrogen. For this purpose the whole of the silver is precipitated by a slight excess of a 3 per cent. sodium chloride solution; the volume of the liquid and precipitate is measured (say 25 or 50 c.c.), and the whole thrown on to a perfectly dry filter, which is not washed. The clear filtered liquid is first measured (say 22 to 40 c.c.), and then poured into a test-glass, and there is added to it 1 or 2 c.c. of perfectly pure and colourless hydrochloric acid. The quantity of arsenious acid is next estimated by means of a titrated solution of potassium permanganate.

The methods simultaneously applied may be used to estimate with precision a mixture of arsenical and antimonial compounds, and also for the quantitative analysis of arseniuretted hydrogen mixed with antimoniuretted hydrogen.

The method is also applicable to the estimation of arsenic and antimony mixed with organic substances, but it is necessary to first destroy these substances.

Although this method is only directly applicable to those antimonial and arsenical compounds which admit of being reduced by nascent hydrogen, such as arsenic and arsenious acids, antimonic acid, &c., the use of this method may be extended to arsenic sulphides and

phosphides, after the previous oxidation of these substances by means of hydrochloric acid and potassium chlorate.

This process of oxidation will always have to be resorted to when arsenic or antimony is to be detected in a compound of unknown composition, because sulphurous, sulphydric, and phosphuretted hydrogen compounds will affect the silver solution in the same manner as arseniuretted and antimoniuretted hydrogen. Pure hydrogen does not reduce silver nitrate solution.

Estimation of Arsenic in Arsenic Tersulphide

To estimate the arsenic contained in arsenic tersulphide—an operation often necessary for the estimation of arsenic—Graebe uses a standard solution of iodine, as in the estimation of arsenious acid. Suspend the arsenic sulphide in water, add some sodium carbonate, then a little starch paste, and the standard solution of iodine. It is necessary that the arsenic sulphide should be freed from sulphuretted hydrogen. For every equivalent of arsenic tersulphide converted into arsenic acid, 5 equivalents of iodine are decolourised by conversion into hydriodic acid, and 3 equivalents of sulphur are precipitated.

Estimation of Arsenic in Arsenic Pentasulphide

A solution of arsenic pentasulphide in ammonium sulphide instantly yields a precipitate of magnesium ammonio-arseniate by a solution of magnesia. Lenssen states that the tin and antimony sulphides are not precipitated under the same conditions. Attempts to found a process of separating arsenic from tin and antimony on this reaction have proved unsuccessful.

Estimation of Arsenic in Ores

(*A*) For estimating the amount of arsenic in ores, Parnell says that the neatest, simplest, and most accurate mode of procedure is to heat the finely divided sample in a gentle stream of chlorine gas to a temperature of about 200° C., and to collect the escaping arsenic chloride in chlorine-water. If free from antimony, the liquid may be well boiled, to expel free chlorine, and the arsenic precipitated with sulphuretted hydrogen, and weighed as pentasulphide.

(*B*) In cases where the arsenic is obtained in the form of arsenio-magnesium phosphate (as in separation of the metal from antimony or copper), the most accurate plan would be to dissolve the precipitate in hydrochloric acid and throw down the arsenic as pentasulphide. When the amount of arsenic is small, it may be weighed as double arseniate. The sample should not, however, be dried at a higher temperature than that of an ordinary water-bath—namely, about 95° C. Perfectly accurate results could, no doubt, be obtained by drying the

precipitate over sulphuric acid, when it retains its 6 equivalents of water. The only objection is that it would take many days for a filter containing a precipitate to be properly dried by this means.

(*C*) MM. de Clermont and Frommel proceed thus :—Supposing we have a mixture of arsenic, antimony, and tin, the whole is converted into sulphides by treatment with sulphuretted hydrogen, after having acidulated with hydrochloric acid, adding also tartaric acid if antimony is present. When the mixture is saturated it is allowed to stand in a warm place till the odour of sulphuretted hydrogen is no longer perceptible, and is then thrown upon a filter and washed with much care, as the least residue of hydrochloric acid would cause a loss of arsenic in the state of chloride. The whole is then transferred into a flask full of water, and heated to a boil. The reaction is more rapid in a retort through which a current of air is passed. If the quantity of arsenic does not exceed 2 decigrammes the distillation of 500 to 600 c.c. of water suffices for the complete dissociation of the sulphides. The residue is then filtered off, and the entire quantity of the arsenious acid is found in the filtrate, and estimated by the ordinary methods.

Separation of Arsenic from Tin

(*A*) Potassium bisulphite dissolves arsenic sulphide, but does not dissolve tin sulphide. The mixture of the two sulphides, oxidised by nitric acid, is allowed to digest with sulphur and caustic potash till solution is complete (or till the formation of a metallic oxysulphide, which is separated by filtration). The liquid, treated by excess of sulphurous acid, is allowed to rest for some time, and is then evaporated till two-thirds of the water and all the sulphurous acid have gone off. Filter off the tin sulphide, and wash it, not with water, which must not be used here, but with a concentrated solution of sodium chloride. This may be removed from the precipitate by means of a slightly acid solution of ammonium acetate, but the liquor so obtained must not be added to the washing-waters charged with salt. The tin sulphide, when dried, may be converted into tin oxide by roasting in contact with air. The arsenic which the liquid contains in the state of arsenious acid may be precipitated by a current of sulphuretted hydrogen.

(*B*) Arsenic sulphides, even upon very long boiling with oxalic acid, are almost unattacked. Very minute traces of the metal sometimes go into solution, but may be reprecipitated by a bubble or two of sulphuretted hydrogen. Accordingly, the presence even of an enormous excess of oxalic acid does not hinder the precipitation of arsenic as sulphide. Both tin sulphides, if moist and freshly precipitated, are readily decomposed by moderately long boiling with an excess of oxalic acid, sulphuretted hydrogen being given off.

To separate the two metals proceed as follows :—To the solution containing arsenic and tin (this solution being prepared in the usual

manner for the precipitation of the sulphides) add oxalic acid, in the proportion of about 20 grammes of the reagent for every gramme of tin, taking care to have the whole so concentrated that the acid will crystallise out in the cold. Then heat to boiling, and pass in sulphuretted hydrogen for about twenty minutes. No precipitate appears at first ; but as soon as the liquid is saturated with the gas arsenic sulphide begins to fall, and in a very few moments is completely thrown down. Then, as usual, the whole should be allowed to stand about half an hour in a warm place, before filtering. Every trace of arsenic is precipitated, so that, in the filtrate from the sulphides, it cannot be discovered by Marsh's test. The precipitated arsenic sulphide is absolutely free from tin.

Solution of Arsenical and Antimonial Compounds

Rammelsberg's method of separating arsenic and antimony from the metals of the fifth group, by fusion with sodium carbonate and sulphur and solution in water, has the drawback that the aqueous solutions contain highly sulphuretted compounds, which, on exposure to the air, deposit incrustations of sulphur, and on decomposition with hydrochloric acid precipitate the arsenic and antimony sulphides mixed with much sulphur, which is very inconvenient in dissolving the arsenic sulphide, or in converting the antimony sulphide into antimonic acid. By using sodium thiosulphate previously completely dehydrated by cautious fusion in a capsule, this inconvenience is avoided, and the sulphides thrown down from the aqueous solution of the melt are contaminated with but little free sulphur.

Separation of Arsenic from Antimony

(*A*) An accurate method of separating these two bodies is founded on the fact that recently precipitated arsenic sulphide is soluble in potassium bisulphide, while antimony sulphide is insoluble. If, for example, we have to analyse commercial grey antimony sulphide, or metallic antimony, it can be done as follows :—Mix the finely pulverised and weighed substance with a little sulphur, and digest in a solution of potassium protosulphide : the mass dissolves, generally leaving a black residue, consisting of a mixture of lead, iron, and copper sulphides, which must be filtered off and examined separately. The liquid is mixed and digested with a large excess of water saturated with sulphurous acid, then heated and kept in ebullition till two-thirds of the water has boiled away and there is no smell of sulphurous acid. Antimony sulphide will be precipitated, and from the filtrate from this the arsenic may be precipitated by a stream of sulphuretted hydrogen gas.

(*B*) Among the many methods for separating arsenic from antimony, the one which is based upon the dissimilar deportment of

arseniuretted and antimoniuretted hydrogen with silver nitrate, deserves to be favourably mentioned; the former yielding arsenious acid, which passes into solution; the latter giving rise to the formation of silver antimonide, which is insoluble in water. The arsenic may be recognised in solution by ammonia, if there be an excess of silver, or by sulphuretted hydrogen, if the silver has been entirely precipitated. By boiling the mixture of silver and silver antimonide (after the arsenious acid has been carefully washed out by boiling water) with tartaric acid, this dissolves the antimony alone, and the solution thus obtained yields at once the characteristic orange-yellow precipitate with sulphuretted hydrogen.

With minute quantities this process proves successful, inasmuch as 5 milligrammes of either metal in the presence of 100 times the amount of the other can be satisfactorily exhibited. In evolving the hydrogen compounds of arsenic and antimony, care must be taken to add as little nitric acid as possible to the hydrochloric acid used in dissolving the sulphides of the metals, since the presence of even moderate quantities of this acid greatly interferes with the free disengagement of the gases. It is also preferable to employ magnesium instead of zinc for this purpose (see page 391).

(*C*) R. Bunsen dissolves the antimony and arsenic sulphides, while still moist, upon the filter in an excess of solution of potash, which must have been purified by means of alcohol. The solution, together with the concentrated washings, is introduced into a porcelain crucible holding about 150 c.c., and a rapid current of chlorine is introduced into the liquid through a hole in the watch-glass which serves as a cover, till all the alkali is neutralised. The crucible, still covered with the watch-glass, is heated in the water-bath, and concentrated hydrochloric acid in great excess is dropped in by means of a pipette. The liquid is evaporated down to half its bulk, the loss is again made up with an equal volume of concentrated hydrochloric acid, and the liquid is again concentrated down to one half or third, in order to expel all free chlorine. It can now be diluted to a perfectly limpid solution, by the addition of very weak hydrochloric acid, without tartaric acid, which interferes with the separation. To this solution there are now added, for every decigramme of antimonic acid probably present, about 100 c.c. of a recently prepared and *saturated* solution of sulphuretted hydrogen, when antimony pentasulphide is precipitated immediately or after a short time, according to its larger or smaller proportion. As soon as this precipitate has separated itself, the excess of sulphuretted hydrogen is immediately removed from the solution, by forcing through it a violent current of air, filtered through cotton-wool. This is easily effected by means of the blast of a glass-blowing table. To prevent loss by spirting, the beaker must be kept covered with a perforated watch-glass, the air-pipe entering through its aperture. In about fifteen to twenty minutes the gas is expelled and the liquid becomes inodorous.

The precipitate is then thrown upon a weighed filter and washed with the filter-pump, the filter being filled in succession eight or ten times with water, twice with alcohol, four times with carbon disulphide, and finally three times with alcohol. The precipitate is dried at 110° in the salt-bath, at which temperature it remains for any length of time perfectly constant in weight. The washings, even in not very experienced hands, do not require more than an hour. The filtrate which contains the arsenic as arsenic acid does not retain the least trace of antimony. The antimonial precipitate may in certain cases retain quite insignificant traces of arsenic. But if, after washing with water, it is redissolved in potassium hydrate, and the process of separation repeated, the antimony is obtained free from any trace of arsenic. The estimation of arsenic in the filtrate and washings is not less simple. The collected liquid, after the addition of a few drops of chlorine, is heated on the water-bath and treated with a prolonged current of sulphuretted hydrogen both while hot and during cooling.

The precipitate is allowed to settle for a day at a gentle heat, and is then placed upon a weighed filter. If care has been taken to leave a sufficient excess of hydrogen sulphide in the liquid during heating and cooling, the precipitate consists of a little sulphur and arsenic pentasulphide without the least admixture of trisulphide. Before weighing it is treated exactly like the antimonial precipitate. Its composition and weight are constant after drying at 110° C.

Detection of Arsenic in Tartar Emetic

(*A*) Tartar emetic has sometimes been found to contain arsenic. This impurity may be detected in the following manner:—Two grammes of the suspected tartar emetic are reduced to a fine powder and dissolved in 4 grammes of pure hydrochloric acid (sp. gr. 1·124). The glass vessel wherein this solution is made ought to be narrow, and capable of being well closed, and of sufficient size to contain an additional quantity of at least 30 grammes of hydrochloric acid. A quantity of pure hydrochloric acid should be thoroughly saturated with sulphuretted hydrogen gas, and of this acid at least 30 grammes are added to the solution of the tartar emetic. The glass vessel containing the solution is well corked, and, after having been shaken up, is set aside; the turbidity which at first appears soon subsides (if it does not do so, it is due to the too great saturation of the hydrochloric acid with sulphuretted hydrogen, and should be remedied by the addition of pure hydrochloric acid). If no arsenic is present, the liquid remains colourless; but the slightest trace of arsenic gives rise to a yellow colouration, and soon after to a perfectly perceptible pure yellow precipitate of arsenic sulphide.

(*B*) Ignite the antimonial preparation to be tested with four times its weight of pure sodium nitrate, exhaust the residue with water,

acidulate the solution slightly with nitric acid, concentrate by means of evaporation, and add first silver nitrate, and next, very carefully, some ammonia: the result will be the formation of a more or less deep brown-red-coloured precipitate, indicating the presence of arsenic.

Dr. Von Ankum states that, having taken only 10 grammes of tartar emetic, containing in that quantity less than $\frac{1}{2}$ milligramme of arsenic, he was enabled to detect the latter very readily by the method described.

Electrolytic Separation of Arsenic from Antimony [1]

(*A*) Classen finds that arsenious acid is oxidised to arsenic acid by the current in an alkaline solution. But if we electrolyse a liquid which contains antimony along with arsenious acid, a mixture of metallic antimony and arsenic is deposited. The case is different if the arsenic is present in solution as arsenic acid. In presence of free alkali and concentrated solution in sodium sulphide the antimony alone deposits. Hence, for separating the two metals the arsenic, if present as arsenious acid, must be oxidised to arsenic acid. It is heated either with concentrated nitric acid or with aqua regia, the acid is completely removed by evaporation on the water-bath, the residue is covered with 50 or 60 c.c. sodium sulphide (sp. gr. 1·22 or 1·225), concentrated soda-lye is added, containing about 1 gramme sodium hydrate, and the liquid is electrolysed with a current corresponding to 1·5 or 2 c.c. detonating gas per minute. The subsequent separation is effected exactly like that of antimony from tin.

(*B*) If antimony and arsenic have to be separated in a solution of alkaline polysulphides we proceed exactly as for antimony. In order to determine arsenic after the elimination of antimony the liquid is acidified with dilute sulphuric acid, heated in the water-bath to expel sulphuretted hydrogen, filtered, and the washed precipitate is dissolved in hydrochloric acid with the addition of potassium chlorate. This solution is supersaturated with ammonia, and the arsenic acid precipitated with magnesia mixture as magnesium-ammonium arseniate.

The precipitate is either after filtration dried at 110° and weighed on a tared filter, or it is converted into magnesium pyro-arseniate by cautious heating in a porcelain crucible.

Separation of Arsenic, Antimony, and Tin

(*A*) On the supposition that arsenic is present as arsenic acid, antimony alone is precipitated from a solution of the three metals in concentrated sodium sulphide in presence of soda-lye. Classen finds that tin and arsenic remain entirely in solution. For converting arsenic into arsenic acid, and for the precipitation of antimony, he proceeds exactly as given above.

[1] For details of operation see chapter on Electrolytic Analysis.

(*B*) For the separation of tin from arsenic in the liquid decanted from the antimony, the sulpho-salts are decomposed with dilute sulphuric or hydrochloric acid, the mixture of arsenic sulphide, tin sulphide, and sulphur is filtered off, oxidised with hydrochloric acid and potassium chlorate, and the arsenic is separated as given below. In order to determine the tin, the liquid freed from arsenic is saturated with sulphuretted hydrogen and filtered, and the tin sulphide is dissolved in ammonium sulphide.

For the electrolytic determination of the tin proceed as in the section on Tin.

(*C*) For the analysis of a substance containing arsenic, antimony, and tin, we may, according to the method proposed by E. Fischer and Hufschmidt and simplified by R. Ludwig and A. Classen,[1] first eliminate the arsenic and separate the tin from the antimony in the remaining liquid.

(*D*) For the separation of the metallic sulphides they are oxidised with hydrochloric acid and potassium chlorate, the acid being driven off in the water-bath. The residue is rinsed with fuming hydrochloric acid into a boiling-flask of the capacity of 500 to 600 c.c., mixed with 20 to 25 c.c. of a saturated solution of ferrous chloride, or preferably with about 25 grammes of double sulphate of iron and ammonium, adding so much fuming hydrochloric acid that the total volume makes from 150 to 200 c.c. Into this solution there is passed a rapid current of hydrochloric acid, which is continued for at least half an hour after the apparent saturation of the liquid. Without using a refrigerator the solution is distilled off down to about 50 c.c. A flask holding about 1 litre is used as a receiver, and containing 400 to 500 c.c. of water. If the flask is well cooled during the distillation not a trace of arsenic passes over into a second receiver, even if its quantity amounts to 0·5 gramme calculated as arsenic oxide. In the distillate the arsenic may be either titrated with a solution of iodine, after previous supersaturation with pure sodium carbonate, or it may be precipitated as arsenic sulphide with sulphuretted hydrogen, and determined as such upon a weighed filter; or the arsenic may be calculated from the weight of the sulphur present.

(*E*) For determining the antimony and tin the strong hydrochloric ferriferous solution which remains in the boiling-flask after distillation can be diluted with three times its volume of water. Antimony and tin are precipitated by introducing a current of sulphuretted hydrogen. After being allowed to deposit for a short time, the liquid is poured upon a filter, the precipitate is washed repeatedly by decantation with hot water and finally washed with hot water on the filter until hydrochloric acid can be no longer detected in the filtrate. Traces of sulphides often adhere to the sides of the vessel in which the precipitation has been effected. It is therefore rinsed out with a

[1] *Berichte*, xviii. 1110.

concentrated solution of sodium sulphide, which is then poured into the filter containing the metallic sulphides. The filtrate is collected in a tared platinum capsule, the filter is washed out with sodium sulphide, the necessary quantity of pure soda-lye is added to the filtrate, and the electrolytic separation of antimony and tin is effected in the manner described above.

Detection of Arsenic in Bismuth

Bismuth subnitrate occasionally contains arsenic. This may be detected in the following manner:—About $\frac{1}{2}$ gramme of the subnitrate is placed in a test-tube, and 1 c.c. of pure and concentrated sulphuric acid is next added, to expel the nitric acid. After this has been driven off, the tube being kept in a vertical position, from 4 to 5 c.c. of pure hydrochloric acid are added, and when the liquid has become quite clear, about 1·5 to 2 grammes of pure tin protochloride. When the salt is dissolved, about 3 c.c. of strong and pure sulphuric acid are added; and if the mixture does not then become very hot, it is heated just to the boiling-point. If no arsenic is present, the liquid remains clear and colourless, even after standing for some time; but if even a trace of arsenic is present, the liquid becomes at first pale yellowish, next brownish coloured, and at last metallic arsenic is deposited as a deep greyish-brown flocculent substance. Even when the arsenic is present with the bismuth in the proportion of 1 to 500,000, a colouration ensues.

Separation of Arsenic from Copper

E. W. Parnell has carried out some accurate experiments on the best means of separating these metals.

(*A*) **Separation by Treatment of the Mixed Sulphides with Sodium Sulphide.**—To a mixture of the two metals excess of hydrochloric acid is added; the metals are then thrown down by sulphuretted hydrogen, the mixed sulphides introduced into a flask, covered with a colourless solution of sodium sulphide, and maintained at a gentle heat on the water-bath for about twelve hours. The liquid is then filtered off, the filtrate separated, and the copper sulphide on the filter washed with boiling water, to remove every trace of soluble arsenic. The copper sulphide is then dissolved in nitric acid, the solution evaporated with a small quantity of sulphuric acid, the residue dissolved in water, again treated with sulphuretted hydrogen, the precipitate treated as before with perfectly pure sodium sulphide, and filtered. The clear solution (which will contain any arsenic that has remained with the copper in the first instance) is decomposed with hydrochloric acid, the precipitated sulphur collected, washed, and treated with ammonia, which will dissolve any arsenic sulphide that may be mixed with it. A little sodium carbonate is added to the ammoniacal solution,

and the liquid evaporated to dryness in a small porcelain dish, the residue mixed with a little potassium cyanide, and the mixture examined for arsenic, by heating it in a glass tube in a slow stream of carbonic acid. A very faint mirror of metallic arsenic is obtained, probably not exceeding $\frac{1}{10}$ of a milligramme.

The filtrate from the first treatment with sodium sulphide is next decomposed with hydrochloric acid, the precipitate thoroughly washed and dried, and carefully sublimed. No trace of copper remains as a residue. From this, therefore, it is evident that a satisfactory separation can be effected by using a colourless solution of sodium sulphide.

As ammonium sulphide dissolves small quantities of copper sulphide it cannot be used instead of sodium sulphide.

(*B*) **Separation by Means of Chlorine Gas in the Wet Way.**—To a mixed solution of the metals arsenic and copper, excess of a solution of potash is added, and a slow stream of chlorine conducted into the liquid until the latter is thoroughly saturated with the gas. The mixture is then boiled, filtered, the insoluble part well washed, and the precipitate and filtrate examined respectively for arsenic and copper. The copper is perfectly free from arsenic; but the filtrate may contain a small quantity of copper (probably due to minute particles of copper oxide being carried through the filter, as the oxide is in an exceedingly fine condition; the amount is very small). Care should be taken to ensure a decided excess of the chlorine, or a considerable quantity of arsenic may remain with the copper.

(*C*) **Separation by Means of Chlorine Gas in the Dry Way.**—Excess of hydrochloric acid is added to the mixed solution, the metals thrown down by sulphuretted hydrogen, the precipitate thoroughly dried, placed in a small porcelain boat, and introduced into a glass tube; this latter passes through an air-bath, fitted with a thermometer to enable the tube to be maintained at a fixed temperature. The tube is allowed to project for about 4 inches beyond the air-bath. Perfectly dry chlorine is then conducted over the mixture, maintained at a temperature of about 200° C. for about half an hour. The projecting part of the tube, which has been almost cold during the operation, will be found to contain no trace of copper. The copper in the porcelain boat is completely soluble in weak hydrochloric acid. It is seen, therefore, from these experiments that, if proper precautions be taken to ensure perfect dryness of the mixture and the gas, a complete separation can be effected at a temperature of about 200° C. To avoid the formation of the globule of sulphur, or mixture of sulphur chloride and sulphur, which often takes place in the condensing tube, the precaution should be taken to first saturate the liquid with chlorine, or to use a solution of chlorine for the condensing liquid.

Detection of Arsenic in Copper

The copper is dissolved in nitric acid, a small quantity of solution of ferric nitrate added, the solution nearly neutralised with sodium hydrate (not ammonia) and excess of sodium acetate added. The solution is then heated to boiling, and filtered as rapidly as possible; the precipitate after being well washed is dissolved in hydrochloric acid, the solution made alkaline with ammonia, saturated with sulphuretted hydrogen and filtered from the precipitated iron sulphide. The filtrate is acidified with hydrochloric acid and allowed to stand in a warm place for some time. The arsenic and antimony sulphides are filtered off and dried at 100° C.; the precipitates are removed completely from the paper into a small beaker, and treated with red fuming nitric acid, a few drops of hydrochloric acid being added as soon as the action has ceased. It is then diluted, filtered, the arsenic precipitated as ammonio-magnesium arseniate, and weighed as usual. If the precipitated sulphides cannot be perfectly removed from the filter-paper, the paper must be treated with nitro-hydrochloric acid, filtered, and the filtrate added to the nitric acid solution.

This method is very accurate. It requires, however, some special precautions.

When the sodium acetate is added, the colour of the solution should change from pale blue to dark green; this shows that the solution has been sufficiently neutralised. The beaker must be removed from the heat immediately the solution begins to boil; if the solution be left boiling (and sometimes when it is not) a greenish-white precipitate of basic copper acetate falls. This can generally be removed by the addition of a few drops of hydrochloric acid, but in cases where it has separated on the surface of the beaker, or where it will not readily dissolve, it is best to throw out the solution and commence again. This is very troublesome to those using this method for the first time, but after a little experience has been gained the precipitation very rarely happens.

The precipitate should have the dark red colour of ferric acetate; if it is paler it is due either to there not being sufficient iron, or to the co-precipitation of some basic copper acetate. The filtrate should be blue or pale green; sometimes it is dark green and turbid, from the presence of iron acetate carried through the filter; in that case the first portions must be passed through the filter again.

The precipitate must be washed till it is free from copper, and when it is dissolved in hydrochloric acid the solution must have the yellow colour of ferric chloride. If it is at all green, the solution must be neutralised, a little more sodium acetate added, and the iron and arsenic reprecipitated.

With equal quantities of iron and arsenic a small quantity of arsenic remains in solution, and the iron arsenic precipitate is of a

pale colour. With 1·5 part of iron to 1 of arsenic the precipitation is complete. In order to make sure it is well to add about twice as much iron as it is expected there is arsenic present. Then, even if a little iron remains unprecipitated, all the arsenic will be thrown down.

Since copper sulphide retains so much arsenic, it might be expected that iron sulphide would act in a similar manner, but it does not; if there be no copper present, the precipitate is quite free from arsenic, but if copper is present a considerable quantity of arsenic may be retained. Hence the importance of thoroughly washing the acetate precipitate and reprecipitating it if necessary.

Electrolytic Separation of Arsenic from Antimony and Copper[1]

(*A*) According to Classen, the separation of copper from the two metals can be effected in the solution of the double oxalates, or in the acid solution only, if the quantity of antimony and arsenic is small, and if the current is not allowed to act longer than is needful for the reduction of the copper. Directions have already been given as to how to proceed when small quantities of antimony or arsenic have been deposited upon the copper. If the proportion of arsenic exceeds 0·2 per cent. after the electrolysis is completed, the copper is of a more or less dark colour, and when weighed gives too high a result.

(*B*) It has been proposed to ignite the desiccated electrode for a short time to volatilise the arsenic, to dissolve the remaining copper oxide, and to repeat the electrolysis. This method is applicable for very small quantities of arsenic. Experiments made with arsenical pyrites, &c., showed that with large proportions of arsenic the separation of copper from a nitric solution is not quantitative, and that it is impracticable in this manner to volatilise large quantities of arsenic. After the electrode has been slightly ignited there always remains upon it a residue insoluble in nitric acid. The electrolysis of the solution obtained yields also no satisfactory results.

(*C*) In presence of arsenic, therefore, an indirect method has been unavoidable for the determination of copper. But now the determination of copper in arsenical ores, &c., presents no difficulty if they are first treated with bromine. All the arsenic may then be volatilised as arsenic bromide.

As a test, metallic copper and metallic arsenic, both obtained by electrolysis, were dissolved in a hydrochloric solution of bromine, and evaporated down on the water-bath three or four times with the addition of a solution of bromine. In order to decompose the residual bromine compound of copper, it was heated with sulphuric acid, diluted

[1] For details of operation see chapter on Electrolytic Analysis.

with water when cold, the necessary quantity of nitric acid was added, and the whole was electrolysed.

(*D*) Arsenic may be removed from sulphuretted ores by repeated heating with a few c.c. of bromine sufficient to separate the copper free from arsenic. In roasted ores, on the contrary, the elimination cannot be effected with pure bromine, but it can by repeated evaporation with a solution of bromine in hydrochloric acid.

Burnt arsenical pyrites are twice evaporated down on the water-bath, treated with double their weight of concentrated sulphuric acid, heated first on the water-bath, and then on the sand-bath until vapours of sulphuric acid are given off. When cold, 30 c.c. of nitric acid (sp. gr. 1·2) are added. The solution is diluted with water and electrolysed. At first no copper is deposited, but after the greater part of the ferric salt has been reduced to the ferric state by the current, the precipitation of copper sets in. In cases of plumbiferous products it is well first to filter the sulphuric solution obtained as above, and then to add the necessary proportion of nitric acid to the filtrate.

(*E*) According to E. F. Smith, copper may be obtained free from arsenic, provided the arsenic exists in solution as an arseniate, if potassium cyanide is added in excess and a current giving 1·5 to 5 c.c. per minute is used for the electrolysis.

(*F*) Smith has also used the above method for separating cadmium and silver from arsenic. For this purpose a current giving 0·4 c.c. per minute is sufficient.

Separation of Arsenic from Vanadium

Experiments made by C. Field and Edgar F. Smith[1] on the behaviour of vanadates[2] and arsenates[3] heated in an atmosphere of hydrochloric acid gas, in which both acids were volatilised, suggested the thought that if the sulphides of vanadium and arsenic were exposed to the same vapours, perhaps they would show a variation in deportment. And so it has proved. Perfectly dry arsenic trisulphide, previously washed with alcohol, carbon disulphide, and ether, then dried at 100° C., when exposed in a porcelain boat, placed in a combustion tube, was almost completely expelled from the retaining vessel at the ordinary temperature. The last traces were driven out at a temperature a little above 150° C. Brown vanadium sulphide, in a perfectly dry condition, treated in the same manner, was not altered. It only remained then to prepare mixtures of known amounts of the two sulphides and subject them to the action of the acid vapour. To this end the following experiments were made:—

I. 0·1303 gramme of vanadium sulphide,
0·1302 gramme of arsenic sulphide.

[1] *Chemical News*, Jan. 15, 1897.
[2] *Journ. Am. Chem. Soc.* vol. xvi. p. 578.
[3] *Ibid.* vol. xvii. p. 682.

The arsenic sulphide was volatilised without difficulty, and left 0·1297 gramme of vanadium sulphide.

II. 0·1290 gramme of vanadium sulphide,
0·2242 gramme of arsenic sulphide,
gave, after exposure of one hour to hydrochloric acid vapour, a residue of vanadium sulphide, weighing 0·1297 gramme.

III. 0·0828 gramme of vanadium sulphide,
0·0582 gramme of arsenic sulphide,
left 0·0827 gramme of vanadium sulphide.

IV. 0·1306 gramme of vanadium sulphide,
0·2028 gramme of arsenic sulphide,
gave a residue of 0·1308 gramme of vanadium sulphide.

V. 0·1403 gramme of vanadium sulphide,
0·2409 gramme of arsenic sulphide,
left 0·1404 gramme of vanadium sulphide.

The temperature in these experiments was not allowed to exceed 250° C., as beyond that point there is danger of affecting the vanadium and causing its partial volatilisation.

Separation of Arsenic from Mercury and Palladium [1]

Classen finds that the behaviour of the double metallic cyanides with the current is available for separating mercury from the two other metals. For the separation of arsenic we electrolyse the solution previously mixed with an excess of potassium cyanide with a current of 0·3 c.c. detonating gas. And for the separation of palladium with one of 0·1 to 0·2 c.c. detonating gas.

Estimation of Small Quantities of Arsenic in Sulphur

(*A*) H. Schæppi proceeds as follows :—Ten grammes of sulphur, pulverised as finely as possible, are covered with hot water, and a few drops of nitric acid, digested for some time, filtered and washed till the washings have no longer an acid reaction. Thus calcium chloride and sulphate are removed, and calcium sulphide, if present, is destroyed. The sulphur thus prepared is covered with water at 70° to 80°, a few drops of ammonia are added, and the mixture is digested for a quarter of an hour. All the arsenic present as sulphide is dissolved, and the ammoniacal liquid is variously treated according to the degree of accuracy required. For perfectly accurate estimations the ammoniacal solution is mixed with silver nitrate, and all the sulphur present in the state of arsenic sulphide is thrown down as silver sulphide, acidified with nitric acid, filtered, and washed. The precipitate of silver sulphide

[1] For details of operation see chapter on Electrolytic Analysis.

is dissolved in hot nitric acid and estimated as silver chloride. From the weight of the latter the arsenic sulphide is calculated.

(*B*) As a less accurate but more rapid method, the ammoniacal solution of arsenic sulphide is cautiously neutralised with pure dilute nitric acid and considerably diluted. It is then titrated with decinormal silver nitrate till a drop of the solution is turned brown with neutral chromate. The arsenic is easily calculated from the quantity of silver nitrate consumed. For very rough estimations it is sufficient to treat 10 grammes of finely ground sulphur with nitric acid, to extract with ammonia, and to add silver nitrate. From the intensity of the colour, or the quantity of the precipitate of silver sulphide, it may be judged if the sulphur is approximately free from arsenic, or strongly contaminated. The author states that, contrary to the general belief, reddish-yellow sulphur is more free from arsenic than such as is of a full yellow colour.

TELLURIUM AND SELENIUM

Separation of Tellurium from Selenium and Sulphur

(*A*) Dr. Oppenheim separates these elements by the different way in which they are acted upon by potassium cyanide. Sulphur is dissolved when fused with this compound, and is not precipitated by hydrochloric acid. Selenium is likewise dissolved, but is reprecipitated by any acid. Tellurium not only refuses to form a tellurocyanide when fused with potassium cyanide, but takes the place of the cyanogen therein, forming potassium telluride, which dissolves in water, with a purple colour, and is speedily decomposed, by the action of the air, into potash and metallic tellurium. This process, however, is imperfect, on account of a slight loss, which was first ascribed to the volatility of the elements at the temperature employed. The loss, it is found, occurs chiefly on the side of tellurium, which, of the three elements, is the least volatile, and it is owing principally to part of the tellurium being oxidised and dissolved as potassium tellurate.

Instead of melting the elements with potassium cyanide, it suffices to heat them with a solution of the salt. Sulphur and selenium are thus completely dissolved. A small proportion of tellurium forms potassium tellurite, and the rest remains in the metallic state. The separation of the elements is, therefore, conducted in the following manner:—A mixture of them, reduced to a fine powder, is boiled with a solution of potassium cyanide in a water-bath for about eight hours. Tellurium is then collected on a filter. Selenium is precipitated in the filtrate by means of hydrochloric acid, and the second filtrate is mixed with sodium sulphite, heated, and allowed to stand for twenty-four hours. The portion of tellurium which has been dissolved as potassium tellurite is thus completely precipitated. It is then added to the other portion collected on the filter, dried in the water-bath, and weighed.

Selenium is estimated in a similar manner, while the quantity of sulphur present is indicated by difference.

The same method may be employed for separating selenium from metals not soluble in potassium cyanide. But if iron, copper, or other metals are present, which form soluble compounds with the reagent, partly precipitated by hydrochloric acid, it is necessary to dissolve the mixture of the elements in acids and to add a quantity of ammonium sulphide sufficient to dissolve the selenium and tellurium. They must then be precipitated from this solution as sulphides and treated with potassium cyanide, as described above. When selenium sulphide is acted upon by potassium cyanide, the selenium is first dissolved, and a residue of sulphur remains behind, which disappears but slowly. The red modification of selenium is dissolved more easily than the black. Selenious acid cannot be reduced by being boiled with potassium cyanide.

(*B*) The opening up of products or minerals containing tellurium, and its separation from accompanying elements, has been successfully accomplished by E. Donath by the following process, which meets all fair demands as regards accuracy and despatch.

From 3 to 4 grammes of the very finely pulverised sample are gradually oxidised in a porcelain capsule with a minimum of concentrated nitric acid, and the thick pasty mass is heated until all excess of nitric acid is eliminated. The temperature must not be raised high enough to decompose the less stable iron, copper, and bismuth nitrates. In this case, there would be formed from the tellurous acid, telluric acid; and, subsequently, very sparingly soluble tellurates, the formation of which must be avoided. The dry mass obtained is ground finely in the capsule with an agate pestle, and moistened with concentrated soda-lye, which becomes strongly heated by the decomposition of the nitrates. After digestion for thirty minutes, a little more soda-lye and a corresponding quantity of water are added, the liquid is filtered off, and the tellurium precipitated in the filtrate by boiling for at most twenty minutes with a pure solution of glucose, and it is either determined as such or as tellurous acid.

(*C*) In precipitating tellurium by glucose in a boiling alkaline solution, the separation is complete and soon effected. The deposit of tellurium can be either weighed on a tared filter or dissolved off the filter by dropping upon it nitric acid, moderately diluted and heated (2 parts nitric acid and 1 part water, with a few drops of sulphuric acid). The solution is then concentrated in a small porcelain capsule, and the residue, after gentle ignition, is weighed as tellurous acid.

(*D*) V. Schroetter, in analysing telluriferous minerals containing gold, treats the ore with aqua regia and precipitates the gold with oxalic acid or glycerin. The liquid after removal of the gold is treated with sulphurous acid, which precipitates selenium and tellurium,

the former element being all contained in the first portions of the precipitate. The mixed precipitate is treated with nitric acid ; the tellurous acid is filtered off, and the filtrate which contains the selenium is distilled. In the precipitation of tellurium by sulphurous acid, a point comes when the precipitation ceases, though tellurium is still held in solution. This portion falls on diluting with water.

(*E*) For the detection of tellurium in ores which contain it as gold telluride, G. Kustel uses sodium amalgam. The powdered ore is placed in a capsule with a little water and mercury, and afterwards with a little sodium amalgam. If tellurium is present, the water takes a violet colour. If it contains sulphur, the water blackens silver-foil. If iron sulphide is present, the violet colour produced by sodium telluride may be masked by the precipitate occasioned. In such cases the water is poured off, a fresh quantity of water added, and the test is recommenced with a fragment of sodium amalgam.

Preparation of Pure Tellurium

In testing a volumetric method for the estimation of tellurium proposed some time ago, James F. Norris, Henry Pay, and D. W. Edgerly[1] were led to study the methods which had been used for the purification of tellurium. As it appeared that a substance of undoubted purity could be obtained only by a very long series of operations, which involved fusion with potassium cyanide, precipitation, and subsequent distillation in hydrogen, a new method was sought. It seemed probable that the basic nitrate of tellurium might be used for this purpose, as it is a well-crystallised compound, very easily obtained. They accordingly prepared it, and having found that the sample did not agree in some of its properties with those which had been assigned to it in the literature, a careful study of it was made. Klein and Morel[2] prepared the compound by dissolving tellurium in nitric acid (sp. gr. 1·25) and evaporating the solution. To the crystals which formed they assigned the formula $4TeO_2.N_2O_5.1\frac{1}{2}H_2O$. Only very small crystals were formed, and these were hygroscopic. The nitrate prepared by the authors by the method of Klein and Morel was obtained in crystals, sometimes a centimetre in length, and were not hygroscopic. An analysis was accordingly made, which showed that the compound has the formula $4TeO_2.N_2O_5.H_2O$, or, better, $Te_2O_3(OH)NO_3$, since the water is not present as water of crystallisation.

In the preparation of the nitrate it is crystallised from nitric acid, and as the impurities present in the tellurium do not form crystalline compounds under these conditions, it was thought that the salt could be obtained quite pure. The tellurium obtained from it would, as a result, be free from those substances with which it is invariably mixed when precipitated from solution by sulphur dioxide or other reducing

[1] *Chemical News*, Oct. 26, 1900. [2] *Bull. Soc. Chim.* [2], vol. xliii. p. 198.

agents. A sample of basic nitrate was recrystallised three times and then subjected to a careful study, with the result that no impurity was discovered.

On account of the fact that the most trustworthy atomic weight determinations of tellurium have given results which place it in the eighth group in the periodic system of the elements, notwithstanding its striking similarity to sulphur and selenium, the hypothesis has been put forward that tellurium is a mixture of true tellurium with an atomic weight of about 125, and another element with a higher atomic weight. Brauner,[1] who spent a number of years studying tellurium, has expressed this as his opinion.

As no known substance was found in the tellurium obtained from the pure nitrate, the element was subjected to a fractionation, to determine whether it could be broken down into two or more substances by this means, which proved so effective in the case of didymium. The double bromide of tellurium and potassium made from tellurium dioxide, hydrobromic acid, and potassium bromide, prepared with the greatest care, was carried through a fractionation which involved over 200 crystallisations. In order to determine whether this fractionation had accomplished any decomposition, the tellurium from the end fractions was converted into the nitrate, and the loss in weight of the latter compound on ignition determined. Any change in atomic weight could be observed in this way. The results obtained with the two fractions were identical within the limits of accuracy of the method. The difference obtained—0·4 of a unit in the atomic weight—was probably due to inaccuracies in the method. The conversion of the nitrate into the oxide, as at present carried out, does not appear to give results from which the atomic weight of tellurium can be determined with great accuracy.

Preparation of Basic Tellurium Nitrate

The tellurium used was obtained from a residue left in the electrolytic refining of copper. This residue was a solution which consisted principally of the sodium salts of tellurous, selenous, and silicic acids, with the last-named acid in great excess. Whitehead[2] has described the process by which the copper is refined, and how the liquid is obtained. Tellurium was separated from this liquid in two ways. At first the solution was diluted with water, and neutralised with sulphuric acid, which threw out a heavy white precipitate of tellurous acid and silica. This mixture was evaporated to dryness twice with hydrochloric acid to render the silica insoluble, and the residue extracted several times with strong hydrochloric acid. From the solution of the chloride so formed, the tellurium was obtained by precipitation

[1] *Journ. Chem. Soc.* vol. lxv. p. 382; and vol. lxvii. p. 549.
[2] *Journ. Am. Chem. Soc.* vol. xvii. p. 849.

with acid sodium sulphite. In later experiments the tellurium was precipitated from the hot alkaline solution with commercial glucose. The tellurium obtained by both methods contained silica and other impurities. The crude metal was added to warm dilute nitric acid (sp. gr. 1·25), and the resulting solution evaporated to dryness in order to ensure the complete removal of silica. The mixture of basic nitrate and oxide was ignited till free from nitric acid, and was then extracted a number of times with strong hydrochloric acid. The solution in hydrochloric acid was filtered through asbestos, and precipitated with acid sodium sulphite. The sulphite was added slowly until the precipitate formed was black, thus showing that most of the selenium was precipitated. After the mixed precipitates of selenium and tellurium had settled, the solution was decanted, filtered, and the precipitation continued. The tellurium, which had been freed from a large share of its impurities by this second precipitation, was again dissolved in nitric acid (sp. gr. 1·25), and the basic nitrate obtained from the solution by crystallisation. The nitrate was twice recrystallised. This was best done as follows:—The salt was stirred with a large amount of nitric acid (sp. gr. 1·25) heated to about 70° C. At a higher temperature the nitrate was decomposed into a mixture of amorphous and crystalline oxide, which was not readily dissolved by the acid. The solution was filtered through asbestos, and evaporated at a temperature of about 80°. In some cases the solution was allowed to cool after crystals appeared. In other cases the evaporation was continued while the crystals were separating from the liquid. By the latter method larger crystals were obtained, which were at times 0·5 centimetre in length. The nitrate crystallises in orthorhombic prisms, terminated by macrodomes and truncated by well-developed macropinacoids and small brachypinacoids. The salt is not hygroscopic, some crystals having stood in the open air for over a month without losing their bright lustre.

Purity of the Basic Nitrate of Tellurium

The purity of the basic nitrate of tellurium, which had been twice recrystallised, was studied. It was again recrystallised from nitric acid, and a qualitative analysis of the crystals was made. The mother-liquor was evaporated to dryness, and also analysed. The presence of no foreign element was detected in either case. Whitehead [1] and Keller [2] have determined what substances are present in the crude copper from which the tellurium used in this work was obtained. These are silver, gold, bismuth, arsenic, antimony, and selenium. As none of these elements forms a crystalline compound which is difficultly soluble in nitric acid, it is seen that the basic nitrate of tellurium was readily obtained in a pure condition. Brauner has shown that pure tellurium

[1] *Journ. Am. Chem. Soc.* vol. xvii. p. 849. [2] *Ibid.* vol. xix. p. 778.

cannot be obtained by precipitation, and that repeated distillation of the metal is necessary to free it from the heavy metals.

In order to test for minute traces of selenium—a common impurity in tellurium—the following method was devised, based on the difference in behaviour of the oxides of selenium and tellurium with hydriodic acid. The former oxide is reduced and iodine set free, while the latter is converted into the tetraiodide. The test is made in this way: About 0·15 to 0·2 gramme of the oxide to be tested is dissolved in 2 cubic centimetres of a 10-per-cent. solution of sodium hydroxide, and 3 cubic centimetres of hydrochloric acid (sp. gr. 1·12) are added. The solution is then cooled to the room temperature, carbon bisulphide and 2 drops of a dilute solution of potassium iodide (2 grammes in 100 cubic centimetres water) are added, and the tube is shaken. Under the above conditions, if selenium is present, the carbon bisulphide will be coloured by the iodine liberated, and the small amount of tellurium tetraiodide formed will remain in solution. It is necessary to avoid a large amount of potassium iodide in order to prevent the formation of much tellurium tetraiodide, which would dissolve in the carbon bisulphide, and so obscure the colour of the iodine. Any doubt whether the colour is due to liberated iodine or to tellurium tetraiodide can be decided definitely by shaking the carbon bisulphide with water. The colour produced by the iodine is not altered, while the tellurium tetraiodide is decomposed, and the carbon bisulphide again becomes colourless. The accuracy of the method was tested by mixing known amounts of selenium dioxide with the tellurium to be tested. Using the amounts given above, 0·0012 milligramme selenium can be detected in the presence of 0·160 gramme of tellurium dioxide—that is, about 1 part in 150,000. No selenium could be detected in the oxide obtained from the pure nitrate when this very delicate test was applied.

It is of interest to note here that a strong solution of potassium iodide acidified with hydrochloric acid is a very delicate test for tellurium. The dark colour produced is quite characteristic, resembling somewhat, in strong solution, the colour of platinum solutions containing iodides. The difference is readily shown, however, by dilution, when the colour produced by platinum persists as a pink, while the colour produced by tellurium disappears on account of the decomposition of the iodide.

No foreign substance was found in the tellurium from the nitrate by careful qualitative analysis, yet it was subjected to additional tests. Brauner and Wills found that the purest tellurium obtained by precipitation invariably left a residue when distilled in hydrogen. A sample of the oxide prepared from the nitrate was dissolved in pure hydrochloric acid, and the tellurium precipitated with sulphur dioxide, and washed until free from hydrochloric acid. The tellurium was then distilled in a stream of hydrogen, which was prepared by the action of sulphuric acid

on zinc. The gas was purified by the method used by Wills [1] in preparing pure tellurium for a determination of its atomic weight. After the distillation a bright stain was left on the porcelain boat. The tellurium was redistilled a number of times, with the same result. The grey shiny spot on the boat was not affected by hot sodium hydroxide, hydrochloric or nitric acid, and was not volatilised by the heat of a blast-lamp.

From the following experiments it was shown that this residue was due to the union of a small amount of tellurium with the porcelain of the boat at the high temperature required for the distillation. Some tellurium prepared from the nitrate was next distilled in a vacuum. After the first distillation a light grey substance was left in the boat. This was flocculent, dissolved completely in dilute hydrochloric acid and sodium hydroxide, and evidently was tellurium dioxide, which is always present in precipitated tellurium. The tellurium, when redistilled in vacuum, left no residue, but when distilled in hydrogen a stain was left on the boat as before. Some pure tellurium, obtained by distillation in a vacuum, was heated on porcelain in a blast-lamp flame. A stain was left which was caused by the combination of a small amount of the tellurium with the porcelain. This does not take place when the metal is distilled in a vacuum, as the temperature of distillation is lower.

The oxide prepared from the nitrate was also completely volatile without leaving a residue. It was heated to redness on a platinum foil placed inside of a porcelain crucible. The above experiments show that a careful examination of the tellurium obtained by recrystallisation of the basic nitrate did not show the presence of any known substance.

Separation of Tellurium from Antimony

A. Guthier has given the following method :—

Separation by Means of Hydrate of Hydrazine.—The solution should be a hydrochloric one, and free from sulphuric and nitric acids. To the slightly acid solution we add a large excess of tartaric acid and an excess of a dilute solution of hydrate of hydrazine. The tellurium is precipitated ; the antimony remains in solution. The latter is boiled with concentrated hydrochloric acid, diluted with warm water, and precipitated with sulphuretted hydrogen. Instead of the hydrate of hydrazine, we might use the hydrochlorate, but not the sulphate. The separation is quite general. The antimony and the tellurium might be precipitated first of all as sulphides, and these subsequently oxidised with nitric acid or aqua regia.

Estimation of Selenium

(*A*) Sulphurous acid is the best reagent to precipitate selenium when this element exists in the state of selenious acid ; the precipitation

[1] *Journ. Chem. Soc.* vol. xxxv. p.704.

should be preformed in the presence of hydrochloric acid. Sulphurous acid may also be replaced by phosphorous acid, likewise in the presence of hydrochloric acid; but the reduction takes place much slower than when sulphurous acid is used.

(*B*) As already pointed out, selenium may be estimated by fusing the body containing it with potassium cyanide, dissolving the fused mass in water, and then supersaturating the solution with hydrochloric acid, which effects the complete precipitation of the selenium at the end of a few hours. The fusion ought to be performed in an atmosphere of hydrogen; it is advisable, when the substance contains free selenious acid, to previously saturate this acid with an alkaline carbonate, so as to avoid volatilising small portions before the potassium cyanide has had time to react upon it.

The solution obtained by treating the fused mass with water contains potassium selenocyanide, together with a small quantity of selenide; it is necessary, on this account, to boil the liquid for some time before the addition of hydrochloric acid, to convert the selenide into selenocyanide. Without this precaution, a portion of the selenium might be disengaged in the form of seleniuretted hydrogen.

When the selenium acids are fused with alkaline carbonates in an atmosphere of hydrogen they are reduced to alkaline selenides; from a solution of these latter a slow current of atmospheric air entirely precipitates the selenium. This process may serve for estimating selenium, but it is less accurate than the preceding.

Sulphuretted hydrogen completely precipitates selenious acid from its solutions in the form of selenium disulphide, from the weight of which the selenium may be estimated.

Selenious acid may be estimated in its aqueous solution, or, in the presence of nitric and hydrochloric acid, by simple evaporation, taking care not to exceed a temperature of 100° C., above which a portion of the acid may volatilise.

(*C*) The ordinary process for the estimation of selenic acid, which consists, as is known, of precipitating this acid as a barium salt, is, according to Rose, far from deserving the confidence with which it is usually regarded. On the one hand, barium seleniate is much more soluble than the sulphate; on the other hand, it possesses, in a much greater degree than this latter salt, the property of carrying down with it considerable quantities of the soluble salts which are contained in the liquid. It is better to reduce the selenic acid to selenious acid with hydrochloric acid, and then to precipitate the selenium with sulphurous acid.

When it is desired to estimate the selenic acid in an insoluble combination, particularly in barium seleniate, this combination is decomposed by an alkaline carbonate; the transformation into an alkaline seleniate takes place even in the cold, and it is then easy to reduce the selenic to selenious acid by means of hydrochloric acid.

Separation of Selenium from Metals

Selenium cannot be separated from the metals with which it is combined when the sulphides of these metals are insoluble in ammonium sulphide, by making use of the solubility of selenium in this reagent. The insoluble metallic sulphide is almost always mixed with selenide. Most frequently, selenium may be separated from metals by heating the mixture in a current of chlorine; the selenium chlorides are sufficiently volatile to render the separation generally easy. In acid solutions of the selenites of metals not precipitable by sulphuretted hydrogen, the selenium may be precipitated by this gas in the state of selenium sulphide.

To estimate the alkalies and alkaline earths combined with selenium acids, it is sufficient to fuse them with ammonium chloride. The alkali or alkaline earth remains in the state of chloride. One single fusion, or two at the most, are sufficient to drive off all the selenium.

Preparation of Selenium from Seleniferous Flue-dust

This is a mixture of selenium and metallic selenides with soot, sand, &c., which accumulates in some of the flues leading to the leaden chambers from the burners where some kinds of pyrites are burned. With some ores at Mansfeld it contains as much as 30 or 40 per cent. of selenium.

The dark-coloured mass, after being first moistened with sulphuric acid and then washed and thoroughly dried, is placed in a porcelain or luted glass retort. It is then strongly heated, the temperature towards the end of the operation approaching that at which the glass softens. Most of the selenium will now distil over perfectly pure.

The residue, consisting of selenides mixed with carbon and other impurities, should be dissolved in hydrochloric acid containing a little nitric acid. Precipitate the iron and copper with caustic soda, filter, and precipitate the selenium in the filtrate either by saturating the liquid with sulphurous acid, or by evaporating with an excess of sal-ammoniac and heating until this begins to volatilise. The alkaline salt is then removed with water. If the selenium were precipitated by sulphurous acid before removing the copper from the liquid, the precipitate would retain somewhat considerable quantities of this metal.

Detection of Sulphur in Selenium

Dissolve the selenium in very strong nitric acid, add a little hydrochloric acid, and boil. Any sulphur which may be present can then be detected by barium chloride, as it will be in the form of sulphuric acid. Remove the excess of barium from the filtered liquid by addition of sulphuric acid, and reduce the selenium with sulphurous acid.

Preparation of Selenious Acid

Act upon selenium with concentrated nitric acid, and evaporate the solution until selenious acid begins to sublime; the residue is dissolved in water. This solution may contain, besides selenious acid, some sulphuric and selenic acids; in order to separate these from each other, baryta-water is added. Since barium selenite is readily soluble in an excess of selenious acid, the addition of baryta-water is continued until a small quantity of the liquid, having been filtered, no longer gives a permanent precipitate on the addition of more baryta-water. The liquid, having been filtered, is evaporated to dryness and sublimed; the selenious acid thus obtained is quite free from selenic and sulphuric acids.

Preparation of Selenic Acid

(*A*) Selenic acid is prepared from selenious acid by dissolving the latter in water, and precipitating the solution with silver nitrate; the insoluble silver selenite is shaken up with a mixture of water and bromine until the latter is in slight excess. The solution, having been filtered and concentrated by evaporation, yields selenic acid, free from sulphuric or selenious acid.

(*B*) Another good method of preparing selenic acid is given by Wöhler:—Saturate selenious acid with copper carbonate, and then pass a current of chlorine into the liquid, until the precipitate is completely dissolved. The solution, after being again saturated with copper carbonate, is concentrated by evaporation; the copper seleniate is then precipitated by alcohol, in which the copper chloride dissolves. Wash the copper seleniate with alcohol, then dissolve in water and remove the copper by a current of sulphuretted hydrogen.

CHAPTER IX

GOLD, PLATINUM, PALLADIUM, IRIDIUM, OSMIUM, RHODIUM, RUTHENIUM

GOLD

Detection of Minute Traces of Gold in Minerals

(*A*) The large number of non-auriferous or but slightly auriferous specimens of quartz and pyrites which have sometimes to be examined for gold renders it desirable that some quicker, less laborious, and, if possible, more exhaustive, method of analysis than the current one (that by amalgamation) should be employed. After many experiments, Mr. Skey, Analyst to the Geological Survey of New Zealand, has devised a plan which gives very good results, even when small quantities of mineral are operated on. He employs iodine or bromine for the purpose of dissolving out the gold. Both of these substances differ from chlorine especially in their relatively feeble affinities for hydrogen, so that there is less fear that from the generation of hydrogen acids any great preponderance of other matters would be dissolved along with the gold. Either of these substances can be safely and advantageously employed for the separation of gold from its matrix.

The following particulars of experiments made in this method will be useful in showing what is approximately the smallest quantity of gold that can be positively separated and identified, when operating upon a limited quantity.

1st. Two grammes of roasted 'buddle headings' from a quartz mine at the Thames, N.Z., known to contain gold at the rate of 1 ounce or so to the ton, was well shaken for a little while with its own volume of alcoholic solution of iodine, then allowed to subside. A piece of Swedish filter-paper was then saturated with the clear supernatant liquid, and afterwards burned to an ash; the ash, in the place of being white, as it would be if pure, was coloured purple; the colouring matter was quickly removed by bromine—a clear indication of the presence of gold. The time occupied by the whole process was twenty minutes.

2nd. One gramme of the same 'buddle headings,' mixed with such a quantity of earth as to reduce the proportion of gold present to 2 dwts. per ton, was kept in contact with its own volume of the tincture of iodine for two hours, with occasional stirring; a piece of filter-paper was then saturated with the liquid, and dried, five times consecutively, and finally burnt off as before: in this case, also, the colour of the residual ash was purple, and it gave the reaction of gold.

3rd. Thirty-two grammes of siliceous hæmatite, finely pounded, were thoroughly mixed with precipitated gold to the amount of 2 dwts. per ton, then ignited and treated with bromine-water. After two hours the solution was filtered, and evaporated to a bulk of 20 minims; this gave a good reaction of gold to the 'tin chloride' test.

4th. One hundred grammes of the hæmatite, with precipitated gold at the rate of ½ dwt. per ton, treated as before, but this time well washed at the expiration of two hours; the washings evaporated along with the first filtrate gave a fainter, but still decided, reaction of gold to the same test.

5th. Iodine, as tincture, substituted for bromine in Experiments 3 and 4, gave similar results; the only variation made was, that, as a precautionary measure allowing for its slower action, they were kept in contact for twelve hours.

Careful experiments have been made to compare the results of the common amalgamation process with the foregoing, and it has been found that it is not certain, with the same expenditure of labour, to get reliable indications of gold, when present in less quantity than 2 dwts. per ton, operating upon about 100 grammes of material.

In summing up the results of these experiments, it appears, then, that for qualitative examinations for gold, or for quantitative estimations in certain cases, iodine and bromine are each superior to mercury. It also appears that a proportion of gold equal to ½ dwt. per ton, upon a bulk of 100 grammes (about 4 ounces) of ferruginous matter, can be easily and rapidly detected. Of course, by operating upon larger quantities, gold could be discovered by this process, were it present in far less quantities, but this is sufficiently near for the majority of cases.

These processes are especially adapted for the separation of gold from sulphides, as the preliminary roasting is extremely favourable to them, the loss in the substitution of oxygen for sulphur amounting to 25 per cent. by weight, while the volume remains constant (or nearly so); hence there is a corresponding porosity in the product, by which every particle of it is thrown open to contact with the solution. This mechanical accessibility obviously cannot be taken advantage of by mercury.

With sulphides these processes are practically exhaustive, while, at the same time, the simultaneous extraction of other matters is so trifling, that the proper tests for gold can be safely applied directly to the concentrated solution. In the roasting of pyrites it is necessary to

raise the temperature towards the end to a full red heat, in order to decompose the ferruginous sulphates, since if these remained iron would get into the solution. In the case of an excess of calcium carbonate being present, it is proper to gently re-ignite the roasted mineral, &c. with ammonium carbonate, or much lime might get into the iodine or bromine solution. On the other hand, a very high temperature is to be avoided, for a considerable quantity of fine gold can escape detection in this way, by the partial vitrification of the more fusible of the silicates.

The identification of gold by the combustion of its salts with filter-paper seems to promise a rapid method of estimating it, comparatively, by the aid of a series of prepared test-papers, representing gold in different degrees of dilution.

(*B*) Sergius Kern proposes the following method of detecting gold. The gold of the sample under analysis is first separated from foreign metals, and next converted by means of sodium chloride into sodio-gold chloride; the solution is then concentrated by evaporation. In order to detect gold, an aqueous solution of potassium sulphocyanide is used, containing for 1 part of the salt about 15 to 20 parts of water. About 6 grammes of this solution are poured into a test-tube, and some drops of the concentrated solution obtained by treating the samples as described above are added. If gold is present a red-orange turbidity is immediately obtained, which soon falls in the form of a precipitate; on gently heating the contents of the test-tube the precipitate dissolves, and the solution turns colourless.

The reagent is so delicate that one drop of a solution of sodio-gold chloride (1 gramme of the salt dissolved in 40 grammes of water) gives a very clear solution.

(*C*) Colonel Ross was the first to give gold among the metals whose sublimates can be obtained with the common blowpipe, which is owing to the fact that it can be easily produced and seen on aluminium, though not on ordinary charcoal. Ross appears to have produced it only from a bead of gold and lead, and he makes no mention of getting it from pure gold. In his book is a coloured representation of a very beautiful sublimate obtained from gold with a little lead, and it appears that he regards the lead as necessary for the operation, attributing the colours to gold *oxide*, formed and volatilised by the action on the gold of the lead oxide produced.

(*D*) Blossom finds that a very fine gold sublimate can be obtained in two or three minutes by strongly heating a little ball of perfectly pure gold on a charcoal-slip on the ledge. The mouth-blowpipe suffices, but it is got more quickly, and better, by using a stand blow-pipe and hand-blower. After two minutes blowing the appearance on the plate is as follows:—Nearest the charcoal, where the heat on the plate has been greatest, is a small arch of pale yellow colour, just a thin film of gilding over the aluminium. Beyond this is a strip, $\frac{1}{4}$ to $\frac{1}{2}$ inch

wide, of a beautiful violet or purplish-violet colour, and dotted all over the sublimate are little specks and splashes of gold carried over mechanically. By heating for a much longer time, with frequent stopping to let the plate cool, very fine sublimates may be produced. The purplish violet obtained is clearly the same as the deposit on white paper held under a fine gold wire through which a powerful electric discharge passes; and it is certainly interesting to be able to obtain the same appearance by means of the blowpipe.

Estimation of Gold in Pyrites

(*A*) Melt 100 grammes of pyrites with 46·6 grammes of fine iron turnings under a layer of common salt. The monosulphide formed is powdered, and attacked with dilute sulphuric acid in a gas apparatus, the sulphuretted hydrogen being received in ammonia. The matter insoluble in acid is collected, washed, dried, and roasted. It is then mixed with borax and about 2 grammes of granulated lead, and the mixture melted in a muffle until the lead collects in a single globule floating in ferruginous scoriæ. This globule is detached and submitted to cupellation.

On this process it may be remarked that by simply fusing the pyrites alone at a strong heat, with such flux as the gangue, if any is present, may require, a very much smaller regulus will result, equally sure to contain all the gold and equally suitable for treatment with acid.

The simplest mode of treating the insoluble residue after acting upon the regulus with acid, is to collect it on a small filter, dry it, lay it upon a scorifier, cover with assay-lead, fuse, and scorify in a muffle, finally cupelling the lead-button. This method of assay may be advisable in cases where *very small* amounts of gold are to be estimated; but in most cases it cannot compare, for convenience, with the direct treatment of the ore by scorification or by reduction of litharge, concentration of two or three lead-buttons so obtained, and cupellation.

(*B*) The following method may be useful in certain cases:—One pound, or even 18 ounces (avoirdupois) of fine marble-dust is mixed with 8 ounces of finely pulverised and sifted pyrites; the whole is then resifted and put into a Hessian crucible, which should be about one-third filled by the mixture. The crucible is set as usual on a fire-brick, and a fire of hard coal is made around it, the coals being heaped up to within an inch of the top. The crucible is covered with a piece of brick or sheet-iron. During the first half-hour the contents should be stirred once or twice. As the fire grows brighter the carbonic acid evolved keeps the contents of the crucible in brisk movement, and the mixture should be stirred well every five or ten minutes. On stirring during this time, the iron rod used seems to meet with but little

resistance from the light mass, but at the end of about an hour and a half the evolution of gas suddenly ceases, the red-hot mass becomes heavy, sinks, and requires considerable force to keep it stirred. It must be stirred well and vigorously, however, for about half an hour, not leaving it unstirred for more than a minute, otherwise the mass will fuse or cake, and the assay will be almost inevitably ruined.

When a sample taken out in an iron spoon gives off *no* smell of sulphur, the entire contents of the crucible must be turned into a stoneware pot, or a wooden bucket, half filled with water, and well stirred. When the powder—which should be uniform and free from lumps or fused pieces—has settled, the water must be poured off, the wet mass allowed to drain, and then transferred to a large earthen bowl or porcelain mortar. Here it is to be amalgamated with about 2 ounces of mercury, to which a little bit of sodium amalgam has been added. The amalgamation, as well as the stirring in the fire, is a tedious process. It does not consist in merely grinding with a pestle the mercury in among the particles of the roasted ore, but this ore itself must be ground in contact with the mercury until the particles are so fine that they will float suspended in water for several seconds. At the end of, say, ten minutes' thorough grinding, the contents of the bowl are to be brought into one mass in the bottom of the vessel, the bowl then sunk in a tub of water, and the contents 'washed down,' an operation not easily described, but familiar enough to every mining engineer. It consists essentially in shaking the bowl half full of ore and water in such a way that the mercury, gold particles, and unground ore sink to the bottom, while the light and finely ground ore is floated off into the tub. The ore remaining is reground and rewashed, and these processes are repeated till nothing but the mercury remains in the bottom of the bowl or mortar. This mercury is then dried with filter-paper and heated in a porcelain capsule over a Bunsen flame, very gently, until it is sublimed and the gold remains behind. The film of gold may then be scraped up and melted, with a little sodium borate and potassium nitrate, in the very smallest-sized Hessian crucible, either with the foot blowpipe or in a charcoal furnace, by which means a round, clean button of gold suitable for weighing will be obtained.

This method is tedious, laborious, and, to a considerable degree, uncertain, but it will indicate the presence of gold, and will bring it out in a weighable form from pyritic ores, where the assay by smelting will not show a trace of the precious metal; and when the fire assay shows a certain percentage this will invariably bring out a larger amount.

Separation of Gold by Quartation with Zinc

(*A*) On melting zinc with the alloy, in an open porcelain crucible, the former is partially oxidised, the film of zinc oxide hindering the

contact of the metals. If the fusion is performed under a layer of resin, the vapours become ignited, and the resin is often burnt away before the fusion is effected. Even in a covered crucible the resin is soon volatilised, while particles of carbon are deposited on the lid and the sides, and falling back into the crucible contaminate the alloy. The finer particles of carbon render the solution in nitric acid turbid, and cannot be entirely removed by washing.

(*B*) Balling, therefore, modifies Jüptner's process as follows:—He uses cadmium, which is more readily fusible, for quartation, instead of zinc, and takes potassium cyanide as a cover. The metals unite readily under the melted cyanide at the heat of a Berzelius spirit-lamp, and a homogeneous regulus is soon obtained. The crucible, when cold, is placed in a beaker, and the potassium cyanide is dissolved in water. The solution is poured away and the metal is washed with water. It is then introduced into a flask and boiled once with nitric acid of sp. gr. 1·2, and then thrice with nitric acid of sp. gr. 1·3. The cadmium is completely dissolved. Two and a half parts of this metal suffice for quartation. The granule of gold retains the form of the original metal, and is transferred to a small crucible for ignition.

(*C*) Cabell Whitehead, Assayer to the United States Mint, finds cadmium to be a most efficient aid in the estimation of small quantities of silver in gold bullion containing considerable amounts of copper or platinum.

Five hundred milligrammes are weighed into a porcelain crucible and covered with 10 grammes of potassium cyanide. The potassium cyanide is melted over a Bunsen burner or preferably a blast-lamp. When the cyanide is in quiet fusion 1 gramme of cadmium is dropped into the crucible, where it quickly melts and forms a bright, homogeneous alloy with the gold. After gently shaking, so as to bring the cadmium in contact with every particle of bullion, the crucible is removed and the contents poured on to a clean porcelain slab, where they soon solidify. The alloy will be found in one piece, easily detached from the potassium cyanide. It is now washed in warm water, dried, and placed in a diamond mortar, when several sharp blows with a hammer quickly reduce it to powder.

This powder is carefully transferred to an assay bottle, 1004 milligrammes of pure silver added, and 10 c.c. of nitric acid—32° Baumé—poured on. In from five to ten minutes (depending upon the heat used) the solution is complete and all action has ceased. The bottle is now cooled and 100 c.c. of normal salt solution is charged, and the bottle shaken. The precipitation is finished with the decinormal solution.

This assay is accompanied by another called a 'proof,' made of 1004 milligrammes of pure silver dissolved in the same amount of acid. Now the excess of silver found in the assay, over that shown in the

'proof,' is the amount contained in 500 milligrammes of coin. This doubled gives parts of silver per 1000.

Example:—An alloy composed of 499 milligrammes pure gold, 1 milligramme of silver, and 1 gramme of cadmium, treated as above described, after being charged with 100 c.c. normal salt solution, required 5 c.c. decinormal solution for complete precipitation of the silver present. A proof assay, carried along as check, upon 1004 milligrammes of pure silver, required in addition to 100 c.c. of normal salt solution 4 c.c. of decinormal solution for complete precipitation = 1004 c.c. decinormal solution. Hence, each c.c. decinormal equals 1 milligramme silver, and 1 c.c. decinormal solution required by the bullion, in excess of that called for by the silver added, shows the bullion to contain 1 milligramme silver in 500, or 2 parts per 1000.

It may be ask by those not familiar with mint appliances and usages, 'Why not titrate directly the silver brought into solution with the cadmium, instead of adding a known weight of pure silver and finding the desired result by difference?'

The reply is that the small amount of silver present in this class of bullion would, as chloride, not 'clear' on shaking, and much time would be consumed in finding the end of the reaction. By the method described the usual apparatus and solutions may be used and results rapidly obtained.

When no such reasons exist the sulphocyanide method alluded to at the end of this article is recommended.

(*D*) An approximate assay gives by cupellation 0·035 silver, hence 500 milligrammes will contain about 17·5 milligrammes of that metal, and 986·5 milligrammes must be added to bring the total silver up to 1004 milligrammes. If copper is not present, about 50 milligrammes are added, it being found that the alloy of copper with cadmium is very brittle, and the resulting button is easily crushed to powder.

The sample having been fused with cadmium in presence of potassium cyanide is powdered and subjected to treatment with nitric acid as above described.

After charging with 100 c.c. normal salt solution, and shaking, the assay required 4·5 c.c. decinormal solution for the end reaction. A 'proof' consisting of 1004 milligrammes pure silver in solution, treated in the same manner, required but 3 c.c. decinormal solution.

Hence the assay contained 4·5—3=1·5 milligramme more silver than the proof, or 1004+1·5=1005·5 milligrammes in silver in all. This, less the 986·5 milligrammes silver purposely added, gives 19 milligrammes as the silver present in 500 milligrammes of bullion taken, or 38 parts in each 1000 instead of 35 parts found by cupellation.

In favour of the new method it may be said—

(1) That the ready solubility of cadmium in nitric acid of any strength makes it possible to dilute (if the term may be used) the silver present in gold bullion to any desired extent, while, on the other

hand, the difficult solubility of lead necessarily limits the dilution possible by the time required for its imperfect extraction.

The inevitable small portion of other metals retained by the gold after treatment with nitric acid may therefore, by the use of cadmium, be reduced to but an infinitesimal quantity of silver.

(2) The brittleness of the button obtained permits its being crushed to a powder, in which condition the alloy rapidly yields its soluble portion to nitric acid, and the time required for an assay is materially shortened.

(3) The low temperature required enables the chemist to dispense with all special appliances. A Bunsen burner will well answer the requirements for heating purposes, and little more is needed beyond a standard salt solution. No muffle or rolls are wanted.

(*E*) In a laboratory where few assays are made, the following method might be used and very satisfactory results obtained. After alloying and crushing, treat in a parting flask with 15 c.c. of nitric acid—32° Baumé—for ten minutes; pour off this acid into a beaker, add 15 c.c. of acid the same strength, and boil for ten minutes longer; pour off again in the same beaker, wash with hot water and take out in an annealing cup, dry and heat over a blast-lamp, weigh and deduct 0·25 milligramme for cadmium retained. Twice this weight gives the gold fineness.

The acid and washings are evaporated to drive off free nitric acid, and the silver is determined either as chloride, or volumetrically with sulphocyanide, with a ferric indicator. Cadmium nitrate does not interfere in the least with the determination of silver, either as chloride or as sulphocyanide.

Electrolytic Separation of Gold from other Metals[1]

(*A*) E. F. Smith proposes the behaviour of the metallic cyanides as a means of separating gold from palladium, copper, nickel, zinc, and platinum. If 3 grammes potassium cyanide are dissolved in 150 c.c. of liquid, a current representing 0·5 to 1 c.c. of detonating gas per minute throws down pure gold without the accompanying metals.

This process serves for separating silver or mercury from platinum. The two former metals are precipitated quite free from platinum.

(*B*) According to Classen, gold may be deposited in a fine compact form from the solution of its compounds in potassium cyanide, using the same process as that indicated for silver. As the gold can only be dissolved away from the platinum capsule by means of aqua regia, it is previously coated with a dense layer of metallic silver.

[1] For details of operation see chapter on Electrolytic Analysis.

Micrometric Assay of Gold Ores

It often happens in the assay of poor gold ores, and of slimes, tailings, and other residues from the treatment of auriferous minerals, that the gold bead resulting from the assay, when placed in the balance, is so light that it cannot be weighed with any degree of accuracy. Harkort and Plattner (*Probirkunst*) measured the small beads, obtained by the cupellation of these ores, by means of two lines ruled on ivory similar to those in a Wedgwood pyrometer, and graduated by the help of spheres of gold of known weight.

The results obtained were not very exact, as the beads were flattened on one side and contaminated with silver. Goldschmidt proposed using a micrometer to measure the spheres, and Gozdorf [1] devised the method of forming the gold into a perfect sphere by fusing it in a bead of boric acid.

Guerreau [2] has made a number of assays to check the correctness of this method, which, up to the present, has not been generally made use of in practical assaying.

The gold and silver bead is obtained in the ordinary manner, but the parting with nitric acid must be done with great care, so that the attack may proceed very slowly, and that if the gold is divided it may divide as little as possible. The flattened bead is placed in a small porcelain crucible, and treated with cold nitric acid of 1·18 density (22° B.) for about five minutes; next it is heated gently for ten minutes; then the temperature is raised, and it is treated for ten minutes with nitric acid of 1·29 density (32° B.). If, at the commencement of the attack, too strong an acid or too high a temperature is used, the gold will be reduced to such a fine state of division that it would be difficult to avoid losses. It is then washed with water, decanted, and dried in the oven.

It is necessary to use a very gentle heat to drive off the last traces of moisture; in fact, if the water is driven off too rapidly, and, above all, if it is boiled, the gold will be disintegrated, and losses will occur.

As a general rule, inquartation is not necessary, as the silver contained in the assay litharge is amply sufficient.

A borax bead is melted in the blowpipe flame on a platinum wire, and, while still warm, it is pressed on the gold, which adheres to it firmly. On remelting the bead the gold collects in the form of a sphere. It sometimes happens that two spheres of gold are obtained instead of one; it is impossible to make these two unite in the interior of the bead; in such a case the boric acid must be dissolved and the operation recommenced. Although the great viscosity of the melted medium prevents the gold from becoming alloyed with the platinum, it is always advisable to make the borax bead as large as possible.

[1] *Chemical News*, Nov. 5, 1886. [2] *Ibid.* Oct. 17, 1902.

The boric acid is dissolved, and the sphere of gold measured under the microscope on a watch-glass. An enlargement of 100 to 150 times is most convenient for these assays, but the true value of the divisions of the ocular should be verified by means of a millimetre objective divided into 100 parts.

The sphere should be measured in six or eight different positions, and the mean of the values obtained taken. By operating in this manner, differences in diameter up to 0·03 millimetre have no appreciable influence on the results.

Generally speaking, the spheres are very regular ; the greatest variations were observed on a large sphere of 0·799 millimetre diameter, weighing 5·3 milligrammes. The difference between the two extreme measurements was 0·036 millimetre, or 4·5 per cent. On small spheres the difference is nil ; if, however, too great a variation is found it will be necessary to remelt the sphere. As a general rule, it may be said that the smaller the sphere the better are the results. It is not advisable to estimate quantities of gold of more than 6 or 7 milligrammes by this method ; but, on the other hand, there is, so to speak, no limit to the smallness of spheres of which the valuation is possible. The smallest sphere obtained weighed 0·04 milligramme. Gozdorf measured the very small spheres in the borax bead, but this method does not give good results.

The weight of a sphere of a substance of which the density is known is deduced from the formula :

$$W = \frac{\eta \times d_3 \times D}{6}$$

in which d represents the diameter of the sphere, and D the density of the substance ; from this we get $W = 10{\cdot}123 \times d_3$, a constant with which we determine the weight of a sphere of gold having a diameter of one division of the micrometer. It only remains to multiply the figure thus obtained by the cube of the number of divisions of the sphere to obtain its weight. The sphere may be then weighed on the balance as a check. The density of fused gold is taken as 19·33.

Estimation of Gold

L. Vanino and L. Seemann [1] treat the solution containing gold with peroxide of hydrogen after the addition of an alkaline lye. While other methods require several hours to effect a complete reduction, in this case the gold is precipitated in a few minutes even in the cold, as a black deposit which under the action of heat agglomerates and becomes of a reddish-brown colour :—

$$2AuCl_3 + 3H_2O_2 + 6KOH = 2Au + 6O + 6KCl + 3H_2O.$$

In the case of dilute solutions it is best to apply heat after the precipitation, then acidulate with HCl. For the estimation of gold in

[1] *Chemical News*, Aug. 16, 1900.

commercial chloraurate of sodium it is, however, preferable to effect the reduction by means of formic aldehyde instead of peroxide of hydrogen.

The reaction of peroxide of hydrogen in alkaline solution is much more sensitive qualitatively than any other reaction of gold. With 3 milligrammes of gold per litre we can still perceive a pale reddish colouration, appearing blue by reflected light; this would not be detected by other reagents.

Silver is also precipitated quantitatively under the same conditions, but platinum as well as iridium remains in solution; this affords an excellent method for separating these two metals from gold.

PLATINUM

Detection of Small Quantities of Platinum

When potassium iodide is added in slight excess to a solution of platinum chloride, the platinum iodide is dissolved, and should the solution be concentrated, a dark red liquid is produced. F. Field shows that very minute traces of platinum can be detected in this way, and in many cases where that metal is in combination with a large excess of other metals it may be distinctly recognised. To show the delicacy of the test, 0·1 gramme of platinum was converted into chloride, evaporated to dryness, care being taken that every trace of nitric acid was expelled. This was dissolved in 1000 c.c. of water, each c.c. therefore containing $\frac{1}{10000}$ part of platinum, to which a drop of potassic iodide imparted immediately a dark rich rose colour, strikingly resembling a concentrated solution of cobalt nitrate. 10 c.c. of this was made up to a litre (1000 c.c.), so that every c.c. contained 0·000001, or $\frac{1}{1000000}$ of platinum. One part of platinum in 2,000,000 of liquid can be detected by this test. A drop or two of acid added to the solution accelerates the development of the colour. Sulphuretted hydrogen, sodium sulphite and thiosulphate, sulphurous acid, mercuric chloride, and certain other reagents immediately destroy the colour. When the pink solution is heated the tint disappears.

Purification of Platinum

The tendency of platinum to alloy with other metals at a temperature far below its fusing-point is sufficiently well known to every user of platinum crucibles. It is equally well known that iron, &c., which has been absorbed by platinum cannot be removed, except superficially, by the action of hydrochloric acid for instance, nor even by heating in acid potassium sulphate.

(*A*) Stas, in his memoir on the atomic weight of silver, &c., states that he purified his platinum vessels from iron by causing them to come in contact, at a red heat, with the vapour of ammonium chloride.

The process had to be repeated as often as any yellow sublimate was formed.

(*B*) Instead of ammonium chloride, Sonstadt puts dry double ammonium and magnesium chloride in the platinum vessel intended for purification. The vessel is then heated to near the fusing-point of cast iron for about an hour. In this process not only is ammonium chloride vapour given off for a long while with the double salt, at a temperature much above that at which ammonium chloride alone volatilises, but when that salt is completely expelled the magnesium chloride remaining is continually being decomposed with evolution of free chlorine, and, frequently, the formation of a crystalline crust of periclase lining the crucible.

Platinum thus purified is softer and whiter than ordinary commercial platinum. The method is not only available for the removal of iron, but renews crucibles that have become dark-coloured and brittle from exposure to gas flame, as well as crucibles that have been attacked by silicates during fusion of these with sodium carbonate. In his original paper on this subject Sonstadt draws attention to the extreme facility with which platinum becomes impure by heating in contact with matters containing only a very small proportion of some substance capable of attacking the metal. Thus a platinum crucible becomes sensibly impure after prolonged ignition at a high temperature, bedded in commercial magnesia. On the other hand, a platinum crucible has been kept at a constant weight to the tenth of a milligramme over a series of intense ignitions, when the precaution had been taken to embed it in chemically pure magnesia.

Analysis of Platinum Ores

Platinum ores contain the following substances:—

1. Sand. The whole of the sand is never removed by washing the ore; the sand contains quartz, zirconia, iron chromate, and, in the Russian ores, iron titanate.

2. Iridium osmide.

3. Platinum and iridium.

4. Palladium, iron, and copper, which exist in the ores in a metallic state, for the iron found in the sand is not soluble in acid.

5. Gold and platinum; and, oftener than is supposed, a little silver. The latter metal is generally found with the palladium, and it is very rarely that palladium is obtained quite free from silver when it is prepared by the old processes.

6. Rhodium.

(*A*) **Deville and Debray's Method** of analysing these ores is as follows:—

1. *Sand.*—To estimate the sand take a small assay crucible, or an ordinary crucible with smooth sides, and melt in it a little borax, so as

to glaze the inside. Now introduce from 7 to 10 grammes of pure granulated silver and 2 grammes of the ore, fairly taken and weighed very accurately. Over the platinum put 10 grammes of fused borax, and one or two small pieces of wood charcoal. The silver is now melted, and care must be taken to keep it for some time a little hotter than the melting-point, so that the borax may be very liquid, and may dissolve the vitreous matters which accompany the platinum and constitute the sand. The crucible is now allowed to cool, and, when it is cold, the button, which will contain the silver, osmium, platinum, and all the other metals, is detached, and if necessary digested for a time with weak hydrofluoric acid to remove the last portions of borax. It is now heated to a faint redness and then weighed. The weight of the button subtracted from the sum of the weights of the ore and silver employed will give the amount of sand contained in the ore. It is very important to know this amount, for it represents the only matter absolutely destitute of value which the ore contains; and this simple operation may be considered most important in estimating the value of an ore. It is, besides, performed so quickly that it is as well to do at the same time two or three specimens, taken from different parts of a lot of platinum powder.

2. *Iridium Osmide.*—Another 2 grammes of the ore weighed very accurately are treated with aqua regia at 70° C. until the platinum is entirely dissolved. The aqua regia must be renewed occasionally for twelve or fifteen hours, or until it is no longer coloured. It is best to perform this operation in a large beaker, and to place a cover over it to prevent loss. The solutions must be decanted with the greatest care from the metallic spangles of the iridium osmide and the sand which remain at the bottom of the beaker. If necessary it may be filtered, but as little as possible of the osmide must be allowed to go on the paper. The insoluble residue must be washed by decantation, then dried and weighed, after having added what remained on the filter. By subtracting the weight of this residue from the weight of the sand of the former operation, the weight of the iridium osmide is found.

The button obtained in estimating the sand might be employed in this operation. In that case it is necessary to dissolve out the silver with nitric acid, and then proceed with the residue, as just directed.

3. *Platinum and Iridium.*—The solution in aqua regia obtained in the last operation is evaporated to dryness at a low temperature, and the residue is redissolved in a small quantity of water (if it should not entirely dissolve in the water some more aqua regia must be added, and the evaporation repeated), to which is added about twice its bulk of pure alcohol; lastly add a great excess of sal-ammoniac in crystals. The whole is now slightly warmed, to complete the solution of the sal-ammoniac; it is then stirred, and afterwards set aside for twenty-four hours. The orange-yellow, or even reddish-brown precipitate which is

formed, contains most of the platinum and the iridium, but some remains in the solution. The precipitate must be thrown on a filter and washed with alcohol. Afterwards the filter is dried in a platinum crucible, placed, for greater safety, within a larger one, and afterwards heated by degrees to dull redness. The crucibles are now uncovered, and the filter is burnt at the lowest possible temperature. Once or twice after the incineration of the filter a piece of paper saturated with turpentine should be introduced into the crucible, by which means the iridium oxide will be reduced and the expulsion of the last traces of osmium will be effected. The crucible is now heated to whiteness until it no longer loses weight, or the reduction is finished in a current of hydrogen.

The liquid separated from the platinum-yellow by filtration is evaporated until the ammonium chloride crystallises in large quantity. It is allowed to cool, then decanted, and a small quantity of a deep violet-coloured salt is collected on a filter; this is the iridium ammonio-chloride, mixed with a little of the platinum salt. It is first washed with a solution of sal-ammoniac and then with alcohol. The salt is then ignited, and, if necessary, reduced by hydrogen like the platinum salt. The mixture of platinum and iridium, obtained by the two reductions, is then weighed. The two metals are now digested at about 40° or 50° C., in aqua regia, diluted with about 4 or 5 times its weight of water—the aqua regia being renewed until it is no longer coloured. The residue is pure iridium. To obtain the weight of the platinum, the weight of the iridium is subtracted from that of the mixture of the two. This method of separating the two metals is very accurate if the aqua regia used be weak, and the contact with it is prolonged.

4. *Palladium, Iron, and Copper.*—The liquor charged with sal-ammoniac and alcohol, from which the platinum and iridium have been separated, is evaporated to get rid of the alcohol, and then treated with an excess of nitric acid, which transforms the ammonium chloride into nitrogen and hydrochloric acid. It is now evaporated almost to dryness. The residue is removed to a covered porcelain crucible, which is weighed with great care. When the matter is dry it is moistened with concentrated ammonium sulphide, and afterwards dusted over with 2 or 3 grammes of pure sulphur. After drying, this crucible is placed within a larger one of clay and surrounded with pieces of wood charcoal. The two are covered, and now set in a cold furnace, which is filled up with charcoal, and the fire is lighted at the top to avoid the projection of any matter from the crucible if it were too quickly heated. After reaching a bright red heat, the crucibles are allowed to cool. The porcelain crucible now contains palladium in a metallic state, with the iron and copper sulphides, and also the gold and rhodium. This mixture is moistened with concentrated nitric acid, which, after prolonged digestion at 70°, dissolves the palladium, iron, and copper, forming at

the same time a little sulphuric acid. The solution of the nitrates is poured off the residue, which is washed by decantation, and the solution and washings are evaporated to dryness, and then calcined at a strong red heat. In this way the palladium is reduced, and the iron and copper pass to the state of oxides, which are easily separated from the palladium by means of strong hydrochloric acid. The palladium remains in the crucible, in which it is again strongly ignited and then weighed.

The iron and copper chlorides are now evaporated to dryness at a temperature but little above 100° C., and are then treated with ammonia. The iron sesquichloride, having lost nearly all its acid, has become insoluble; but the copper chloride is readily dissolved, and may be filtered from the iron, which is washed, ignited, and weighed. The copper solution is now evaporated almost to dryness, and then mixed with excess of nitric acid and heated to drive off the ammonium chloride. Afterwards the copper nitrate is ignited and weighed. The weight of the copper is always so small that the hygrometric water the copper oxide may absorb may be neglected.

5. *Gold and Platinum.*—The residue insoluble in nitric acid is weighed and treated with very dilute aqua regia, which takes up the gold, and sometimes, but very rarely, traces of platinum. To ascertain if platinum be present, evaporate to dryness, and redissolve by alcohol and ammonium chloride. If any platinum-yellow remain, it must be ignited and weighed. The difference in the weight of the porcelain crucible before and after the treatment by aqua regia gives the weight of the gold, from which, if any be found, the weight of the platinum must be deducted.

6. *Rhodium.*—The residue left in the crucible is rhodium, which must be reduced in a current of hydrogen.

(*B*) **Bunsen's Method** of analysing platinum residues is as follows:—The residues employed contained no osmium, and were relatively rich in rhodium.

Platinum and Palladium.—It is easy to effect the almost complete separation of platinum and palladium from rhodium, iridium, and ruthenium. The original material is mixed in a Hessian crucible, with from $\frac{1}{2}$ to $\frac{1}{3}$ its weight of ammonium chloride, heated until the latter is completely volatilised, allowed to glow gently until only the vapours of iron sesquichloride show themselves, and then placed in a porcelain dish and evaporated to a syrupy consistency, with from 2 to 3 times its weight of crude nitric acid. By this treatment with ammonium chloride the metals present not belonging to the platinum group will have been partially converted to lower chlorides, the rhodium, iridium, and ruthenium will have been rendered insoluble, and the silica present as gangue converted from a gelatinous mass to a finely pulverulent condition, in which state it will admit of speedy filtering.

The chlorine compounds, produced by the ammonium chloride, give,

upon digestion with nitric acid, just enough hydrochloric acid to dissolve the platinum to bichloride, while the metallic copper and iron present act so far reducingly upon the palladium (in solution in nitric acid) that it remains in solution, not as bichloride, but as the protochloride, which latter is not precipitated with potassium chloride. The mass is diluted with water, filtered, and the solution saturated with potassium chloride, and the greater part of the platinum separated pure as potassium platinochloride, which is washed out, first with potassium chloride, and later with absolute alcohol (the last washings must not be added to the solution).

The filtrate is brought into a large flask (which can be made air-tight), so as not to more than half fill it. Chlorine gas is led into this flask, and it is, from time to time, shaken vigorously, until no further absorption of gas takes place, when all the palladium will have separated as a cinnabar-red precipitate of potassium palladiochloride (somewhat impure, however, from traces of platinum, iridium, and rhodium). The liquid from which these precipitates were obtained is now evaporated, not quite to dryness, with hydrochloric acid; and, upon addition of just so much water as is necessary to dissolve out the potassium chloride and other soluble salts (aiding the operation by rubbing with a pestle), there remains behind a dirty, yellow-coloured precipitate. This is separated by filtration, boiled with caustic soda and a few drops of absolute alcohol. Hydrochloric acid is added to dissolve the precipitate formed, and the liquid then saturated with potassium chloride; the result is a precipitate of chemically pure potassium platinochloride. The mother-liquor contains only copper and no platinum metals.

The purification of the cinnabar-red precipitate of palladium is accomplished as follows:—Dissolve in boiling water, whereby a portion of the chloride dissolves, with evolution of chlorine, to palladium protochloride. Then evaporate with $2\frac{1}{2}$ times its weight of oxalic acid, and dissolve again in a solution of potassium chloride; whereupon potassium platinochloride remains behind, chemically pure. Wash out as before.

The brown liquid is then somewhat concentrated upon the water-bath; and upon cooling, there separate bright green, well-formed crystals of potassium palladio-protochloride (with some potassium chloride), which, upon testing, proves free from the other platinum metals.

The liquid poured off from these crystals is then neutralised carefully with caustic soda, and gives a slight precipitate of copper and iron, which is filtered off. Upon adding potassium iodide to the filtrate, all the palladium separates as palladium iodide. To avoid adding an excess of the reagent, it is best to take, from time to time, a drop from the liquid with a capillary tube, and bring the same upon a watch-glass. As long as the precipitation is incomplete, the drop appears, upon a

white background, *brown*; when complete, it is *colourless*; when the reagent is present in excess, it is *red*. This is tested for its purity by reducing it to metallic palladium, and then heating and dissolving in nitric acid; when pure, it must dissolve completely. The whole mass is now reduced in a slow stream of hydrogen gas (whereby the iodine can be obtained again, as hydriodic acid, by absorbing with water). Lastly the mass must be strongly heated, to decompose slight traces of the palladium subiodide which are formed.

The mother-liquor from which all this platinum and palladium have been obtained may contain some iridium and rhodium; it is, therefore, evaporated to dryness with a little potassium iodide, whereby a mixture of the rhodium and iridium iodides separates. This can either be dissolved in aqua regia and the two metals separated (as will hereafter be described) by sodium bisulphite, or it can be united with the next portion from which these metals will be obtained.

Ruthenium, Rhodium, and Iridium.—The residue from the original material which remains, after treatment with ammonium chloride and nitric acid, is treated as follows, to get the metals in a form adapted to further chemical treatment.

The method depends upon the behaviour of zinc chloride to zinc. If a piece of zinc be melted, it rapidly covers itself with a stratum of oxide. If to the melted metal a metal like iridium be added, the oxide stratum hinders the latter from coming into contact with the zinc, even though it be pushed beneath the surface. If, however, a few grains of ammonium chloride be added to it, ammonia, hydrogen, and zinc chloride will be formed, which last dissolves the oxide stratum to basic zinc chloride. The zinc below resembles mercury in lustre and mobility. As soon as the chloride has dissolved as much of the oxide as possible, the oxide stratum again forms, and is instantly removed by the addition of more ammonium chloride. The melted zinc, strewn with ammonium chloride, also possesses, like mercury, the property of attacking other metals, if the affinity exists of forming alloys with them. By strewing ammonium chloride upon the melted zinc, a quiet surging is kept up, as the ammonia and hydrogen are given off. Many oxides and chlorides (among which are those of the platinum metals), when they come into contact with this atmosphere of reducing gases, and with the basic zinc chloride, are instantly reduced and dissolved by the zinc. In making the solution, the zinc, in a porcelain capsule, should be constantly rotated: the gangue remains in the basic chloride. The regulus, immediately upon solidifying, should be taken from the capsule, out of the yet liquid basic chloride, and washed off with acetic acid until all the basic chloride is dissolved away. The gangue can be quantitatively estimated by filtration and weighing. If the regulus is not immediately removed, the containing vessel will be broken, owing to the unequal expansion of the porcelain and the metal.

The best proportions for a quantitative separation are, to 1 part of the platinum metals, from 20 to 30 parts of zinc. For an ordinary separation, 7 parts of zinc are sufficient.

For the extraction of the residues remaining after the treatment with nitric acid this method is admirably adapted. By fusing only once with zinc for two or three hours, all the platinum metals are extracted. The operation is the following :—

From 3 to 3·5 kilogrammes of commercial zinc are fused in a 2-litre Hessian crucible, ammonium chloride from time to time strewn upon it; 400 grammes of residue, previously heated to faint glowing with ammonium chloride, are added, and the temperature kept, for two or three hours, just above the fusing-point of the alloy, by adding, whenever the mass threatens to solidify, some ammonium chloride. The mass is divided into three strata after solidification has taken place.

The outer stratum, easily broken away by a blow from a hammer, contains no platinum metals. The next contains some particles of the zinc and platinum alloy, embedded in the basic zinc chloride ; it is porous, and not very thick. The inner stratum consists of a beautiful crystalline regulus.

To obtain the alloy from the middle stratum, it is only necessary to wash repeatedly with water ; and the alloy gained is, of course, to be added to the regulus. To obtain this regulus as pure as possible, it is again fused with 500 grammes of zinc and some ammonium chloride, then granulated in water, and the granules dissolved in fuming hydrochloric acid. The acid attacks the regulus with the greatest energy, and the solution is complete in less than an hour. The zinc chloride can be used for the next operation.

The platinum metals are found at the bottom of the vessel, in the form of a finely divided black powder, which is contaminated with zinc, and with traces of iron, copper, &c. from the latter. It cannot be purified with nitric acid, nor with aqua regia, for part of the platinum metals will thereby be dissolved, or, at best, so suspended in the liquid that filtration is impossible. If, however, the powder is treated with hydrochloric acid, singularly enough, all the impurities are dissolved ; not only zinc and iron, but also lead and copper, dissolve easily, with the generation of hydrogen. The explanation is readily found in electrical currents produced by the contact of the metals, the stream passing from the positive zinc, iron, &c. to the negative platinum metals, hydrogen being given off on the latter and chlorine on the former, and uniting with them. The metallic powder, after thorough washing, possesses the property, upon being gently heated, of exploding weakly, and, when highly heated, with violence, the explosion being accompanied with the evolution of light ; thereby neither hydrogen, nor chlorine, nor nitrogen, nor aqueous vapour is given off ; and, as these are the only elements which it is possible

that the metallic powder could have taken up, it must be assumed these metals are, by this treatment, converted into an allotropic condition, and that, upon heating, they return, with more or less energy, to their original condition. The powder contains, mainly, rhodium and iridium; but there are traces present of platinum, palladium, lead, copper, iron, and zinc.

It is intimately mixed with about 3 or 4 times its weight of completely anhydrous barium chloride, and a stream of chlorine gas led over it at a tolerably high temperature. The operation is concluded when particles of iron sesquichloride show themselves on the neck of the flasks containing the powder. These are carefully brushed away with filter-paper. Some water is now added, and the mass of the platinum metals dissolved with the evolution of heat. There remains behind insoluble matter, which, upon reduction with hydrogen, alloying with zinc, and treatment with hydrochloric acid, furnishes ruthenium. From the solution all the barium chloride is removed by the careful addition of sulphuric acid. The platinum metals are now completely freed from all other metals by reduction with hydrogen, the temperature being, throughout the operation, maintained at nearly 100° C. by means of a water-bath. Platinum and palladium chiefly separate first; then mainly rhodium; and the last portions consist almost entirely of iridium. It is best to break off the operation when the liquid has assumed a greenish-yellow colour. The last portions of iridium (obtained by evaporating the solution to dryness, fusing with sodium carbonate, and treatment with aqua regia) are added to the portion, afterwards to be again rendered workable by renewed treatment with barium chloride. The operation of reduction is hastened by concentrating the liquid, in doing which care must be taken to guard against explosion, on account of the hydrogen. The eliminated metals are treated with aqua regia, and the platinum and palladium thus dissolved separated from each other, as already described. The traces of rhodium and iridium in the mother-liquor can be removed entirely by continued boiling with potassium iodide (whereby they are precipitated as iodides); they are then dissolved in aqua regia and added to the insoluble portion.

This insoluble and partly oxidised portion is now again reduced in hydrogen gas, treated, as before described, with barium chloride, and, after the removal of the barium, the last traces of platinum and palladium removed by boiling with caustic soda. Rhodium and iridium now alone remain to be separated.

The brown-red liquid is, for this purpose, evaporated with hydrochloric acid, and, after filtration, treated with sodium bisulphite in great excess, and the whole allowed to remain quietly in the cold for several days. The double rhodium and sodium sulphide separates slowly, giving a lemon-yellow precipitate. The solution becomes lighter and lighter, and finally almost colourless. The colour of the

precipitate changes with that of the liquid, becoming, with it, lighter. This precipitate, upon washing, contains the rhodium almost pure.

Upon heating the liquid gently, a yellow-white precipitate separates, which consists mainly of rhodium, but contains, also, some iridium. After filtering off this precipitate, the solution, upon being concentrated to a small volume, gives yet two precipitates :—

1. A curdy, slowly separating, yellowish-white precipitate, containing nearly chemically pure iridium, with but the faintest traces of rhodium.

2. A heavy, crystalline powder, quickly separating, which is readily freed from the first by decantation. Upon testing, it gives all the reactions for iridium, but likewise some peculiar reactions not shown by the latter. It may possibly contain a new metal.

The complete separation of rhodium from iridium is accomplished by treating the yellow precipitates with concentrated sulphuric acid. They are brought in small portions into the acid, heated in a porcelain capsule until all the sulphurous acid has escaped, and then left upon the sand-bath until the free sulphuric acid has been driven off and the sodium sulphate formed. Upon boiling the mass in water, all the iridium dissolves as sulphate, with a chrome-green colour ; while the rhodium remains behind as a flesh-coloured double sodium and rhodium salt. The latter is boiled in aqua regia, and washed by decantation. It is insoluble in water, hydrochloric or nitric acids, and in aqua regia. The rhodium and iridium are now completely separated.

The first yellow precipitate obtained in the cold by the sodium bisulphate gives, by this treatment, the rhodium quite pure. The second and third precipitates, containing much iridium, give a very fine rhodium, but still slightly contaminated with iridium. The products, therefore, obtained by this treatment with sulphuric acid (which betray their contamination with iridium by their somewhat brownish colour), are collected by themselves, the rhodium separated therefrom by glowing, treated again with barium chloride, and the operation of separation repeated. The green solution, containing only iridium, is gradually heated over an ordinary burner, in a porcelain capsule, and, afterwards, upon the sand-bath, to remove the excess of sulphuric acid ; and finally, the capsule and its contents are highly heated in a Hessian crucible. There are formed thereby sodium sulphate and iridium sesquioxide. Upon boiling the mass with water, the last remains behind as a black, insoluble powder, which is readily washed by decantation.

(*C*) **C. Lea's Process for Analysing Platinum Ores.**—The ores on which these analyses were performed contained chiefly iridium, together with ruthenium, osmium, rhodium, and platinum. It was a Californian osmiridium which had already undergone a preliminary fusion with nitre and caustic potash.

This material is boiled with aqua regia to extract all the soluble portions, the residue then ignited with nitre and caustic soda,[1] and the fused mass heated with water. From the resulting solution small portions of potassium osmite crystallise out. The metallic oxides are next precipitated, and this precipitate, together with the portions insoluble in water, is boiled again with aqua regia, ignited, &c. These ignitions still leave a small portion of unattacked residue.

The boiling with aqua regia is continued for a long time, in order to get rid as thoroughly as possible of the osmic acid. Even after 200 hours' boiling, osmium is still left in the solution in easily recognisable but comparatively small quantity. The greatest advantage is found throughout the whole of this part of the operation from the use of a blowing apparatus, with the aid of which all inconvenience from the fumes of osmic acid is avoided. The apparatus is constantly swept clear by a powerful air current, and the osmic acid is removed as fast as it is volatilised. As the ignition of the ore with alkaline nitrate and caustic alkali scarcely drives off any osmium, and as almost all inconvenience in manipulating the resulting solutions can be avoided by throwing down the metals with alcohol from the hot alkaline solution, in place of using acid, it is clear that the difficulties arising from the noxious effects of osmic acid can be almost wholly removed from each of the various stages of the process.

A very prolonged treatment with aqua regia is found to have the great advantage of converting nearly the whole of the ruthenium into bichloride. The separation of ruthenium in this form from the other metals is so easy in comparison with the difficulties presented by the separation of the sesquichloride, that this advantage cannot be looked upon as other than a very material one.

Sal-ammoniac is next added to the mixed solution in quantity sufficient to saturate it. The sandy crystalline precipitate (A) is thoroughly washed out, first with saturated and then with dilute sal-ammoniac solution. The saturated solution of ammonium salt carries through with it nearly the whole of the ruthenium as bichloride (B); the dilute solution is found to contain small quantities of iridium, rhodium, and ruthenium (C).

Over (A), water acidulated with hydrochloric acid is placed, and allowed to stand for some days. This is treated with ammonia and boiled. The precipitate, when treated with hydrochloric acid, furnishes green osmium chloride, with traces of ruthenium.

In these preliminary steps Claus's process has been followed, which undoubtedly offers advantages over any other, and best brings the

[1] Attention is necessary to the order in which these substances are employed. If the caustic soda is melted first, it attacks the iron vessel strongly, and may even go through. If added last it causes sudden and violent effervescence, with danger of boiling over. Therefore, place the nitre first in the vessel, and when it is fused add the caustic soda. When a red heat is obtained add the osmiridium by degrees.

metals into a convenient state for separation, varying it only by prolonging the treatment with aqua regia, and converting the ruthenium principally into bichloride instead of sesquichloride.

We have now three portions of material:—(A), consisting of ammonium iridiochloride, containing also ruthenium, osmium, rhodium, and platinum in small quantities. (The ore under examination contained no palladium, which metal, if present, has always its own peculiar mode of separation, and does not enhance the difficulties of operation.) (B), containing ruthenium bichloride, together with iron in quantity, copper, and other base metals which may be present. Finally, (C), containing chiefly ruthenium bichloride, mixed with small quantities of iridium and rhodium.

The next step in the process is to introduce the ammonium iridiochloride (A) into a large flask with 20 to 25 times its weight of water, and apply heat until the solution is brought to the boiling-point; the whole of the ammonium iridiochloride should be brought into solution in order that the reduction to be effected may not occupy too long a time, as otherwise the platinum and ruthenium salts, if any be present, might likewise be attacked. Crystals of oxalic acid are thrown in as soon as the solution actually boils, whereupon a lively effervescence takes place, and the iridium salt is rapidly reduced. As fast as the effervescence subsides, more oxalic acid is added, until further additions cease to produce any effect. When this is the case, the liquid is allowed to boil for two or three minutes longer, not more; the heat is to be removed, and the flask plunged into cold water.

By this treatment any platinum present is unaffected. Sal-ammoniac in crystals is added, about half enough to saturate the quantity of water present. The sal-ammoniac may be added immediately before the flask is removed from the fire. After cooling, the solution should be left for a few days in a shallow basin, whereby the ammonium platinochloride will separate out as a yellow, a reddish, or even (especially if the quantity of water used was insufficient) as a black crystalline powder, according to the quantity of iridium which it may contain.

The mother-liquor is to be again placed in a flask and boiled with aqua regia. On cooling, the ammonium iridiochloride crystallises out, and any traces of rhodium and ruthenium which may be present remain in solution. The iridium salt is to be washed with a mixture of 2 parts of saturated solution of sal-ammoniac and 3 parts of water, and may then be regarded as pure.

The treatment by oxalic acid affords iridium free from all traces of ruthenium. The detection of very small quantities of ruthenium in presence of much iridium has been hitherto an impossibility, or could only be effected by Claus's method of allowing a small quantity of water acidulated by hydrochloric acid to remain in contact with the ammonium iridiochloride for some days. The ruthenium salt, by its

superior solubility, tended to dissolve first; hence the acidulated water, after standing, contained ruthenium in larger relative proportion than the original crystals; the ruthenium reactions were more marked, and if it was present, and in sufficient quantity, it could be detected by potassium sulphocyanide, or, better, to an experienced eye, by lead acetate. The objections to this method are sufficiently obvious.

The treatment of solutions (B) and (C) presents no difficulty. With (B) the best plan is to place the solution aside in a beaker covered with filter-paper for some time. Treated in this way, the bichloride gradually crystallises out, and by recrystallisations may be obtained in a state of perfect purity.

Solution (C) is to be evaporated to dryness, and reduced to an impalpable powder. It is then to be thrown upon a filter, and thoroughly washed with a perfectly saturated solution of sal-ammoniac. The ruthenium bichloride is thus carried through, with perhaps a trace of rhodium sesquichloride, from which, however, it is easily freed by crystallisation. From the residue, the rhodium-ammonium sesquichloride is removed by a dilute solution of sal-ammoniac. It is perfectly free from the iridium, which is left behind.

In connection with this separation, Lea makes a remark which, though of special reference to this particular case, is also applicable to all those cases in which the double chlorides of the platinum metals are to be separated by their various solubilities in solution of sal-ammoniac. This most valuable process—for which we are indebted, as for so much else, to Claus, whose untiring labours have made him the father of this department of chemistry—requires to be applied with some attention to minutiæ.

The crystalline matter must be reduced to the finest powder, and after being thrown upon the filter, it must be washed continuously until the separation is effected. Any interruption of the washing is followed by more or less crystallisation of sal-ammoniac through the material, which precludes an effectual separation. The same material which in a state of coarse powder will hardly yield up enough ruthenium bichloride to colour the sal-ammoniac solution, will, when thoroughly pulverised, give an almost opaque blood-red filtrate.

Solution (C) may be subjected to a different treatment from the foregoing, and oxalic acid may be used to effect the separation. The solution is to be brought to the boiling-point, and oxalic acid added as long as effervescence is produced. The iridium bichloride is thereby reduced, the ruthenium bichloride and the rhodium sesquichloride are not affected. Sal-ammoniac is then to be dissolved in the solution to thorough saturation. By standing and repose the double rhodium and ammonium chloride separates out. The solution is then reoxidised by boiling with aqua regia; by standing for some days in a cool place, the ammonium iridiochloride crystallises out, and the supernatant solution

contains the double ammonium chloride and ruthenium bichloride, which may be rendered pure by several recrystallisations.

For purifying the double iridium and ammonium chloride, the oxalic process is decidedly the best. It is simpler and easier, and there is the further advantage that the platinum is left in the condition of double chloride, whereas when the usual method of treating with aqueous sulphuretted hydrogen is used, the platinum is apt to be converted partly into sulphide, together with any traces of rhodium and ruthenium which may be present. When oxalic acid is used, the platinum remains behind as a reddish powder, containing some iridium, from which it may be freed in the ordinary manner, if it is present in quantity sufficient to be worth working.

For treating a mixture such as that which is here designated as (c), containing no platinum, and only ruthenium present in the form of ammonium rutheniochloride, it is unnecessary to apply reducing agents, and the first method described is the best. But if it be proposed to effect the separation by the reduction of the iridium compound, the method here described is preferable to that based on the use of sulphuretted hydrogen even in this case.

The action of oxalic acid on the platinum metals is interesting; its reducing effect upon iridium bichloride at the boiling-point is immediate. On ruthenium bichloride it seems to have no effect whatever, and they may be boiled together for a length of time without sensible result. In a trial made with ruthenium and ammonium sesquichloride, the oxalic acid was boiled with the metallic salt for a considerable time without any apparent effect becoming visible, but by long-continued boiling a gradual precipitation took place. When ammonium platinochloride was boiled with oxalic acid, no effect was produced for a considerable time, but gradually the platinum salt diminished in quantity, and the liquid acquired a stronger yellow colour, perhaps owing to formation of soluble platinic oxalate. This process will not, however, furnish an easy and convenient method of purifying commercial platinum from the iridium always found in it, as the reduction of very small quantities of double iridium and ammonium chloride in the presence of a large proportion of the corresponding platinum salt is difficult and slow, and the platinum salt itself is evidently attacked.

(*D*) **Wolcott Gibbs's Process** for the analysis of platinum ores is as follows:—The metals are first obtained in a nitrohydrochloric solution, and the liquid is then evaporated to dryness with an excess of sodium chloride. The mass of double chlorides obtained as already mentioned is to be rubbed to a fine powder, introduced into a deep porcelain evaporating-dish, and mixed with 4 or 5 times its volume of boiling water. A solution of sodium nitrite is then to be added in small quantities at a time, the solution being continually stirred, and occasionally neutralised by addition of sodium carbonate. The liquid soon becomes olive-green, and the greater part of the

mass dissolves ; it is advantageous, when the quantity of the mixed chlorides is large, to pour off the liquid as soon as it appears saturated, and to repeat the operation with a fresh quantity of water. The undissolved mass, which consists chiefly of the impurities of the ore, when these have not been removed before the process of oxidation, is then to be thrown upon a filter and washed with boiling water until the washings are colourless. By keeping the solution somewhat alkaline, the whole of the iron remains upon the filter as sesquioxide, with other impurities. The filtrate contains iridium and rhodium as sesquichlorides, ruthenium partly as bichloride and partly as protochloride, platinum as bichloride. When the operations already mentioned have been well performed, no determinable quantities of osmium and palladium are present. On cooling, the greater part of the platinum is deposited as potassium platinochloride mixed with a little of the corresponding iridium salt, and is to be separated by pouring off the olive-green supernatant liquid. The quantity of the alkaline nitrite to be added in this process need not exceed half of the weight of the mass of double chlorides, but with a little experience it will be found unnecessary to weigh the nitrite added, the process of the reduction of the potassium iridiochloride being evident to the eye.

To the filtrate a solution of sodium nitrite is to be added, and the whole boiled until the liquid assumes a clear orange colour. Sodium nitrite should be used in this process, because the resulting double iridium and sodium nitrite is easily decomposed by boiling with hydrochloric acid, which is not the case with the potassium salt. When potassium nitrite is used, a small quantity of the white insoluble double salt already mentioned is usually formed and renders the solution turbid.

To the clear yellow, or orange-yellow, boiling solution, sodium sulphide is to be added until a portion of the dark brown precipitate of the ruthenium, rhodium, and platinum sulphides is dissolved with a brown-yellow colour, and an excess of the alkaline sulphide is, consequently, present. The liquid is then to be allowed to cool, and treated with dilute hydrochloric acid, until a distinctly acid reaction is produced. In this manner the whole of the platinum, ruthenium, and rhodium present in the solution are thrown down as insoluble sulphides. After complete subsidence, the sulphides are to be thrown on a double filter and thoroughly and continuously washed with boiling water. When the operation is carefully performed, the filtrate and washings contain only iridium. It is best to neutralise this solution with sodium carbonate, boil a second time with a little additional sodium nitrite, and treat as before with sodium sulphide and hydrochloric acid. In this manner very small additional quantities of the platinum, ruthenium, and rhodium sulphides may sometimes be separated.

The filtrate is to be evaporated and boiled with an excess of strong

hydrochloric acid, which completely decomposes the double iridium and sodium nitrite, yielding the sodium iridiochloride, which is very soluble in water. An excess of a pure and strong solution of ammonium chloride is then to be added, the whole evaporated to dryness, and the dry mass washed with cold water, and then with a cold and strong solution of sal-ammoniac. There remains a mass of pure ammonium iridiochloride, which may be advantageously rubbed to a fine powder, dissolved in boiling water, and allowed to crystallise. The resulting salt is chemically pure, and the crystals possess an extraordinary beauty and lustre. The mass of mixed sulphides, together with the filter, are to be treated with strong hydrochloric acid, and nitric acid added in small portions at a time. By the aid of a gentle heat the sulphides are readily oxidised and dissolved. After sufficient dilution, the liquid is to be filtered, the pulp of undestroyed filter-paper washed, the filtrate evaporated to dryness, the dry mass digested with concentrated hydrochloric acid, and again evaporated to dryness. The dry mass of chlorides and sulphates is to be redissolved in water, and the platinum, ruthenium, and rhodium precipitated by metallic zinc, after addition of hydrochloric acid. The finely divided metals, after filtration, washing, and drying, are then to be mixed with potassium chloride, and treated with dry chlorine at a dull red heat. In this manner the metals are again brought into the form of double chlorides, and the difficulties which arise from the presence of the sulphates are avoided.

The mixed double chlorides are to be boiled with potassium nitrite, evaporated to dryness, and the soluble ruthenium and potassium nitrites dissolved out with absolute alcohol in the manner described in speaking of the separation of platinum from ruthenium (page 476, *B*). The ruthenium may then be obtained pure by converting it into the double mercury and ruthendiamin chloride (page 477).

The mass undissolved by alcohol consists of potassium platinochloride mixed with both the soluble and the insoluble double rhodium and potassium nitrites. It is to be boiled with dilute hydrochloric acid, neutralised with potassium carbonate, again evaporated to dryness after the addition of potassium nitrite, and again boiled with absolute alcohol, which sometimes dissolves a trace of ruthenium. The undissolved mass is then to be treated with hot water, and again evaporated to dryness, and this process repeated two or three times, so as to convert the whole of the soluble rhodium salt into the insoluble salt. The potassium platinochloride may then, after reducing the mass to fine powder, be dissolved out by boiling water, when the rhodium salt remains pure, as a fine orange-yellow crystalline powder. This may be dissolved in hot hydrochloric acid, evaporated to dryness with an excess of pure ammonium chloride, and ignited in a clean porcelain crucible, when pure metallic rhodium remains as a porous mass mixed with potassium chloride.

When the process above described has been carefully conducted, and especially when the quantity of sodium nitrite added is sufficient, the mixed sulphides will be found to contain only platinum, rhodium, and ruthenium, and to be free from iridium. If, however, after converting the sulphides into double chlorides in the manner pointed out, iridium is found to be present, the process to be pursued is still the same so far as regards the separation of the ruthenium; the remaining mass is then to be dissolved in water with addition of hydrochloric acid, the solution nearly neutralised with ammonia, the platinum and rhodium separated as sulphides in the manner already pointed out, brought into the form of double chlorides, and then separated by potassium nitrite as before.

For the complete success of this method it is absolutely necessary that the mass of mixed double chlorides be freed from osmium as completely as possible. This may be done in the usual manner by repeated evaporation with nitrohydrochloric acid.

Separation of the Metals of the Platinum Group

The methods at present in use for the extraction of platinum and iridium leave residues of which the analysis is of great interest, as they are the sole source of a certain number of the rare metals, viz. osmium, ruthenium, palladium, and rhodium, besides the iridium and platinum they still contain. The following method, devised by Leidié,[1] based on the properties of the double alkaline nitrites of these metals, enables us to effect their separation much more easily than by the dry methods of H. Sainte-Claire Deville and Debray.

I. **Elimination of the Foreign Metals, and Transformation of the Metals of the Platinum Group into Double Alkaline Nitrites.**—The residues of the platinum group are roasted at a dull red heat with free access of air, and are then reduced by hydrogen; the residue is washed first with water and then with dilute hydrochloric acid; finally it is again reduced by hydrogen. This preliminary operation is for the purpose of destroying the compounds in which the residual metals occur, bringing them into the metallic state, and eliminating the soluble alkaline salts, as well as the greater part of the iron and zinc which may have been introduced during the course of the operations.

The metallic matter is then mixed with twice its weight of fused, powdered chloride of sodium, and the mixture is heated in a current of dry chlorine to a dull red heat; the products of volatilisation, which might get lost, are condensed by means of a suitable apparatus.

In this manner all the metals are transformed into chlorides or double chlorides of more or less solubility. Both the fixed and volatilised products are treated with water containing a little hydrochloric acid and filtered; if necessary, on account of the unattacked residue

[1] *Chemical News*, Jan. 11, 1901.

being too great, the operation is repeated. By using a quantity of water equal to 20 or 25 times the weight of the metal, but little of the chloride of lead is dissolved, and nearly the whole of the chloride of silver is removed by means of the chloride of sodium.

The solution, which must be partially neutralised with carbonate of sodium, is brought nearly to boiling-point, and gradually treated with nitrite of sodium until it becomes neutral to litmus; at this moment carbonate of sodium must be further added until the precipitate no longer increases; it is then boiled for a few moments, allowed to cool, and filtered. The nitrite of sodium has precipitated the iron in the state of sesquioxide, and the gold in the metallic state; the carbonate of sodium has precipitated in the form of carbonates all the other metals, such as lead, silver, zinc, tin, bismuth, copper, &c., which were originally in the mineral or which may have been introduced accidentally during the series of operations which this latter has undergone. The metals of the platinum group have remained in solution in the state of soluble double nitrites of sodium, having the following respective formulæ :—

Nitrite of ruthenium and sodium	.	.	$Ru_2(No_2)_6.4NO_2Na$
„ platinum „	.	.	$Pt(NO_2)_2.2NO_2Na$
„ palladium „	.	.	$Pd(NO_2)_2.2NO_2Na$
„ iridium „	.	.	$Ir_2(NO_2)_6.6NO_2Na$
„ rhodium „	.	.	$Rh_2(NO_2)_6.6NO_2Na$

The osmium is present in the form of chloro-osmite, $OsCl_3.3NaCl$.

Osmium, Ruthenium.—The above-mentioned nitrites have the property of not being precipitated either by the alkalies or the alkaline carbonates. Their solution is treated with caustic soda, and a current of chlorine is then passed through; this operation is carried out in a distilling apparatus made of glass, and of which all the parts are connected by ground joints (as for the preparation of perruthenic anhydride), and the volatile products are collected in water containing a little alcohol. The salts of osmium and of ruthenium are thus transformed into peroxides of osmium and of ruthenium, OsO_4 and RuO_4, which are volatile; gentle heat is applied towards the end of the operation to cause them to distil over with the steam; they are reduced by the alcohol to the state of osmium and ruthenium. The mixture of these two bodies is collected and the osmium separated from the ruthenium by H. Sainte-Claire Deville and Debray's method.[1]

Iridium, Rhodium.—The alkaline solution, freed from osmium and ruthenium, is acidulated with hydrochloric acid and boiled; then, to reconvert the chlorides which were formed under the influence of the chlorine into nitrites, nitrite of sodium is added until the solution is neutral; it is then allowed to cool. Chloride of ammonium is then

[1] *Annales de Chimie et de Physique*, [5], vol. lvi. pp. 476, 480.

added almost to saturation point. The iridium and the rhodium are then precipitated in the form of double nitrites of ammonium, $Ir_2(NO_2)_6.6(NO_2.NH_4)$ and $Rh_2(NO_2)_6.6(NO_2.NH_4)$, which are insoluble in solutions of sal-ammoniac. The precipitate is collected after twenty-four hours and treated several times with hot aqua regia, so as to transform it into iridic chloride ($IrCl_4$) and hydrated sesquichloride of rhodium (Rh_2Cl_6). The aqua regia is driven off by evaporation, and the residue taken up with cold water saturated with chlorine. This solution is then saturated with chloride of ammonium.

The iridium is precipitated in the form of chloroiridiate of ammonium; this latter is collected, dried, mixed with its own weight of sea-salt, and heated to 440° to 450° in a current of chlorine. The ammoniacal salt is decomposed, and the iridium remains in the state of chloroiridiate of sodium, soluble in water; the rhodium which might have been entangled with it is found in the form of anhydrous sesquichloride, insoluble in water. The chloroiridiate of sodium is, by double decomposition, again transformed into chloroiridiate of ammonium. This latter, reduced at a red heat in a current of hydrogen, gives iridium.

The solution from which the iridium has been precipitated is evaporated until it crystallises. The crystals of chlororhodite of ammonium ($Rh_2Cl_6.6NH_4Cl$) are separated from those of the chloride of ammonium. The salt of rhodium is dissolved in water, transformed into the double nitrite of sodium, which is then precipitated in the form of double nitrite of ammonium (the salt of iridium, being a little more soluble, will remain in the mother-liquors). This double nitrite is re-transformed by hydrochloric acid into chlororhodite of ammonium, and the latter, by reduction at a red heat in a current of hydrogen, gives rhodium.

Platinum, Palladium.—The solution, freed from iridium and rhodium, now contains only platinum and palladium in the form of double nitrites; it is evaporated to dryness after the addition of hydrochloric acid to transform the nitrites into chlorides.

As the presence of chloride of sodium, which has by this time become fairly considerable, would interfere with the complete precipitation of the platinum, the dry residue is reduced in hydrogen, and the product of the reduction washed in water, so as to leave nothing but the two metals, platinum and palladium, in the metallic form. These are dissolved in aqua regia, the excess of which is driven off by suitable evaporation, and the residue is taken up with water.

As this solution contains platinic chloride, palladic chloride, and sometimes, if the operations have been carelessly performed, *traces* of iridic chloride, and as all three are precipitable by chloride of ammonium, the second metal is transformed into palladous chloride and the third into hydrated sesquichloride of iridium, which are not precipitable. For this purpose their solution, placed in a flask which it nearly fills,

is submitted to the action of a current of carbonic acid gas to drive off the air, then to a current of binoxide of nitrogen which acts as a reducing agent,[1] and finally to a second current of carbonic acid to drive off the binoxide of nitrogen.

The solution is then saturated with chloride of ammonium, the chloroplatinate of ammonium is collected after twenty-four hours, and crystallised two or three times in boiling water; this substance, by reduction at a red heat in a current of hydrogen, gives platinum.

To the mother-liquors mercuric cyanide is added; the palladium is precipitated in the form of palladous cyanide, $PdCy_2$. This latter is decomposed by heat, the palladium is dissolved in nitric acid, the nitrate is transformed into palladous chloride, then into nitrite of palladium and potassium; finally this latter, by the action of hydrochloric acid, is transformed into chloropalladite of potassium, which can be crystallised. This salt is then reduced at a red heat in a current of hydrogen, and the residue, cooled in a current of carbonic acid, is washed with water to remove the chloride of potassium; in this manner palladium is obtained.

The metals thus prepared are in the form of a porous sponge. To obtain them in ingots they must be melted. The osmium and the ruthenium can be melted in Ducretet and Lejeune's electric furnace, in which the operation can be carried out away from contact with the air in an inert atmosphere; the others in a Sainte-Claire Deville and Debray's lime furnace, by means of a blowpipe supplied with coal-gas in the case of platinum and palladium, and with hydrogen for the iridium and rhodium.

The method just described has as its principal advantages, first of all the elimination, from the very commencement, of all foreign materials, the complete volatilisation of the ruthenium by which the iridium obtained by the other methods is always contaminated, and finally the fact that it does not necessitate the installation of special apparatus as in the case of the dry methods.

Attack of Osmide of Iridium

Leidié and Quennessen[2] melt, in a nickel crucible, 10 grammes of hydrate of sodium (previously fused), and into this gradually throw an intimate mixture of 10 grammes of osmide of iridium and 40 grammes of binoxide of sodium; this must be stirred continuously with a nickel spatula, and heated sufficiently to keep the mixture in a semi-fluid condition. The operation should not last more than about

[1] This reducing agent is much to be preferred to those which are generally used, such as sulphurous acid or sulphydric acid. The first gives double sulphites possessing little known properties; the second, sulphides which cause a loss in the returns.

[2] *Chemical News*, July 3, 1903.

half an hour. The addition of soda has for its object the lowering of the fusing-point of the binoxide, and of diminishing considerably the attack on the crucible. The material is run out on a sheet of nickel. When cold it is broken up, and thrown in small portions at a time into a porcelain vessel covered with a funnel, and containing a litre of water; the portion adhering to the crucible is also treated with water. All the liquors are added together, and when cool they are left to stand in decantation flasks with ground stoppers. The clear liquor is decanted, and the insoluble residue taken up with hypochlorite of soda diluted with its own volume of water to dissolve the binoxide of ruthenium which might be formed by decomposition brought about by the water. The wash-waters are added to the original solution.

The solution thus obtained contains all the osmium and ruthenium in the form of osmiate and rutheniate, with the greater portion of the iridium in the form of iridiate. It may contain also traces of gold and palladium, as well as chromium, aluminium, and manganese from the ore, in the form of alkaline salts. The insoluble portion contains the remainder of the iridium, the iron from the ore, and the nickel from the crucible, with sometimes traces of platinum and rhodium.

Separation of Osmium from Ruthenium

The solution is placed in a glass retort, of which the drawn-out neck is fitted into the neck of a flask having a lateral tube, the central tube forming an hydraulic joint; such a flask is similar to the one used for the condensation of peroxide of ruthenium.[1] This flask is followed by two similar ones forming the condensing apparatus. They are all three plunged into iced water, and two-thirds filled with hydrochloric acid diluted with two volumes of water: by grinding all the joints with emery, all loss of condensible vapours is prevented. The first two flasks will probably be sufficient; the third acts as a control. A current of chlorine is passed through the retort, cold at first, then when the liquid commences to give off bubbles of oxygen, it is heated to about 70°. The osmium and ruthenium are transformed into volatile peroxides, OsO_4 and RuO_4, which condense in the flasks, the iridium into sesquichloride, which remains in the retort in solution, thanks to the excess of soda. The contents of the retort should remain alkaline until the end of the distillation, first on account of the action of hydrochloric acid on RuO_4, and afterwards because the chlorine, passing through the cold recipients, gives hydrate of chlorine which obstructs the tubes. (It is this hydrate that Joly must have mistaken for an emulsion of RuO_4.) If by chance the contents of the retort become acid, soda must be added. The end of the operation can be determined by making sure that the drops, which distil over, do not blacken a solution of sulphuretted hydrogen.

[1] Joly, *Encyclopédie Chimique de Fremy*, vol. iii. No. 3, p. 236.

Under the influence of hydrochloric acid, the peroxide RuO_4 is transformed into the sesquichloride Ru_2Cl_6, which is stable; while the peroxide OsO_4 does not undergo any change. This reaction, commencing in the cold, ought to be completed by the action of heat. For this purpose the contents of the three flasks are placed together in a retort, connected with a system of three condensers similar to those in the preceding apparatus. The flasks are plunged into ice, they are filled up to two-thirds, the first with hydrochloric acid diluted with two volumes of water to arrest the incompletely transformed peroxide RuO_4; the two others are filled with a solution of soda at 12 per cent. of NaOH, treated with 2 per cent. of alcohol, to transform the peroxide OsO_4 into osmiate of sodium. The contents of the flask are heated to about 70° while passing a slow current of air. When no more peroxide of ruthenium distils over (the drops distilled should not colour hydrochloric acid brown), the contents of the first condensing flask are returned to the retort, and the flask is filled up to two-thirds with an alkaline alcoholic solution like that in the next two flasks. The distillation is then pushed to its completion—that is to say, until the drops no longer blacken with sulphuretted hydrogen; as a rule, to obtain this result, it is necessary to distil half the contents of the retort. The osmium is then contained entirely in the condensing flasks, in the form of osmiate, and the ruthenium is in the retort in the form of sesquichloride; these two compounds not being volatile are easily determined in subsequent operations.

To make certain that the separation of the Os and Ru is complete, proceed in the following manner:—A solution containing OsO_4 and RuO_4 becomes brown under the influence of hydrochloric acid, owing to the formation of brown Ru_2Cl_6. A solution containing Ru_2Cl_6 and OsO_4, treated with carbonate of baryta, freshly prepared and free from baryta, gives a precipitate of Ru_2O_3; the solution, freed from the chloride of barium formed by means of So_4Na_2, should not become violet in the presence of an alcoholic solution of soda (formation of violet osmiate).

Separation of Iridium

The contents of the retort from which the osmium and ruthenium have been driven in the first distillation, are acidulated with hydrochloric acid. The residue, insoluble in water, resulting from the attack of the osmide by Na_2O_2, is dissolved in hot dilute hydrochloric acid; this residue is easily soluble, while the other methods of attack (potash and nitrate of potash, for example) give a mass which is very difficult to dissolve, even with aqua regia. If any crystals of unattacked osmide are found, owing to their being insufficiently finely divided they must be collected and subtracted from the original weight. The two solutions are united; the solution then contains all the iridium, as well as the iron in the ore, and the nickel from the crucible; it may

contain traces of gold also, as well as rhodium and platinum, and any other foreign metal associated with the osmide, such as chromium, aluminium, silicon, manganese, copper, &c. The solution is heated, and to precipitate all the foreign metals, it is treated successively with nitrite of sodium and carbonate of sodium, following the instructions given by Leidié *à propos* of the general method for the separation of the metals of the platinum group.[1] Nothing remains in solution but the double nitrite of iridium and sodium ; this is transformed into chloroiridiate by warm hydrochloric acid. Then, as the large amount of chloride of sodium present in the solution might be prejudicial, either to the precipitation of the chloroiridiate by chloride of ammonium, or to the precipitation of the iridium by magnesium, the cooled solution must be saturated with hydrochloric acid gas. The precipitated chloride of sodium is drained and washed with hydrochloric acid ; the solutions, which contain only chloroiridiate of sodium with a little chloride of sodium, are added together.

Estimation of the Metals

Osmium.—The contents of the flasks containing the osmiate of sodium are added together (if they are not decidedly violet they must be heated gently), and strips of aluminium are plunged in ; the osmium is deposited in the metallic form, while the aluminium dissolves in the soda. Care must be taken not to add too much aluminium at first, as the alumina formed, not finding a sufficient quantity of soda to enable it to go into solution, would precipitate an aluminate which is very difficultly soluble both in acids and in alkalies. When the solution is once decolourised, the precipitated osmium, which is very dense, is washed by decantation, first with water to remove the aluminate of soda, and then with 5 per cent. sulphuric acid to remove the remaining excess of aluminium, along with the iron accompanying this metal.

This osmium is thrown on an asbestos filter connected with a filter-pump and well washed ; the filter must have been treated first with 20 per cent. sulphuric acid, then washed, dried, calcined at a red heat, and weighed in a closed tube. The osmium is dried in a bell-glass filled with hydrogen, then heated to dull redness, and cooled in a current of this gas ; the hydrogen is only driven off by the carbonic acid when the whole has been cooled, as the latter gas oxidises the osmium when hot. The filter is weighed again in a closed tube.

As a check, the osmium may be driven off in the form of the peroxide OsO_4 by heating the filter to redness in a current of oxygen, and then weighing it again.

Ruthenium.—The hydrochloric solution containing the sesquichloride Ru_2Cl_6 is evaporated gently to a syrupy consistence, so as to

[1] See *ante*, p. 456.

drive off the excess of acid. The residue is taken up with 50 or 60 cubic centimetres of water, and a few fragments of magnesium added gradually; the solution becomes clear and takes a blue tint; this reaction is characteristic of ruthenium, and was wrongly attributed to osmium by Fischer, the latter being completely decolourised. The solution is then decanted, and the powder is washed with 5 per cent. sulphuric acid, so as to remove the excess of magnesium. Throw on a filter, wash with water, dry, and after incinerating the filter at the lowest possible temperature, heat the whole in hydrogen to a red heat, then allow to cool in carbonic acid, and weigh.

Iridium.—The solution containing the chloroiridiate of sodium is evaporated to drive off the large excess of hydrochloric acid present. The residue is taken up with water, and diluted to a volume of 500 cubic centimetres. From this we take 50 or 100 cubic centimetres, according to the probable proportion of iridium present, and add gradually some fragments of magnesium until it is completely decolourised. The powder is washed with 5 per cent. sulphuric acid, then with water, and dried; after the incineration of the filter, it is heated to redness in hydrogen, cooled in a current of carbonic acid, and weighed.

In all these operations we use sulphuric acid rather than hydrochloric acid, which would dissolve a portion of the precious metal.

Separation of Palladium from other Metals by Means of Hydrazine

P. Jannasch and W. Bettges[1] take a weighed quantity of the metal dissolved in about 5 cubic centimetres of aqua regia, warmed for a short time on the water-bath, covered, and allowed to stand for some minutes. It is then heated more strongly, and finally evaporated to dryness. The residue is taken up with a little water to which about 20 drops of dilute hydrochloric acid have been added. It readily dissolves on warming on the water-bath, and the solution is then made up to about 120 cubic centimetres. To determine the metal, the faintly acid solution is heated almost to boiling, and the palladium is precipitated with 1 gramme of hydrazine sulphate (dissolved in about 20 cubic centimetres of water). The metal begins to separate out at once with energetic evolution of nitrogen, and after warming for twenty minutes the reaction is complete. The fine black precipitate first obtained collects to form a spongy mass, which is washed and dried at 120° to 130° in a weighed asbestos ignition tube, and then reduced in a current of hydrogen. The palladium thus obtained is a dull silver-grey mass. The precipitation of palladium in acid solution by means of hydrazine may be used to separate the metal from potassium, sodium, magnesium, zinc, and iron.

[1] *Chemical News*, July 22, 1904.

Purification of Rhodium

Purification of rhodium is obtained by the reduction of the ammonio-chloride by means of hydrogen. The chloride, prepared according to the method already described by S. M. Jörgensen,[1] is not chemically pure, but contains a little iridium. The purification is easily effected by dissolving 10 grammes of the salt in 250 cubic centimetres of HNO_3 (D=1·40), and heating on the water-bath until a small quantity diluted with water does not become cloudy with nitrate of silver. On cooling, we obtain the chloropentammonic nitrate. Dilute with its own volume of water, filter, and wash with HNO_3 (1 vol. of acid, D=1·4+2 vols. of water), then with alcohol. The salt obtained is dissolved in water and filtered, and the filtrate is collected in concentrated hydrochloric acid. The precipitated chloride, washed with dilute hydrochloric acid, then with alcohol after a second treatment with nitric acid, is dissolved in dilute soda and then precipitated by boiling with hydrochloric acid. Dissolve in boiling water and precipitate again with hydrochloric acid. After three solutions and reprecipitations the precipitate is free from soda and from HNO_3.

Electrolytic Precipitation of Platinum [2]

(*A*) Classen finds that the compounds of platinum are very easily decomposed by the galvanic current, when the metal is deposited at the negative electrode. If the current of two Bunsen elements arranged parallel are used for electrolysis, the reduction is so rapid that the platinum is thrown down as platinum black, in which state it cannot be determined. If a single Bunsen element is used, the metal is separated in so dense a state that it cannot be distinguished from forged platinum. In this manner it is easily practicable to deposit uniformly large quantities of platinum upon the platinum capsule used as a negative electrode, without altering its external appearance.

For the determination of platinum in its salts, the solution may be either slightly acidulated with hydrochloric or sulphuric acid, or mixed with ammonium or potassium oxalate, and electrolysed at a gentle heat. The deposition of the platinum is effected in a relatively short time; *e.g.* 0·5 gramme platinum was deposited in five hours from a solution of platinum chloride diluted to 200 c.c. and containing 0·6 gramme platinum.

(*B*) If the quantity of platinum to be deposited amounts to about 0·4 gramme, according to the results reached in the Munich laboratory, the solution of the platinum salt mixed with 2 per cent. by volume of dilute sulphuric acid (1 : 5) is heated and electrolysed with a current

[1] *Journ. für prakt. Chem.* [2], vol. xxvii. p. 435.

[2] For details of operation see chapter on Electrolytic Analysis.

of N.D. 100=0·01 to 0·03. The deposition is completed in about five hours.

(*C*) E. F. Smith adds to the solution of platinum 30 c.c. of sodium diphosphate, 5 c.c. phosphoric acid, and dilutes with water to 150 c.c. With a current giving 0·2 to 0·8 c.c. (maximum) of detonating gas per minute the platinum is deposited upon a platinum cone previously coated with copper.

Iridium is not reduced from its solutions by the current of a Bunsen element. This behaviour may be applied to the quantitative separation of platinum from iridium.

Preparation of Platinum Chloride from Residues

The concentrated alcoholic solutions are reduced, at a boiling temperature, by a mixture of soda solution and glycerin or sugar. Platino-potassium chloride is also completely reduced if gradually added to the boiling mixture, and if sufficient soda is present. The precipitate of platinum black is washed by decantation in a porcelain capsule till all the sulphuric acid and potassium are eliminated, dried, ignited and digested at a gentle heat in hydrochloric acid to extract iron, &c., and then sufficient nitric acid is gradually added. The solution is evaporated down at a gentle heat; the platinous chloride is converted into platinic chloride by the addition of fuming hydrochloric acid and a little nitric acid; the excess of the latter is expelled by the repeated addition of water and hydrochloric acid, and evaporation. The presence of platinous chloride is detrimental for the estimation of potassium, rendering the results too high, while nitric acid occasions an error in the contrary direction. Traces of iridium have little effect on the accuracy of the analysis. The solubility of platino-potassic chloride in alcohol is 1 part in 42,600 absolute, 1 part in 37,300 at 96 per cent., and 1 in 26,400 at 80 per cent. Platino-sodium chloride is soluble in boiling water in almost every proportion. Platino-barium chloride has the important property of being more or less completely decomposed into platinum chloride and barium chloride.

Mending Platinum Crucibles.—T. Garoide gives the following simple method:—I had a platinum dish, which had a small hole on the side, near the bottom, and the dish was consequently useless for most purposes. I was about to consign it to the old platinum, when it struck me that this metal being 'weldable' I might manage to repair it. Having already a mould for this dish, made of plaster of Paris, and not of wood, this served admirably as an anvil. I then cut a piece of moderately thin platinum foil, about 3 millimetres diameter, and rubbed this and the part of the dish where the hole was with sea-sand until perfectly bright and clean. Having fixed the dish and its mould in an upright position, I laid the platinum foil over the hole, and directed the flame from a table blowpipe upon the spot. A pair of

scissors served as a hammer, and by gently tapping with these the two pieces of platinum united perfectly, and made so neat a joint that one would scarcely observe it unless one's attention was called to it. I have used the dish for all kinds of purposes since, and the union is as good as ever. In the above operation the plaster-of-Paris mould, although very dry, was split and cracked by the heat in all directions, nevertheless it had sufficient cohesion to last until the operation was concluded. I find that platinum wires are very easily joined in this way.

PALLADIUM

Test for the Presence of Palladium

Carey Lea proposes sodium thiosulphate as a delicate test for many of the platinum metals. For detecting the presence of palladium he proceeds as follows :—Place a solution of sodium thiosulphate in a test-tube with a little liquid ammonia, and add a drop of the palladium solution, so that it shall communicate a pale lemon colour only to the liquid. By boiling, this rapidly darkens to a wine-brown shade, increasing in intensity until it finally appears black. Dilution, however, shows that this results from its intensity only; the diluted liquid is free from turbidity and has a warm-brown tint.

Electrolytic Separation of Palladium [1]

(*A*) The determination of palladium is effected by Classen in a manner analogous to that of platinum. If we use the current of a single Bunsen element, we obtain the palladium in a fine metallic state.

(*B*) According to E. F. Smith, palladium can be determined in the manner directed for platinum.

Separation of Palladium from Copper

Saturate the solution containing these metals with sulphurous acid gas and add a solution of potassium sulphocyanide. This has no action on the palladium, while it completely precipitates the copper in the form of a white sub-sulphocyanide.

IRIDIUM

Separation of Iridium from Platinum

(*A*) The following process for separating these metals was proposed by Wolcott Gibbs :—The iridium is, in the first place, to be brought into the form of bichloride, by means of a current of chlorine or by nitric acid, and the two metals are then to be precipitated together as

[1] For details of operation see chapter on Electrolytic Analysis.

potassium double chlorides, by the addition of a concentrated solution of potassium chloride. The colour of the mixed salts varies from orange to almost black, according to the quantity of iridium present. The mass of crystals is to be rubbed fine in an unglazed porcelain mortar, and boiling water added in the proportion of three volumes of water to one of salt. A dilute solution of potassium nitrite is then to be added until the liquid becomes deep olive-green, sodium carbonate being thrown in from time to time in quantity sufficient to prevent the solution from becoming strongly acid. The iridium is instantly reduced to sesquichloride, while the platinum salt remains as a reddish-orange powder. The deep olive-green solution is to be poured off, and the undissolved mass treated a second time with hot water and nitrite. This process must be repeated as long as the liquid remains olive-green. The mixed solutions on cooling, or after evaporation, deposit a beautiful mass of crystals of the double potassium chloride and iridium sesquichloride. By re-solution and repeated crystallisation, the iridium salt may be obtained perfectly free from platinum. The undissolved mass and the mother-liquors from the iridium salt contain a large quantity of platinum with a comparatively small quantity of iridium. When the absolute quantity of platinum salt is not very large, it may be dissolved in boiling water, a small quantity of alkaline nitrite added, and the solution allowed to crystallise; the resulting potassium chloroplatinate contains only a trace of iridium.

This process gives satisfactory results when carefully executed, but requires attention to two points. In the first place the alkaline nitrite must be added in quantity just sufficient to reduce the iridium from bichloride to sesquichloride, but not so as to produce further chemical changes by the formation of the double iridium and potassium nitrite or sodium; with a very little experience this is easily managed. In consequence of the facility with which the double iridium and sodium nitrite is decomposed by boiling with hydrochloric acid into the double chloride, $IrCl_2,NaCl$, it is better to use sodium nitrite in the above process, because, in case an excess of nitrite is used, the mixed solution of double chloride and double nitrite can easily be brought to the form of the double chloride, $Ir_2Cl_3,3NaCl$, by boiling with hydrochloric acid, neutralising with sodium carbonate, and then reducing the iridium to sesquichloride by cautiously adding a very dilute solution of sodium nitrite.

In the second place, it may happen, as in working with crude platinum solutions obtained not from osmiridium but from platinum ores, that the quantity of platinum is very large when compared with that of iridium. The process applies equally well to this case as far as the iridium is concerned, but it is difficult and troublesome to recrystallise large quantities of a salt so insoluble as potassium platinochloride, and small quantities of the corresponding iridium salt are difficult to remove.

(*B*) The following process can be recommended for giving chemically pure iridium when platinum is the only other metal present :— The greater portion of the platinum is first to be separated in the manner above pointed out. The solution of double iridium and sodium chloride, $Ir_2Cl_3,3NaCl$, is then to be filtered, an excess of sodium nitrite added, and the solution boiled until it assumes a clear orange-yellow colour. To the boiling solution sodium sulphide is added drop by drop as long as this produces a cloudiness, and until a small quantity of the precipitated platinum sulphide is redissolved. Dilute hydrochloric acid is then to be added cautiously until the liquid, previously allowed to become cold, is distinctly though faintly acid, when it is to be filtered and the platinum sulphide in the filter washed continuously with hot water. The filtrate is then to be boiled with hydrochloric acid in excess, and the resulting sodium iridiochloride evaporated, precipitated by a cold and strong solution of sal-ammoniac, and washed with the same. This salt, on ignition, yields pure iridium if the operation has been well conducted. It is, however, in all cases advisable, after separating the platinum sulphide by filtration, to neutralise the filtrate with sodium carbonate, boil a second time with a little additional sodium nitrite, and then add sodium sulphide and proceed as before. In this manner every trace of platinum is removed, and the resulting iridium salt is chemically pure.

Electrolytic Separation of Iridium from Platinum [1]

According to Classen, platinum can be deposited as such by means of a very weak current in a solution acidified with hydrochloric acid. This behaviour serves for its separation from iridium. If in the circuit of a battery consisting of 2 or 3 Meidinger elements or of a single Bunsen element we introduce the acidified solution of platinum and iridium, the platinum is deposited without any trace of iridium.

Separation of Iridium from Rhodium

(*A*) Iridium may be approximately separated from rhodium by the process recommended by Claus, which consists in taking advantage of the solubility of the double rhodium and ammonium chloride in moderately strong solutions of ammonium chloride, in which the ammonium iridiochloride is nearly insoluble. This method is difficult of application when the quantity of rhodium is small, and is at best tedious and unsatisfactory.

(*B*) A better method is the following :—To the solution containing the two metals, sodium nitrite is to be added in excess, together with a sufficient quantity of sodium carbonate to keep the liquid neutral or alkaline ; the whole is then to be boiled until the solution assumes a clear orange-yellow or orange colour. If a green tint should be

[1] For details of operation see chapter on Electrolytic Analysis.

perceptible, more sodium nitrite must be added and the solution again boiled. Both iridium and rhodium are converted into soluble double nitrites. A solution of sodium sulphide is then to be added in slight excess, the liquid rendered slightly acid, filtered, and the dark brown rhodium sulphide thoroughly washed. The filtrate is perfectly free from rhodium. This is boiled with excess of hydrochloric acid, evaporated, precipitated with sal-ammoniac, and treated as described in the method of preparing pure iridium given above. The rhodium sulphide, together with the filter, is to be treated with strong hydrochloric acid, and sal-ammoniac added in quantity sufficient to form ammonium rhodiochloride. Nitric acid is to be added from time to time in small quantities, until, with the aid of heat, the whole of the rhodium sulphide is oxidised and dissolved. The liquid is then to be filtered, the filter well washed, and the filtrate and washings evaporated to dryness on a water-bath, when, after washing out the soluble salts with a strong solution of sal-ammoniac, the double rhodium and ammonium chloride is left behind. This is insoluble in a cold saturated solution of sal-ammoniac, in which it may be washed once or twice to remove alkaline salts and any traces of iridium which may be present as sulphate. The rhodium salt is then to be purified by crystallisation, or converted into the chloride of Claus's rhodium-ammonium base by evaporation on a water-bath with a solution of ammonia. Iridium sulphate does not give a basic compound under these circumstances. The chloride is then to be further purified by crystallisation.

OSMIUM

Reduction of Osmic Acid

A solution of osmic acid on addition of potassium nitrite is reduced to osmious acid, which unites with the alkali, forming the well-known beautiful red salt. The solution may be evaporated to dryness without decomposition. The nitrite may, therefore, be added with great advantage when solutions containing free osmic acid are to be evaporated, or even transferred from one vessel to another. No other reducing agent answers the same purpose, as the osmium is obtained at once in a very convenient form for preservation. When a solution of osmic acid, to which potassium nitrite has been added, is evaporated sufficiently and then allowed to cool, beautiful garnet-red octahedral crystals of potassium osmite separate.

These should be dried over sulphuric acid, and not in contact with paper or organic matter, which partly reduces the osmious acid to the brown osmium sesquioxide. Potassium nitrite exerts no sensible action when boiled with a solution of potassium osmiochloride; any salt which may be formed is very soluble in water.

Separation of Osmium from Iridium (Analysis of Osmiridium)

(*A*) **Wöhler's Method** of resolving osmiridium consists in passing moist chlorine over the ore mixed with common salt and heated to dull redness in a glass or porcelain tube. This method is invaluable in analysis, and gives excellent results in working the ore upon a small scale. In all cases, however, several repetitions of the process are necessary for complete resolution or reduction to a soluble form. On the other hand, it can scarcely be doubted that this method could be advantageously employed upon the large scale, if vessels of porcelain of large size and of a proper shape could be obtained. Such vessels might be constructed in the form of long and flattened ellipsoids, furnished at each extremity with wide tubes several inches in length, and would be of great utility in various chemical processes. No process of fusion with oxidising agents compares with Wöhler's method in point of elegance, as no iron or other impurities afterwards to be removed are introduced by the process itself.

(*B*) **Fritzsche and Struve's Process** is to treat the ore with a mixture of equal parts of potassium hydrate and chlorate, by which a more or less complete oxidation is effected, without any sensible evolution of osmic acid. The temperature required in this process is not high, but large vessels must be employed, as the mixture froths very much at first. This process does not appear to possess any sensible advantage over that of Claus, which is, moreover, less expensive, and can be carried out with smaller vessels.

(*C*) **Claus's Method** of resolving the ore consists in fusing for an hour, at a red heat, a mixture of 1 part of ore with 1 part of caustic potash and 2 of saltpetre. The fused mass is to be poured out upon a stone, allowed to cool, broken into small pieces or powdered, and then introduced into a flask, which is to be filled with cold water and allowed to stand for twenty-four hours. The clear deep orange-red solution of potassium osmiate and rutheniate is then to be drawn off by means of a syphon, and the black mass remaining again washed in the same manner. The finely divided oxidised portion of the insoluble matter may now be separated from the unattacked ore by diffusion in water and pouring off, after the subsidence of the heavier ore. The unattacked ore is then to be fused a second time with potash and saltpetre and treated as before. Claus asserts that he has been able in this manner to resolve the Siberian osmiridium completely in two operations.

(*D*) **Wolcott Gibbs,** to whom the chemistry of the platinum metals is so greatly indebted, recommends the following process for the analysis of osmiridium :—The ore, which is usually very impure, is in the first place to be fused with 3 times its weight of dry sodium carbonate. The fused mass after cooling is to be treated with

hot water, to remove all the soluble portions, and then the lighter portions are to be separated by washing from the heavy unattacked ore. In this manner the greater part of the silica and other impurities present may be removed. A previous purification of this kind is not indispensable, and may be omitted altogether when the ore is in plates or large grains, but it is very desirable when the ore is in fine powder, and greatly facilitates the subsequent action of the oxidising mixture. By cutting off the top of a mercury bottle a wrought-iron crucible is obtained, in which 600 grammes of osmiridium may be fused at one operation with potash and saltpetre as above. There is usually little or no foaming, and if any occur it may easily be checked by stirring with an iron rod. No sensible quantity of osmic acid is given off during the process, which with a little care is entirely free from danger. In this manner 1500 grammes of ore have been worked up in a few hours in three successive operations. The fused mass is to be broken into pieces with a hammer, and put into a clean iron pot. Boiling water, containing about $\frac{1}{10}$ of its volume of strong alcohol, is then to be added, and the whole is to be boiled over an open fire until the fused mass is completely disintegrated. The potassium osmiate is, in this manner, reduced to osmite, while the potassium rutheniate is completely decomposed, the ruthenium being precipitated as a black powder. It is advantageous, after boiling for some time, to pour off the supernatant liquid with the lighter portions of the oxides, and boil a second time with a fresh mixture of alcohol and water. In this manner we obtain a solution of potassium osmite, a large quantity of black oxides, and a heavy black and coarse powder. This last consists chiefly of undecomposed ore, mixed with a small quantity of the iridium oxides, &c., with scales of iron oxide from the crucible, and, if the ore has not been previously purified, with the impurities of the ore itself. The greater specific gravity of this residual mass renders it very easy to pour off from it the mixture of black oxides with the solution of potassium osmite and alkaline salts. This solution with the suspended powder is to be poured into a beaker and allowed to settle. The heavy black powder remaining in the iron pot is then to be perfectly dried over the fire, and fused a second time with potash and saltpetre as before. The fused mass is to be treated exactly as after the first fusion. The heavy portions remaining after this operation may be fused a third time with the oxidising mixture. When, however, the ore has been previously purified by fusion with sodium carbonate or when it was originally in the form of clean scales, the heavy portion remaining after two successive oxidations will be found to consist chiefly of scales of iron oxide.

The solutions containing potassium osmite and alkaline salts are to be carefully drawn off by a syphon from the black oxides which have settled to the bottom of the containing vessels. The oxides may then be washed with hot water containing a little alcohol, and

introduced into a capacious retort. By this process, when carefully executed, no trace of osmic acid escapes—an advantage not to be despised, as the deleterious effects of this body upon the lungs and eyes have not been exaggerated, and too much care cannot be taken to avoid inhaling it.

The solution of alkaline salts contains only a portion of the osmium in the ore. The other portion exists in the mixture of oxide, and must be separated by distillation. For this purpose the retort should be provided with a safety-tube, passing through the tubulure, and with a receiver kept cool, and connected by a wide bent tube with a series of two or three two-necked bottles containing a strong solution of caustic potash with a little alcohol, and also kept cold. All the tubulures and connections must be made perfectly tight. Strong hydrochloric acid is then to be cautiously poured into the retort, through the safety-tube, in small portions at a time. The reaction which ensues is often violent; great heat is evolved, and a portion of the osmic acid distils over immediately, and condenses in the receiver in the form of colourless needles. When a large excess of acid has been added, the action has entirely ceased, and the retort has become cold, heat may be applied by means of a sand-bath. The osmic acid gradually distils over, and condenses in the receiver and in the two-necked bottles. Especial care must be taken that the neck of the retort is not too small at the extremity, as it may otherwise become completely stopped up with the condensed osmic acid. The same applies to the tubes connecting the receivers and two-necked bottles. The distillation should be continued for some time after osmic acid ceases to appear in the neck of the retort; when this has once become hot, the acid condenses and passes into the receiver in the form of oily drops.

When the distillation is finished, the retort is to be allowed to cool, and then separated from the receiver, which is to be immediately closed with a cork. By gently heating the receiver in a water-bath, the contained osmic acid may be driven over into the two-necked bottles, where it condenses in the alkaline solution, and is reduced by the alcohol to potassium osmite. The solution thus obtained may be added to that obtained directly from the fused mass of ore, and on evaporation in a water-bath and cooling, will yield crystals of potassium osmite, the salt being but slightly soluble in strong saline solutions. The mother-liquor from the crystals contains only traces of osmium, and may be thrown away as worthless.

The dissolved portions drawn off from the retort have a very dark brown-red colour. The solution is to be evaporated to dryness, redissolved in hot water and again evaporated, after adding a little hydrochloric acid, and this process repeated till no smell of osmic acid can be perceived. A cold and saturated solution of potassium chloride is then to be added in large excess. This dissolves the iron and palladium chlorides which may be present, leaving platinum, iridium, rhodium,

and ruthenium as double chlorides, insoluble in a strong solution of the alkaline chloride.

The undissolved mass is to be well washed with a saturated solution of potassium chloride, which is preferable to sal-ammoniac. In this manner nearly the whole of the iron and palladium may be removed, while any insoluble impurities contained in the ore remain with the mixed double chlorides.

For the separation of osmium from the other metals of the group, the best plan seems to be the one which is universally employed—namely, the volatilisation of the osmium in the form of osmic acid.

RHODIUM

Separation of Rhodium from Platinum

(*A*) The usual method of approximately separating these metals is, to convert them into their potassium or ammonium double chlorides, and then to carefully wash out the rhodium salt by small successive portions of cold water, or, better, by a moderately concentrated solution of potassium or ammonium chloride. By recrystallising the platinum and rhodium salts respectively, they may be obtained in a state of purity, since they are not isomorphous.

(*B*) To obtain rhodium absolutely free from platinum, Wolcott Gibbs advises to convert the two metals into the ammonium double chlorides, separate the rhodium salt as completely as possible by washing with a solution of sal-ammoniac, and then evaporate the double rhodium and ammonium chloride with a solution of ammonia. In this manner the rhodium is converted into the chloride of the ammonia-rhodium base, discovered by Claus, while the platinum forms no well-defined or crystallisable compound. The chloride of Claus's base may then be purified by repeated crystallisation.

RUTHENIUM

Preparation of Ruthenium from Iridium Osmide (Osmiridium)

(*A*) Osmiridium almost always contains ruthenium, the amount of the latter metal increasing as that of the iridium decreases. The following process is the one recommended by Dr. Claus, the discoverer of ruthenium, for preparing this metal.

Osmiridium is melted in the ordinary way with nitre and caustic potash, and moistened with water; then nearly neutralise with sulphuric acid, in order to precipitate the metallic acids in solution, always leaving the liquid with a slight alkaline reaction; add alcohol and boil. Throw the mixture on a filter, and carefully wash in order

to free it as far as possible from potassium salts. The black metallic powder thus obtained still contains sufficient potassium in the state of acid potassium iridiate to convert the greater portion of the iridium into double iridic chloride during the subsequent solution of the metallic powder. For this reason evaporate to a considerable extent the aqua regia solution separated from the powder until all the osmium is disengaged as osmic acid; then, if left to cool, most of the iridium is deposited in the state of potassium iridiochloride, and the liquid contains all the ruthenium in a much greater degree of concentration, although always associated with some iridium.

Afterwards filter and add powdered sal-ammoniac, which causes the deposition of yet more iridium as a black crystalline precipitate. The solution generally contains ruthenium so concentrated as to be separable from the iridium by precipitation. Now evaporate again and add more sal-ammoniac until the liquid begins to lose its colour, and most of the platinum metals are deposited as double salts. Then leave it for several days, collect the residue on a filter and wash it with water containing sal-ammoniac in solution, which completely eliminates iron and copper, and does not affect the ruthenium. In this way there is obtained a residue of iridium salts containing ruthenium, which, dissolved and boiled with the addition of a little ammonia, yields a precipitate of ruthenium sesquioxide.

(*B*) Commenting on the above process, Wolcott Gibbs says that this method of treating the fused mass to separate ruthenium and osmium is liable to two sources of inconvenience. In the first place, the quantity of water required to dissolve out the soluble portions is very large, and the subsequent treatment of such bulky solutions by distillation with acids is tedious, very large retorts being necessary. In the next place, it is impossible in this way to avoid exposure to the vapour of osmic acid, especially in transferring the solutions from one vessel to another. He therefore recommends the process which we have given at page 467.

Estimation of Ruthenium

When it is necessary to estimate ruthenium precisely, the osmium must not be expelled previously by means of aqua regia, otherwise there would be some loss of ruthenium. For the estimation of ruthenium, a larger quantity of the alloy than is generally used is required—that is to say, at least 10 grammes, which must all be reserved for the search for ruthenium, disregarding all the other constituents. Melt the pulverised ore with potash and saltpetre, dissolve it in water, carefully neutralise it with an acid, and, adding some alcohol, heat it; then carefully wash the precipitate, which is a black metallic powder, in water, to eliminate the saltpetre and other potassium salts. Dissolve this powder in hydrochloric acid, heat it in a retort with potassium chlorate and hydrochloric acid, and collect the

volatile products in condensers containing alcohol. By this means ruthenium and osmium are obtained together, but their separation can be effected by alcohol, which instantly decomposes the ruthenic acid, though it takes some time to reduce the osmic acid; or the two metals may be precipitated from their solution by sulphuretted hydrogen, and the sulphides thus obtained heated in a small platinum vessel, in an oxygen current, which disengages sulphur and osmium as acids, while the ruthenium remains as ruthenic oxide.

There is no appreciable loss in melting ruthenium with caustic potash and saltpetre. A piece of paper soaked with alcohol does not blacken if held even for a long time over the heated mixture, and no smell of ruthenic acid is observable, though during the solution of the mixture a feeble odour of it is always given off. If ruthenious sesquioxide, which is obtained by treating this solution with alcohol, is dissolved in hydrochloric acid, the solution takes place without forming a volatile ruthenic combination; but there is some likelihood of loss if aqua regia is used as a solvent, for ruthenium is then placed under circumstances similar to those produced by the simultaneous action of potassium chlorate and hydrochloric acid.

Detection of Ruthenium in the Presence of Iridium, &c.

(*A*) The reactions of ruthenium are remarkably affected by the presence of iridium; and in proportion as this last-named metal is present in larger quantity, the indications afforded by most of the tests hitherto proposed grow less and less decided, and some lose all efficacy. C. Lea has discovered in sodium thiosulphate a very delicate test for ruthenium.

When a solution of sodium thiosulphate is mixed with ammonia, and a few drops of solution of ruthenium sesquichloride are added, and the whole boiled, a magnificent red-purple liquid is produced, which, unless the solutions are very dilute, is black by transmitted light. The colouration is permanent, and the liquid may be exposed to the air without alteration. This reaction is obtained with great ease and certainty, and, in the opinion of the discoverer, is far superior to any known test for ruthenium. In order to determine the limits of the sensibility of this reagent, experiments were made with ruthenium solutions of different strengths. The following results were obtained:—

With $\frac{1}{5000}$ of ruthenium sesquichloride, bright rose-purple.

With $\frac{1}{20000}$ and $\frac{1}{30000}$, fine rose colour.

With $\frac{1}{50000}$, paler, but still perfectly distinct.

With $\frac{1}{100000}$, the colour, though very pale, was still unmistakably present.

Where the solutions are so very dilute as these last, the boiling must be continued for some minutes.

When the presence of ruthenium in very small quantity, or in very

dilute solution, is suspected, it is often advisable to boil the solution with a little hydrochloric acid, previous to the application of the thiosulphate test. The acidulated solution must be rendered alkaline by addition of ammonia before heating with thiosulphate.

This reagent is the best test that is capable of detecting ruthenium in the presence of any excess of iridium. No precautions are necessary, and the reaction is always obtained with the greatest facility. The iridium solution is to be rendered alkaline with ammonia, a crystal of sodium thiosulphate is dropped into it, and the whole is boiled for two or three minutes. If no indication of a red-purple tint appears (or, in case of small quantities of ruthenium, a rose colour), the iridium solution may be pronounced free from ruthenium.

(*B*) Wolcott Gibbs has discovered another delicate test for ruthenium, which likewise can be employed in the presence of other platinum metals. When a solution of potassium nitrite is added in excess to ruthenium sesquichloride, either free, or in combination with potassium or ammonium chloride, a yellow or orange-yellow colour is produced, but no precipitate is formed. A precisely similar change occurs when the ruthenium is in the form of bichloride; but in this case the change of colour is produced more slowly, and usually requires heating or even boiling. The change of colour is due in both cases to the formation of an orange-yellow ruthenium and potassium double salt, which is very soluble in water and alcohol; its relations to alcohol in particular enable us to distinguish ruthenium from the other platinum metals more perfectly than has hitherto been possible. When a few drops of ammonium sulphide are added to a solution of this double salt, a magnificent crimson colour is produced. This reaction furnishes a characteristic test of the greatest value, since it is not materially affected by the presence of the other metals of the same group.

The test may be most advantageously applied as follows:—The liquid supposed to contain ruthenium is first to be rendered alkaline by the addition of sodium or potassium carbonate. Potassium nitrite in solution is then to be added, the liquid boiled for an instant, allowed to become perfectly cold, and a drop or two of colourless ammonium sulphide added. On shaking, the colour appears, and rapidly deepens to the finest red. When the quantity of ruthenium present is very small, or when large quantities of the other platinum metals are also present, it is better, after adding the alkaline carbonate and nitrite, to evaporate the whole to perfect dryness on a water-bath, and treat the dry and powdered mass with a small quantity of absolute alcohol. The alcoholic solution is then to be filtered off, and tested directly with ammonium sulphide. In this way the smallest trace of ruthenium may be detected even in the presence of very large quantities of the other platinum metals.

(*C*) Claus detects ruthenium qualitatively in the presence of

iridium by making use of the following reactions :—A solution of pure iridium, containing no ruthenium, is instantly decolourised by the addition of excess of caustic potash or ammonia. It remains thus for a long time perfectly transparent, and then, after several days, takes a beautiful blue colour. But if the iridium contains traces of ruthenium, the colour of the solution becomes fainter during the reaction, but does not disappear ; it passes to a yellow-brown or reddish hue, and does not become decolourised for some time, at which point the solution becomes turbid, and a slight brown or yellow precipitate is formed. If the iridium contains more ruthenium, yet not sufficient to produce a visible precipitate, its presence is betrayed by the intense red-purple colour assumed by the liquid, especially if potash is used.

Separation of Ruthenium from Iridium

The quantitative separation of ruthenium from iridium is much more difficult than the mere detection of ruthenium in the presence of iridium. Their separation cannot be effected by igniting them with a mixture of saltpetre and caustic potash. The following is an accurate means of separating the two metals, based upon Gibbs's discovery of the reaction of alkaline nitrites on ruthenium salts, already described :—

(*A*) To the solution containing the two metals, sodium nitrite is to be added in excess, together with sufficient sodium carbonate to keep the liquid neutral or alkaline. The whole is to be boiled until the solution assumes a clear orange-yellow or orange colour. If a green tint should be perceptible, more sodium nitrite must be added, and the solution again boiled. Both ruthenium and iridium are converted into soluble double nitrites. A solution of sodium sulphide is then to be added, in small quantities at a time, until a little of the precipitated ruthenium sulphide is dissolved in the excess of alkaline sulphide. The first addition of the sulphide gives the characteristic crimson tint due to the presence of ruthenium, but this quickly disappears and gives place to a bright chocolate-coloured precipitate. The solution is then boiled for a few minutes, allowed to become perfectly cold, and then dilute hydrochloric acid added cautiously until the dissolved ruthenium sulphide is precipitated and the reaction is just perceptibly acid. The solution is then to be filtered through a double filter, and the ruthenium sulphide washed continuously and thoroughly with boiling water. The filtrate is perfectly free from ruthenium ; it is to be evaporated with hydrochloric acid, and treated with sal-ammoniac in the manner already pointed out in speaking of the separation of iridium from platinum (page 463, *A*). The washed ruthenium sulphide is to be treated, together with the filter, with strong hydrochloric acid, and ammonium chloride added in sufficient quantity to form ammonium ruthenio-chloride. Nitric acid is to be added from time to time, in small quantities, until, with the aid of heat, the whole of the ruthenium

sulphide is oxidised and dissolved. The liquid is then to be filtered, the filter well washed, and the filtrate and washings evaporated to dryness on a water-bath, when, after washing out the soluble salt with strong solution of ammonium chloride, the ammonium rutheniochloride remains almost chemically pure. It is to be dissolved and converted into the compound of mercury and ruthendiamin chloride (see Separation of Ruthenium from Platinum). From this salt chemically pure ruthenium may be obtained by ignition, which is best effected in an atmosphere of hydrogen, as the reduced metal is easily oxidised in the air.

It may happen that the precipitated ruthenium sulphide contains traces of iridium. This can only arise from imperfect washing or want of proper care in precipitating with sodium sulphide. In this case, the washings from the ammonium rutheniochloride are yellow, and contain iridium sulphate. The quantity of iridium in such cases is too small to be worth the trouble of separate treatment.

(*B*) When a solution contains iridium and ruthenium in the form of bichlorides, the ruthenium may be easily and completely separated by boiling the solution with potassium nitrite in excess, adding, at the same time, enough potassium carbonate to give an alkaline reaction, evaporating to dryness, and dissolving out the double ruthenium and potassium nitrite by means of absolute alcohol. The undissolved mass in this case contains two double iridium and potassium nitrites. By adding a strong solution of ammonium chloride, evaporating to dryness, igniting the dry mass in a porcelain crucible, and dissolving out the soluble salts, metallic iridium remains in a state of purity. This method may be used for quantitative separation of iridium from ruthenium; but when the object is simply to prepare both metals in a state of chemical purity, the separation by means of sodium sulphide is preferable.

Separation of Ruthenium from Rhodium

The separation of ruthenium from rhodium is best effected by means of potassium nitrite. The mixed solution of the two metals is to be boiled for a short time with an excess of the nitrite, together with a little potassium carbonate to keep the solution neutral or slightly alkaline. The yellow or orange-yellow solution is then to be evaporated to dryness upon a water-bath, the dry mass rubbed to fine powder and then treated in a flask with absolute alcohol in the manner pointed out for the separation of ruthenium from platinum. After filtration and washing with absolute alcohol, the rhodium remains undissolved in the form of a mixture of the two double rhodium and potassium nitrites. These may be ignited with a large excess of sal-ammoniac, so as to yield, after washing, metallic rhodium; or the nitrites may be dissolved in hot hydrochloric acid, ammonia added, and the rhodium precipitated

as sulphide, which is then treated in the manner already pointed out (page 465, *A*), so as to convert the rhodium into the double rhodium and ammonium chloride. To remove the last traces of ruthenium the rhodium salt may be treated a second time with potassium nitrite, as above, and again washed with alcohol. The presence of the least trace of ruthenium is easily detected by adding a drop of colourless ammonium sulphide to the alcoholic solution. The method of obtaining pure ruthenium from the double ruthenium and potassium nitrite has already been given.

Separation of Ruthenium from Platinum

(*A*) The approximate separation of ruthenium from platinum may be effected by precipitating the two metals with potassium chloride and washing out the potassium rutheniochloride with cold water, in which it is readily soluble. The mixed solutions should be evaporated to dryness with an excess of the alkaline chloride, and the dry mass rubbed to a fine powder in a mortar, after which almost the whole of the ruthenium may be washed out with water, or with a cold and moderately strong solution of potassium chloride. The undissolved platinum salt may then be purified by crystallisation, but it usually contains traces of ruthenium. The rose-red solution of the ruthenium salt contains a small quantity of platinum, from which it cannot be wholly freed by the difference in solubility of the two salts. Ammonium chloride may be employed in this process in place of potassium chloride.

(*B*) To obtain a complete separation, Gibbs's process may be followed with advantage:—The potassium rutheniochloride, separated as far as possible from the platinum salt, is to be heated with a solution of potassium nitrite in quantity sufficient to convert the whole of the ruthenium into the soluble yellow double ruthenium and potassium nitrite, potassium carbonate being added in small quantities so as to keep the solution neutral or alkaline. The yellow or orange solution is to be evaporated to dryness in a water-bath, the dry mass reduced to powder and boiled with absolute alcohol until the ruthenium salt is completely dissolved. This is best effected in a flask furnished with a condensing-tube bent upwards, so that the alcohol vapour may be condensed and flow back into the flask. The boiling need not be continued for a very long time, as the ruthenium salt is readily soluble in alcohol. The solution is then to be filtered off from the undissolved salts, and these are to be washed with absolute alcohol until the washings are colourless, or until they no longer give the characteristic ruthenium reaction with ammonium sulphide. The filtrate and washings may then be distilled, to separate and save the alcohol, water being added in small quantity. The residue in the retort or flask is then to be evaporated with hydrochloric acid, which readily decomposes the double nitrite, and yields a fine deep rose-red solution of the

potassium rutheniochloride, containing at most only a trace of platinum. The mass of salts undissolved by the alcohol contains nearly all the platinum in the form of potassium platinochloride, which is easily separated. The solution of the potassium rutheniochloride is now so pure that it gives the reactions of a chemically pure salt.

To obtain the ruthenium in a state of absolute purity, the solution is to be evaporated to dryness with a saturated solution of sal-ammoniac in excess, redissolved, again evaporated, and the dry mass washed with a little cold water to remove the alkaline chlorides. The potassium rutheniochloride is in this manner, for the most part at least, converted into the corresponding ammonium salt. This salt is then to be dissolved in hot water, a solution of ammonia added, and the liquid boiled until it assumes a clear yellow or orange-yellow colour, after which it is to be evaporated to dryness on a water-bath. In this manner the ruthenium is converted into ruthendiamin chloride, discovered by Claus. The yellow mass is to be dissolved in boiling water, and a solution of mercury chloride added. A beautiful yellow crystalline double salt is precipitated, and the mother-liquor, when cold, contains only traces of ruthenium and platinum. The double mercury and ruthendiamin chloride is almost insoluble in cold water, but is soluble in boiling water, and is easily rendered absolutely pure by recrystallisation. On ignition, this salt yields chemically pure metallic ruthenium as a silver-white porous mass.

When, in a mixture of solutions of ruthenium and platinum, the ruthenium is present either partly or wholly as sesquichloride, the liquid is to be boiled with potassium nitrite and carbonate as above, evaporated to dryness, boiled with excess of hydrochloric acid to convert the double ruthenium and potassium nitrite into potassium rutheniochloride, and the resulting solution treated by the process already described.

CHAPTER X

SULPHUR, PHOSPHORUS, NITROGEN

SULPHUR

Estimation of Sulphur in Pyrites

The following is a useful modification of the potassium chlorate method:—Half a gramme of finely ground pyrites (sifting is not absolutely necessary) is mixed in a large platinum capsule with the well-known mixture of 6 parts sodium carbonate and 1 part potassium chlorate. The mixing is effected with a platinum spatula, and is then made more complete by gentle rubbing with an agate pestle fixed to a wooden handle. The whole is then fused over the blow-lamp. The aqueous solution of the melt is first poured into a beaker to avoid spirting, and then into another tall beaker containing an excess of hydrochloric acid. The filtered solution is heated and precipitated with hot barium chloride, heated gently upon the sand-bath for a time, until the liquid standing above the precipitate has become clear, and is filtered at once. The burnt ores in sulphuric acid works have been for a long time assayed for sulphur by this process. From 20 to 25 grammes of chlorate mixture are required for 2 grammes of burnt ore.

If sulphur is fused with a sufficient excess of alkali, it is converted entirely into sulphite, and not into a mixture of thiosulphate and sulphide, and if still more alkali is present, the result is a mixture of sulphite and sulphate. To oxidise the sulphite to sulphate, bromine is used. This analytical principle may be successfully applied to organic sulphur compounds, to free sulphur, and metallic sulphides. The fusion of sulphur or a metallic sulphide with potash yields a sulphide without any loss; it is then oxidised by means of bromine and hydrochloric acid, forming sulphuric acid, which is estimated in the ordinary manner. Where metallic oxides are separated after the fusion, in an insoluble state, they are removed by filtration before the bromine and hydrochloric acid are added. Arsenic, antimony, zinc, &c. sulphides all yield, after melting, a fusible mass, while in the case of iron and copper sulphides these metals are left behind in the state of oxides. Even in pyritic silicates the sulphur can be accurately estimated in

this manner. Care must be taken that not less than 25 grammes pure caustic potash are taken to every 0·1 gramme of sulphur supposed to be present. The operation is performed in a silver crucible, and the fusion is continued till all the mixture becomes tranquil—say from fifteen to twenty minutes—or till the vapours of alkali begin to condense along the upper part of the crucible, which after use shows a clean surface if sufficient alkali has been used. When cold the mass is dissolved in cold water, freed from oxides, &c. by filtration, mixed with from 75 to 100 c.c. bromine-water, and hydrochloric acid added till a distinctly acid reaction is obtained. Heat is then applied till the liquid is colourless.

The pyrites may also be burnt in a current of oxygen, and the products of combustion titrated. The operation is carried on in a tube of hard glass, placed in a furnace for organic analysis. One end of the tube is sealed, and to the other is fitted a stopper with two holes. One of these serves for the escape of the gaseous products of combustion, which are received in a Liebig's bulb apparatus containing standard caustic soda. Through the other hole passes a long narrow tube which conveys oxygen, free from water and carbonic acid, to a small platinum boat placed near the closed end of the combustion-tube, and containing $\frac{1}{2}$ gramme of the pyrites spread out in a thin layer. A plug of asbestos is placed about the middle of the tube, to avoid projections. Heat is first applied towards the open end of the tube, and as it approaches redness it is gradually extended towards the closed end. The current of oxygen is regulated so as to be always in excess. The disappearance of the white vapours formed in the bulb-tube during the operation is a sign that the sulphurous acid is expelled from the combustion-tube. The open end of the tube and the stopper are then washed, and the washings are added to the liquid in the bulb-tube, the sulphurous acid in which is then estimated in the usual manner. If the pyrites contain carbonates, standard solutions cannot be used. It is then necessary to oxidise the sulphurous acid and estimate the sulphuric acid formed.

Estimation of Sulphur in the Presence of Iron (Pyrites)

O. N. Heidenreich[1] recommends the following method:—To prevent the carrying down of ferric sulphate by sulphate of barium precipitated in a solution rich in iron, first reduce the iron by means of metallic zinc before proceeding with the precipitation of the sulphuric acid. The ferrous sulphate thus formed is not carried down. The sample of pyrites to be examined is attacked in the ordinary manner with aqua regia, and the solution obtained is diluted to about 250 c.c. and a certain quantity of zinc added. After complete decolouration the solution is rapidly filtered and made up to 600 c.c.; it is then

[1] *Chemical News*, Feb. 2, 1900.

heated to boiling, and precipitated with a boiling solution of chloride of barium.[1]

The following process, due to P. Holland, will be useful in laboratories which do not possess large platinum crucibles. A test-tube or piece of sealed combustion-tube, about 6 inches long and ½ inch internal diameter, is fitted with a cork and delivery-tube, the latter bent at a right angle and long enough to reach to the bottom of the flask in which it is intended to make the titration. The fusion mixture consists of equal parts of nitre and ignited acid sodium carbonate both free from sulphur, dry, and in fine powder. 9 to 10 grammes are taken in an operation, together with one of pyrites (the latter must be in exceedingly fine powder); the two are mixed in a warm porcelain dish, or agate mortar, and transferred to the tube without loss. The delivery-tube is then inserted with its extremity dipping into the flask. A channel is made on the surface of the mixture, and the tube, suitably supported, is heated in small portions at a time with a Bunsen gas-flame, commencing as usual with the anterior portion. When the operation is progressing favourably, the deflagration proceeds for a few seconds after removing the flame.

There is no danger to be apprehended, and with proper care the tube does not crack or blow out. When the tube has been heated throughout, and the deflagration has ceased, it is then more strongly heated with a Herapath or powerful gas-flame. It is a good plan at this stage to slip a coil of wire gauze over the tube, which helps to accumulate the heat. It is not, however, necessary that the contents should be fused a second time. The sulphur ores examined yielded their sulphur readily.

The gaseous products of the combustion which mechanically carry over with them small quantities of sulphates or sulphuric acid, being heavier than air, collect in the flask, and are washed by shaking with a little water, closing the flask with the palm of the hand. The delivery-tube is also washed. That containing the fused mass is carefully broken and put in the flask, together with sufficient hydrochloric acid to dissolve nearly the whole of the oxide; then ammonia is added until a precipitate of oxide reappears, and, lastly, as much free hydrochloric acid and water as are necessary to bring the liquid to the conditions which were obtained when the barium solution was standardised: 2 c.c. of free acid may be used when the total volume of solution is 200 c.c.

A. H. Pearson gives the following very accurate method of estimating sulphur in pyrites:—Weigh out 1 gramme or less of the powdered ore, place it in a porcelain dish together with a small quantity of potassium chlorate, pour upon it some 50 c.c. of pure nitric acid of 39° B., and cover the mixture with an inverted glass funnel with bent stem; set the dish upon a water-bath, and heat the water to boiling.

[1] *Zeitschr. Anorg. Chem.*, 1899, vol. xx. p. 233.

From time to time throw crystals of potassium chlorate into the hot acid. By adding rather large crystals of the chlorate at frequent intervals, it is easy to oxidise the whole of the sulphide in half an hour; but, since the solution obtained in that case is highly charged with saline matter, it will usually be found more advantageous to use less of the potassium chlorate and to allow a somewhat longer time for the process of oxidation.

When all the sulphur has been oxidised, rinse the funnel with water and remove it from the dish. Evaporate the liquid to a small bulk, then add to it a little concentrated hydrochloric acid, and again evaporate to absolute dryness, in order to render silicic acid insoluble. Moisten the residue with concentrated hydrochloric acid, mix it with water, and filter to separate silicic acid and gangue.

To the filtrate from the silicic acid add a quantity of solid tartaric acid, about as large as that of the pyrites originally taken; heat the liquid almost to boiling, and add to it an excess of barium chloride, to precipitate the sulphuric acid. After the barium sulphate has been allowed to subside, wash it thoroughly by decantation, first with hot water and afterwards with a dilute solution of ammonium acetate (the latter may be prepared at the moment of using by mixing ammonia-water and acetic acid). The purpose of the ammonium acetate is to dissolve any barium nitrate which may adhere to the sulphate; that of the tartaric acid is to prevent the precipitation of iron compounds together with the barium sulphate. In an experiment where 0·7 gramme of pyrites was oxidised with potassium chlorate and nitric acid, and the filtrate from silica was acidulated with hydrochloric acid without the addition of tartaric acid, there was thrown down, on the addition of barium chloride, a bright yellow precipitate, which became darker coloured when the solution was boiled. It was not only found to be impossible to wash out the iron with which this precipitate was contaminated, but the consistency of the precipitate was such that it was a difficult matter even to wash away the saline liquor in which it was formed.

In another experiment the attempt was made to remove the iron in the filtrate from silica, before adding the barium salt to throw down the sulphuric acid; but in that case a considerable portion of the sulphuric acid was dragged down as potassium sulphate by the iron precipitate, and so lost. The precipitation of the iron was effected, in this experiment, by adding an excess of ammonia-water to the acidulated filtrate from silica, and washing the precipitate for a long time by decantation with boiling water. To prove that the iron precipitate really retained sulphuric acid, a quantity of the precipitate was dried, ignited, and powdered, and the powder boiled with water. The clear liquid thus obtained was acidulated with hydrochloric acid, and tested with barium chloride. An abundant precipitate of barium sulphate was at once thrown down.

Errors of 1·5 to 4 per cent. are often made if the nitric acid employed in oxidising the sulphur is not driven off by the subsequent application of an excess of hydrochloric acid. If this precaution is omitted, the barium sulphate thrown down in presence of free nitric acid is somewhat soluble, and, if abundantly washed, the result is too low. If, on the other hand, the washing is but slight, a quantity of barium nitrate may remain mechanically mixed with the sulphate, and the result is too high.

(*A*) R. Fresenius shows that the precipitation of barium sulphate in boiling solutions does not take place instantaneously. Appreciable quantities remain at first in solution. If the solution contains ferric chloride, this has, on the one hand, a solvent action upon the barium sulphate, which, on the other hand, always appears red after ignition, and the ferric oxide producing this colour cannot be removed by treatment with hot hydrochloric acid. These two sources of error act in opposite directions, but the solvent action of the hydrochloric acid and the ferric chloride preponderates. In an examination of Lunge's process (precipitation of the boiling liquid containing ferric chloride, and some hydrochloric acid, with boiling barium chloride and immediate filtration), Fresenius has obtained deficiencies of 1 to 1·7 per cent. in a pyrites containing 43·8 per cent. of sulphur, as ascertained by his own method.

(*B*) On the other hand, G. Lunge maintains that his process, though yielding results less absolutely accurate than those obtained by the method of Fresenius, is yet preferable for use in chemical works where time is the first object. He thinks that the larger proportion of sulphur obtained by the process of Fresenius is partly due to the fact that both galena and heavy spar—bodies frequently found in pyrites—are attacked by the dry process.

Lead sulphide, and lead and copper ores in which it occurs, cannot be dissolved in nitric acid without the deposition of lead sulphate, which contains, also, lead antimoniate, if antimony is present. The estimation of the metals in such cases is easy if the compound is dissolved by boiling in hydrochloric acid. Even ores rich in copper dissolve completely. The hot solution is finally allowed to flow into dilute sulphuric acid, to prevent the deposition of lead chloride.

(*C*) P. Waage calls attention to the drawbacks of nitric acid, chlorine, and potassium chlorate with hydrochloric acid, and recommends bromine, which he has used with success for two and a half years for sulphur, magnetic pyrites, copper pyrites, mispickel, nickel mattes, and precipitated sulphides, both for the estimation of sulphuric acid and the metals.

Sulphur, shaken with bromine and water, is easily converted into hydrobromic and sulphuric acids, if for every atom of sulphur 3 of bromine are present, or 15 by weight of bromine to 1 of sulphur. If

sulphur has to be estimated in this way, it is best to add all the bromine at once, so that no bromine sulphide can be formed.

In the treatment of pyrites no necessity will exist for pulverising them very finely, as they are oxidised by bromine quite easily even in larger pieces ; but it is best to add water first, and then bromine with constant stirring, that the action may not become too violent.

Bromine-water is the most convenient material for the destruction of hydrosulphuric acid. A few drops of it added to a filtrate from a metallic sulphide will immediately produce a separation of sulphur, which will as quickly be dissolved by a further addition of a few drops of bromine-water.

In dissolving precipitated metallic sulphides proceed in the following manner :—Perforate the filter-paper and wash as much of the precipitate as possible into a beaker. Then pour some of the bromine-water into the funnel, and cover the latter with a watch-glass, when after a few minutes the rest of the sulphide may be washed into the same beaker, and a further addition of bromine-water readily oxidises the rest of the sulphide. We thus get rid altogether of the trouble of burning the filter-paper.

(*D*) Reichardt, however, states that iron pyrites requires to be very finely pulverised, and a prolonged action is necessary. Copper pyrites is dissolved very rapidly if an excess of bromine is used, which is easily expelled by a gentle heat. The sample is placed in a small flask, covered with a little water, and the bromine is added. A gentle heat is sometimes necessary towards the end.

In a direct volumetric estimation of the sulphuric acid resulting from the oxidation of pyrites by the wet method, Philip Holland finds that it is desirable to titrate in presence of but little free hydrochloric acid in the entire absence of nitric acid, and to standardise the barium chloride by iron sulphate as nearly as possible under the conditions which will prevail in a pyrites assay so far as the amount of free acid and the volume of liquid are concerned.

(*E*) Glendenning and Edgar call attention to the inaccuracy introduced in the analysis of pyrites by the use of Wedgwood and porcelain mortars. The percentage of silica is in some cases doubled, and the sulphur necessarily diminished. They recommend that the sample be broken up in a steel mortar and pulverised in an agate mortar.

Estimation of Sulphur in Iron, Steel, and Iron Ores

(*A*) According to C. H. Piesse, a simple and ready method of estimating the sulphur in pig-irons and steels, and one requiring but little attention, is as follows :—Place in a beaker of about 300 c.c. capacity about 3·5 to 4 grammes of the sample in drillings, and pour upon them 35 to 40 c.c. of aqua regia, maintaining the proportion of 10 c.c. of the mixed acids for every gramme of the metal, keeping the beaker covered

as well as possible with a watch-glass. After the first violence of the action has subsided, boil the liquid for a few moments until the whole of the iron is dissolved, then transfer the solution with as little washing as possible to a porcelain basin, and evaporate nearly to dryness on a water-bath. Treat the residue with some concentrated hydrochloric acid, add about an equal bulk of water, and then filter. To the filtrate add a considerable excess of barium chloride solution, allow to stand for about twelve hours, filter, and weigh the precipitated barium sulphate with the usual precautions.

(*B*) Koppmayer introduces 10 grammes of iron, finely powdered and sifted, into a bottle holding from $\frac{1}{2}$ to $\frac{3}{4}$ litre. The stopper has three holes. Through one of these passes a funnel with a ground-glass tap, its neck reaching to the bottom of the bottle. Through the second passes the tube at right angles, fitted with a tap, and reaching also to the bottom of the bottle. Through the third hole passes the delivery-tube, connecting the bottle to the condensing apparatus. This latter consists of a series of bulbs arranged like a staircase, so as to permit the gas to come into the greatest possible contact with the standard solution of iodine in potassium iodide with which the condenser is filled. This solution ought not to be exposed to light. When the apparatus is arranged as above, the air is first driven out of the bottle by means of a current of hydrogen gas introduced by the tube bent at right angles. When it is considered that the air is entirely expelled, the tap of this tube is closed. The funnel is now filled with hydrochloric acid, its tap is opened, and by means of the application of heat the acid is allowed to run down upon the iron without permitting any air to enter. Hydrogen and sulphuretted hydrogen are formed, which pass into the condenser. Acid is thus added until all disengagement of gas ceases. The bottle is then heated until its contents boil, a little water having been first added by means of the funnel. After these operations hydrogen is again allowed to enter so as to sweep out all remaining gases. The iodised solution is then poured in, care being taken to rinse the bulb-tube thoroughly, and titrated with sodium thiosulphate, so as to find the remaining proportion of free iodine. The difference between the original amount of iodine present in the solution and the amount thus found shows the proportion of iodine which has been converted into hydriodic acid, and which is proportional to the sulphur contained in the sample under examination.

Estimation of Sulphur in Vermilion

A mixture of nitric acid and potassium chlorate is the best means of oxidising the sulphur in this substance to sulphuric acid, as no trace of free sulphur is ever seen in the liquid, while when hydrochloric acid is used to decompose the chlorate, globules of sulphur float about and entirely resist solution. About 0·5 or 0·6 of a gramme of the vermilion

is placed in a small glass flask, set in an inclined position upon a wire-gauze support above a lamp. A quantity of nitric acid of 39° B. is poured into the flask, a small quantity of potassium chlorate then added, and the mixture heated. From time to time crystals of potassium chlorate are thrown into the flask, the contents of which are maintained near the boiling-point until all the sulphur has dissolved. It sometimes happens, when the proportion of nitric acid is small, that a considerable quantity of saline matter crystallises in the flask; enough water to redissolve this precipitate may, however, be added to the mixture, without impairing to any material extent the oxidising power of the chlorate subsequently added.

The acid liquor resulting from the action of nitric acid and potassium chlorate upon the vermilion is evaporated to dryness on a water-bath, and the residue treated with strong hydrochloric acid, in order to destroy most of the nitric acid before proceeding to precipitate the sulphuric acid with barium chloride. Before adding the hydrochloric acid to the residue, the latter must be allowed to become perfectly cold, lest the mixture froth violently and portions of it be thrown out of the flask. After the acid has once been added, however, the mixture may be heated gently without risk of loss. The solution must at last be largely diluted with water before adding the barium chloride

Estimation of Sulphur in Mineral Waters

(*A*) F. Maxwell Lyte has devised an ingenious method of estimating free sulphuretted hydrogen in a mineral water when accompanied by iron protosulphate, the presence of which interferes with the usual tests. Some lead sulphate is prepared by precipitation from boiling solutions, and is well washed with boiling distilled water, and, while still fresh and moist, successive portions are added to the mineral water till the brownish-black colour of the precipitate first formed turns to a decided grey, showing that the sulphuretted hydrogen has all been removed from the solution, and that some undecomposed lead salt remains in excess. The supernatant liquid is decanted from the precipitate, which quickly settles down, and the latter is rapidly washed on a filter with boiling distilled water, and subsequently with a hot solution of ammonium acetate to dissolve out the excess of lead sulphate, till the washings are no longer coloured by the addition of an alkaline sulphide. The filter is now carefully incinerated, and the lead sulphide oxidised by an addition of a little nitric acid, and evaporated with a little sulphuric acid until heavy fumes of the latter begin to be evolved. Subsequent dilution with water gives a precipitate of lead sulphate, which is separated by decantation and weighed; from this may be calculated the amount of sulphuretted hydrogen which has been present in the water.

(*B*) For the estimation of hydrosulphuric acid in mineral waters,

W. J. Land gives the following directions:—In an apartment free from direct sunlight, preferably a room lighted by non-actinic rays, prepare a moist precipitate of pure silver carbonate, by dissolving 8·5 grammes of pure silver nitrate in $\frac{1}{4}$ litre of distilled water; also 2·7 grammes of chemically pure dry sodium carbonate in an equal volume of distilled water previously heated to about 180° F. Mix the solutions gradually, simultaneously stirring them with a glass rod. Allow the precipitate to subside, decant the supernatant liquid with a pipette or small syphon, wash with hot distilled water, decanting and washing successively five or six times to obtain a comparatively clean precipitate of silver carbonate, in which substance we have a most excellent reagent for removing every trace of hydrosulphuric acid, small quantities of alkaline sulphides and haloids, from their solution in water. Add to a definite quantity of the water to be operated upon (say 1 litre if strongly impregnated, and 10 litres if weakly impregnated with gas) the still moist precipitate of silver carbonate, until the precipitate, at first black in colour, becomes brown or greyish brown, thus indicating an excess (as desired) of the silver salt. Shake or stir well, warm gently, and allow the precipitate to subside perfectly. Decant the greater part of the liquid, transfer the remainder of the liquid with every trace of the precipitate to a small beaker, and digest the latter with pure dilute nitric acid (1 of acid to about 4 of water), thus removing the excess of silver carbonate. Decant and wash well with distilled water. Transfer to a weighed filter, wash with a moderately dilute solution of ammonia (to remove silver haloids), testing the ammoniacal filtrate occasionally with ammonium sulphide, or other suitable reagent, to discover the presence or absence of the silver haloids in the washings; when all traces of these have disappeared, wash well with distilled water, lastly with pure 95-per-cent. alcohol; dry on a water-bath. Remove the dried silver sulphide from the filter, ignite the latter in a small porcelain crucible with a grain or two of sulphur, heating to incipient redness (to expel excess of sulphur), add the ignited product to the larger quantity of the precipitate, transfer to a desiccator, afterwards weigh. 124 parts of the sulphide correspond to 17 of hydrosulphuric acid sought.

Detection of Sulphur by Means of Sodium or Magnesium

Dr. Schönn recommends the use of either of these two metals for ascertaining the presence of sulphur in the oxidised or non-oxidised state in compounds. The substance to be tested (for instance, calcium or barium sulphate) is thoroughly mixed, previously reduced to powder, and next heated to redness with the metal in a test-tube made of thin hard glass. After the reaction is over, the contents of the tube are, when quite cold, treated with distilled water and tested with sodium nitro-prusside. Care should be taken that only small quantities of

substance are operated upon in this manner, especially as substances like realgar, orpiment, and others containing sulphur and arsenic at the same time, detonate violently when ignited with sodium.

As regards liquids containing sulphur, the author states that a drop of sulphuric acid when brought into contact with sodium yields, among the products of the reaction, sodium sulphide; with magnesium, this reaction does not take place unless heat be applied. Carbon disulphide and essential oil of mustard may be readily proved to contain sulphur by application of the same test. For detecting sulphur in organic substances, especially of animal origin, the same process is available. Hair and feathers, dry skin and nails, may be at once submitted to ignition with the metal. White of egg, emulsin, saliva, or muscle should first be calcined on a piece of platinum, and the animal charcoal so obtained be ignited along with sodium or magnesium. In most cases of this kind sodium nitro-prusside will be required to make the presence of sulphur distinctly evident.

Reagent for Sulphur

(*A*) According to Dr. Schlossberger, a solution of ammonium molybdate in hydrochloric acid, diluted with water, possesses the property of becoming coloured blue if traces of sulphur are present. By this means the presence of sulphur even in a single hair is easily recognisable after it is rendered soluble by the method just given.

(*B*) Brunner mixes the substance under examination with strong potash lye, and adds a few drops of nitro-benzol and alcohol, and allows the mixture to stand at the common temperature. After some time, if sulphur or alkaline sulphides are present, there appears a red colouration from the reduction of nitro-benzol. The inverse reaction can be used for the detection of nitro-benzol.

Obtaining Sulphuretted Hydrogen in the Laboratory

E. Divers and Tetsukichi Schimidzu obtain a regular stream of pure hydrogen sulphide by gently heating a solution of magnesium hydrosulphide. Ordinary hydrogen sulphide (from ferrous sulphide and hydrochloric acid) is passed into water containing magnesia in suspension. The gas is absorbed, and the magnesia dissolves. The decanted solution is colourless, and when heated to 60° or 65° evolves a steady stream of hydrogen sulphide, free from hydrogen and hydrogen arsenide. The magnesia which is precipitated during the evolution of the gas can be reconverted by cooling and passing hydrogen sulphide into it.

Anomalies in the Detection of Sulphuric Acid

In testing for sulphuric acid in the presence of phosphoric acid, attention must be directed to a remarkable case of interference which

appears to have escaped observation until it was pointed out by Spiller.

If to an aqueous solution of glacial phosphoric acid a small proportion of sulphuric acid be added, the mixed liquid does not give the usual indication of a precipitate on adding a few drops of barium chloride, but requires a liberal addition of the last-named reagent in order to induce the formation of the sulphate. By adding dilute hydrochloric acid, or by raising the temperature of the clear barytic solution, the formation of a precipitate is determined; but continued ebullition fails, in many instances, to separate the whole of the barium sulphate. When, however, by the action of heat and of hydrochloric acid conjointly, the white precipitate makes its appearance, it is always found to be markedly different in physical character from the product usually obtained, being thrown down in the form of a semi-transparent flocculent precipitate, very like that obtained through the intervention of an alkaline citrate, as described in Spiller's paper, entitled 'On the Influence of Citric Acid on Chemical Reactions,'[1] read before the Chemical Society.

This remarkable property of obscuring the indication of sulphuric acid appears to be possessed only by the glacial modification of phosphoric acid; for, if the white flakes of phosphoric anhydride (as obtained by the combustion of phosphorus) be dissolved in water, no such result is apparent; nor do the hydrochloric acid solutions of bone-ash and of the ordinary sodium phosphate mask, in any appreciable degree, the presence of sulphuric acid. But if by heat the ordinary crystals of sodium phosphate be converted into pyrophosphate and then dissolved in dilute hydrochloric acid, a solution is obtained which in this particular resembles the glacial modification of phosphoric acid.

Detection of Free Sulphuric Acid in Vinegar

Boil about 50 c.c. of the acid to be tested in a retort with a very small quantity of starch, until half the liquid is distilled; after it has cooled add a drop of tincture of iodine. If, under these circumstances, a blue colouration be produced, no sulphuric acid is present. If the blue colour does not appear, it may be concluded that sulphuric acid is present, which, by reacting on the starch, will have transformed it into glucose. With tincture of iodine, glucose gives no particular colouration.

Quantitative Determination of Sulphur

Don Klobulow has devised the following process for the volumetric determination of the total quantity of sulphur in all such of its compounds as are capable of being decomposed by acids. The products of such decompositions are hydrogen sulphide, sulphurous acid, free

[1] See the *Chemical News*, vol. viii. p. 280.

sulphur, and, in certain special cases, sulphuric acid. The author finds that, under some conditions, nascent hydrogen converts not only sulphuric acid, but even the sulphur liberated from some compounds quantitatively into hydrogen sulphide. Hence the principle of the method consists in the reduction of the decomposition products of sulphur compounds by acids (always excepting sulphuric acid, which, if present, is determined in the ordinary manner) to hydrogen sulphide and its subsequent iodometric determination.

The conditions of the reactions are as follows :—

Sulphurous acid in solutions of a moderate degree of concentration is completely converted into hydrogen sulphide by nascent hydrogen at ordinary temperatures, or, better still, at a gentle heat, if air be excluded, and without any formation of sulphuric acid. The sulphur liberated on the decomposition of some sulphur compounds by dilute mineral acids is completely reduced to hydrogen sulphide in solutions of a moderate concentration, air being excluded, either at ordinary temperatures or, preferably, with slight refrigeration. In the author's method the sulphur compound in question is decomposed in a closed vessel in presence of zinc and hydrochloric acid. The sulphuric acid, which in some cases appears as a final product of the decomposition, remains in the apparatus, and is determined as barium sulphate along with any sulphuric acid pre-existing in the original sample ; while the hydrogen sulphide, which always appears as the other final product, passes into suitable absorption apparatus, filled with the titrated solution of iodine, the excess of which is titrated back after the operation. The apparatus used is as follows :—

A capacious flask, holding about 500 c.c., in which the decomposition of the substance is effected, is connected, on the one hand, with the absorption apparatus, and on the other (by means of a tube reaching to the bottom) with a hydrogen apparatus. A ball funnel, fitted with a glass cock, permits the introduction of the hydrochloric acid required for decomposition.

The absorption apparatus consists of the following parts, arranged in the order mentioned :—A large flask in which the gas delivery-pipe from the decomposition flask reaches to the bottom, containing the bulk of the standard solution of iodine ; a Liebig's potash apparatus, also filled with standard iodine solution ; a second potash apparatus, filled with a solution of potassium iodide, in which any iodine vapour carried along from the former apparatus is absorbed. In carrying out the process a quantity of granulated zinc, free from sulphur and arsenic, is introduced into the decomposition flask along with the weighed substance in question or its solution, and diluted with a sufficiency of water. The flask is then closed, connected with the other pieces of apparatus, and hydrogen is passed in for about ten minutes to expel air, when the decomposition may be commenced. The zinc must be in excess, though too large a quantity makes the

operation more tedious. The following cases must be distinguished:—

(*A*) If there appears as decomposition product, besides hydrogen sulphide, free sulphur—alone or along with sulphurous acid—the decomposition flask is placed either in a dish of cold water or in a vessel with a continual flow of water, and the decomposition is conducted as slowly as possible. Supposing the solution to be originally clear, it becomes milky in consequence of the liberation of sulphur, but this turbidity gradually disappears, and the liquid grows clear again. When the process has reached this stage, which occurs in twenty to twenty-five minutes, the cooling arrangement is removed, more acid is added, and the solution of the residual zinc is promoted by a gentle heat. When the zinc is completely dissolved the flask is heated for a time to 70° to 80°. The current of hydrogen (which does not need to be very strong as long as zinc is still present) is reinforced, and the liquid in the decomposition flask is thus kept in brisk motion, which, on the one hand, hastens the removal of the last traces of hydrogen sulphide from the liquid, and prevents a reflux of the absorptive liquid into the decomposition flask as the latter cools.

(*B*) If, in the decomposition of the substance in question, there appears no sulphur, but merely sulphurous acid and hydrogen sulphide, any refrigeration is superfluous; the decomposition is begun at the ordinary temperature, and afterwards quickened by a gentle heat. In other respects the process is conducted as in Case 1.

Before breaking off the experiment it is well to ascertain, by means of lead-paper, if the sulphuretted hydrogen has been entirely removed from the flask. This test is best applied at the joint between the gas delivery-tube and the first absorption apparatus.

The duration of the entire process is one and a half to two hours; after its completion the absorbent vessels are emptied into one common vessel, and the excess of the iodine solution is titrated back with sodium thiosulphate. The liquid in the decomposition flask contains all the sulphuric acid which has been formed during the decomposition, as well as that—if any—pre-existing in the substance. Its determination is effected in the ordinary manner. The solutions used are decinormal iodine and sodium thiosulphate standardised to each other. The hydrochloric acid used is of the strength 1·1.

Estimating Free Sulphuric Acid in Superphosphates

The following method is recommended by Dr. R. Carter Moffat as being very accurate:—An aqueous solution of the superphosphate being made, evaporate slowly until a small quantity only is left; add about 7 volumes of concentrated alcohol, and allow it to settle in the cold for some hours. This precipitates all sulphates, and leaves in solution, besides phosphates, the free sulphuric acid. Filter, wash

with alcohol, add a large amount of water to the solution, carefully evaporate off the spirit, and estimate the acid in the usual manner by precipitation with barium chloride. The soluble phosphates do not in any way interfere.

Should a more ready, though less accurate, process be required, an aqueous solution of the superphosphate treated with a very dilute normal solution of ammonia gives tolerably fair results.

Precautions in Precipitating Barium Sulphate

(*A*) It is well known that precipitated barium sulphate may retain alkaline salts in quantities of from 1·5 to 2 per cent., which cannot be removed by the most careful washing. Stolba obtains the barium sulphate pure by digesting it (after washing until the wash-waters no longer show the reaction of barium) with 40 to 50 c.c. of a cold saturated solution of neutral copper acetate and some acetic acid, at nearly a boiling heat for ten or fifteen minutes. During the digestion enough acetic acid must be present to prevent the formation of basic salt on boiling. Should basic salt form, which may be readily perceived at the bottom of the vessel, more acetic acid must be added, and the digestion must be renewed for ten or fifteen minutes. During the process the vessel containing the precipitate should be constantly agitated. The alkaline salts retained by the barium sulphate undergo double decomposition with copper acetate, and the resulting products all admit of entire separation from the precipitate by means of hot water. The precipitate is washed until no reaction for copper is manifested on testing the washings with potassium ferrocyanide. This method is also satisfactory for the estimation of sulphuric acid in presence of a large excess of barium nitrate and chloride.

(*B*) The commercial crystallised copper acetate is purified from sulphuric acid, and at the same time saturated with barium sulphate, by adding to its boiling solution a slight excess of barium chloride and acetic acid, and filtering from the precipitate.

(*C*) Fresenius describes a number of very important experiments concerning the influence of various acids and salts on the precipitation of barium sulphate, and the admixtures of foreign salts with the precipitate. His conclusions are:—(1) Barium sulphate does not require 43,000 parts of water for solution, as usually stated, but upwards of 400,000 parts, even in presence of hydrochloric acid, which slightly raises its solubility. (2) Sodium chloride, potassium chloride, and barium nitrate do not increase its solubility very perceptibly, but the alkaline nitrates do so. (3) Hydrochloric acid does the same, and it must therefore be evaporated or partially neutralised before the precipitation. (4) Sodium chloride does not produce any foreign admixture in the precipitate. (5) Potassium chlorate does cause such admixture in a high degree. The precipitate can, however, be purified

by digesting with hot hydrochloric acid, evaporating the same, and washing with water. (6) Sodium, potassium, and barium nitrate cause a very impure precipitate, which cannot be purified by washing with hydrochloric acid, but only by fusion with sodium carbonate, and estimating the sulphates in the aqueous solution of the fused mass.

Purification of Sulphuric Acid from Arsenic

Arsenic almost always exists in commercial sulphuric acid in the form of arsenious acid, which, being volatile, distils over with the sulphuric acid, and prevents its purification by rectification.

(*A*) Bussy and Buignet recommend that a sulphuric acid which contains arsenious acid should be boiled with nitric acid, to oxidise arsenious acid to arsenic acid, then mixed with a little ammonium sulphafe to destroy the excess of nitrous compounds, and distilled with precautions to prevent any particles being carried over by projection. The distillate will be free from arsenic.

(*B*) As there is some theoretical danger that the ammonium sulphate might reduce the arsenic acid to arsenious, which would pass over as before, Blondlot recommends that manganese peroxide should be used to oxidise the arsenious acid. The way he proceeds is as follows :—Manganese peroxide is added in the proportion of 4 to 5 grammes to the kilogramme of sulphuric acid, and the mixture heated to boiling in a porcelain dish, stirring all the time. It is allowed to cool, and is then transferred to a retort and distilled.

(*C*) Maxwell Lyte employs a different mode of purification, chiefly with a view to ensuring the complete absence of all nitrous products, and obtaining a pure acid from the very first, and of thereby obviating the necessity of changing the receiver—a most dangerous operation when distilling sulphuric acid. If the acid contains nitrous compounds, heat it in a porcelain capsule to a temperature of about 110° C., with a small portion of oxalic acid, till the latter is completely decomposed and all effervescence has ceased ; about 0·26 to 0·5 per cent. is amply sufficient for nearly all samples of commercial acid. It is best to add the oxalic acid before heating, and to stir constantly till the reaction is completed. Now allow the acid to cool down to about 100° C., and add to it a solution of potassium bichromate in sulphuric acid, or some of the salt itself in fine powder, until the pure green colour at first produced by the formation of chromium sesquioxide is replaced by a yellowish green, indicating an admixture of chromic acid in the free state. The acid so prepared, being now distilled, passes from the first perfectly free from all impurity. The addition of the bichromate has another advantage, viz. that if it be first of all applied to a small sample of the commercial acid, it indicates the presence of free sulphurous acid as well as of arsenious acid, and either of these being present, we may presume the absence of nitrous compounds.

No doubt permanganates would answer equally well; but the potassium bichromate, which is cheap and easily procured, is so convenient as to leave nothing to be desired.

Detection of Gaseous Impurities in Sulphuric Acid

It is essential for some purposes that oil of vitriol should contain neither sulphurous acid nor any of the lower nitrogen oxides; both of these impurities are met with in some commercial samples of oil of vitriol. R. Warington gives the following method for testing for the presence of sulphurous acid and nitrogen oxides:—

About 2 pounds of the oil of vitriol are placed in a bottle, which the liquid half fills; the bottle is then stoppered and violently shaken for a minute or two. The gases contained in the oil of vitriol are thus washed out by the atmospheric air present in the bottle. Sulphurous acid is then tested for by introducing into the air-space of the bottle a slip of paper coloured blue by iodine and starch; the paper is conveniently held in the bottle by means of a wire and a cork. The bleaching of the paper gives evidence of the presence of sulphurous acid.

The test-paper is best prepared from Swedish filter-paper; this is first passed through a well-made solution of starch and then dried. A slip of this paper is next placed in a weak aqueous solution of iodine, where it remains till it has acquired a distinct blue colour. It is then removed, pressed between blotting-paper, and is now ready for use.

The paper thus prepared gradually loses its colour by exposure to air; it should therefore be used as soon as made; for the same reason its exposure to the gas in the bottle should not exceed two or three minutes; no perceptible change of colour will occur in this time if no sulphurous acid be present. The colour of the paper is also at once destroyed by heat; it cannot therefore be used for testing the gases given off by hot liquids.

The nitric oxides are detected by substituting for the first test-paper one imbued with potassium iodide and starch. N_2O_2 forming N_2O_4 on contact with air, and N_2O_3 producing the same compound on contact with air and moisture, the presence of any one of these three oxides will suffice to liberate iodine on the moist test-paper and colour the starch. Since sulphurous acid destroys the blue starch iodide, the presence of an excess of this gas will prevent the detection of the nitric oxide. The nitric oxide is, on the other hand, without effect on the test-paper employed for the sulphurous acid. If, therefore, the sulphurous acid is not in excess, it is quite possible to obtain the reactions of both gases from the same sample of oil of vitriol, and this is no uncommon occurrence with oil of vitriol which has been imperfectly boiled.

In using the reaction here described for the purposes of general

testing, it is to be remembered that sulphuretted hydrogen produces the same effect as sulphurous acid.

Analysis of Sulphuric Anhydride and Fuming Sulphuric Acid

O. Clar and J. Gaier weigh the fuming acid in thin glass bulbs of 20 millimetres in diameter, provided with two long capillary points opposite to each other. The bulbs are half filled with the acid by suction, and are then sealed up at both ends. After weighing, a point is broken off under water. The anhydride is weighed in small glass bottles 58 millimetres high, 17 millimetres wide, with high ground stoppers, enlarged conically above, and with a small aperture in its summit closed with a minute glass plug. The interior of the stopper is filled with glass wool, slightly moistened. The bottle when charged and weighed is allowed to glide in an inverted position into a 2-litre flask held in a sloping position, and containing about 500 c.c. water at 50° to 60°. After mixture has taken place through the small aperture in the stopper, the liquid is made up to 1 litre, and a portion of 100 c.c. is titrated with 5-normal soda.

Detection of Sulphurous and Thiosulphuric Acid

(*A*) Instead of employing hydrochloric acid and zinc, aluminium and hydrochloric acid are preferable. Zinc may be contaminated with sulphur compounds, while aluminium is always pure in this respect; the latter metal, moreover, dissolves very slowly in dilute hydrochloric acid, and therefore the same piece of aluminium may serve for many testings.

(*B*) Dr. Reichardt has distinctly detected the sulphuretted hydrogen when a solution of 1 part of sulphurous acid in water, diluted with 500,000 parts of water, was treated with hydrochloric acid and aluminium.

Estimation of Sulphides and Hydrosulphites

(*A*) If both salts are present together in solution, it is necessary to find the quantity of iodine which a part of the liquid requires if mixed with acetic acid, and the quantity of barium sulphate which an equal part of the solution yields after complete oxidation with bromine. Two equations are thus obtained with two unknown quantities. If a sulphate is also present its quantity is ascertained by adding to the liquid sodium bicarbonate, passing a current of carbonic acid through the liquid, heating after expulsion of the air, and, after the addition of hydrochloric acid in excess, concentrating to a quarter its volume. The sulphurous acid being thus expelled, the sulphur is filtered off, and the sulphuric acid in the filtrate is estimated in the ordinary manner.

(*B*) For the estimation of sulphurous acid in air, B. Proskauer passes a known volume of air through 50 or 75 c.c. of a solution of permanganate containing 15 grammes of the crystalline salt per litre, and 2 or 3 c.c. of hydrochloric acid. The solution is placed in a Bunsen bulb-tube.

PHOSPHORUS

Detection of Phosphorus

When previously well-dried (previous ignition is often required) inorganic combinations of phosphorus are ignited in a pulverised state in a test-tube with small quantities of magnesium wire, ribbon, or powder, there is formed magnesium phosphide. After cooling, the fused mass, on being moistened with water, will disengage phosphuretted hydrogen gas, which, in many instances, will be found to be the spontaneously inflammable variety. Phosphorus may be detected in the same way in organic substances—as, for instance, brains, muscle, &c.—but these should be previously calcined, and the dry animal charcoal so obtained submitted to the experiment.

For the detection of phosphorus in organic liquids, the following modification of Mitscherlich's process will be found to answer well. It consists of an ordinary flask, connected with a receiving-bottle by means of a glass tube, which passes about 18 inches through a glass cylinder filled with cold water. A long straight tube conducts the gaseous products from the bottle. The lamp and flask, and about three-fourths of the glass cylinder, are surrounded with dark paper. The operation is best performed in a dark room.

The phosphorescence of the liquid increases in intensity with the consistence of the liquid and the quantity of the phosphorus. The gas-bubbles are luminous, rise in the mixture, and apparently burn upon its surface with a bright flame. With the temperature the light increases; a photosphere fills the flask, rises in the tube, and moves up and down within the cooled part. Sometimes only a column or a luminous ring appears stationary at the point where the vapours are cooled, and a luminous fog or sparks gradually sink into the receiver, or a sudden, frequently repeated flash of light is observed. If the heat is raised too high, or the cooling is insufficient, the phosphorescence passes through the long gas-tube, at the mouth of which the gases take fire, if the volatile oils from *Cruciferæ* (mustard, &c.) have been present.

Coffee, mustard, smoked meat, highly seasoned food and beverages, and medicines containing odorous gum-resins, volatile oils, musk, camphor, chlorine, &c., have the property of covering the odour of a small portion of phosphorus.

The reaction is not interfered with by the presence of ipecacuanha, tartar emetic, magnesia, hydrated iron oxide, musk, castor, opium, albumin, neutral acid or basic salts and double salts, volatile organic

acids, chlorides, iodides and sulphides, and free acids; but iodine, and mercury chloride and bichloride in considerable proportion, and metallic sulphides in the presence of free sulphuric acid, and particularly *oleum cinæ* (*Artemisiæ*), interfere with or prevent the reaction.

Numerous experiments, by distilling the brain of various animals, blood, albumin, casein, fibrin, legumin, and other protein compounds, with dilute sulphuric acid, have not yielded the least phosphoric reaction.

Detection of Arsenic in Commercial Phosphorus

In preparing dilute phosphoric acid by the oxidation of commercial phosphorus, the precaution should be taken to pass a current of sulphuretted hydrogen through the solution, in order to free it from all substances precipitable by that agent from acid solutions; by this operation arsenic sulphide is frequently thrown down. In order to estimate the amount, Dr. C. J. Rademaker oxidises 100 grammes of phosphorus with nitric acid, dilutes the solution and precipitates the arsenic as sulphide, by means of sulphuretted hydrogen; the solution is allowed to rest for six days, after which the precipitate is collected on a filter and washed, transferred to a small evaporating-dish, oxidised with nitric acid, reduced by means of sulphurous acid to arsenious acid, and again precipitated by means of sulphuretted hydrogen; the precipitate is digested with ammonia to free it from adhering sulphur, the solution filtered, evaporated, dried, and weighed, when the sample under examination was found to amount to nearly 1 gramme of arsenic sulphide.

Phosphorus Holder.—E. Kernan gives the following ingenious method of making a phosphorus crayon which is perfectly safe in the hand for lecture experiments in luminous writing, &c.:—A few inches of lead tube, $\frac{1}{4}$ inch bore, are contracted to an open cone at one end. As much phosphorus as one may choose is put into the cone of the tube; the phosphorus is made to project slightly from the cone; the upper part of the tube is filled with water and corked. To put in the phosphorus, as much as may be required is melted in a conical glass, or test-tube, the cone of which is larger than that of the lead tube. This is put standing in the melted phosphorus, which fills the cone and tube to its own outside level. When cold, there is a nice projecting crayon, from the form of the glass. Any phosphorus outside the lead tube may be melted off. To renew the writing-point, a test-tube, conical below, is fitted to the cone of the lead; the whole is held in warm water for a minute, when sufficient phosphorus flows out to form a new point.

Preparation of Phosphuretted Hydrogen

Prepare zinc phosphide by mixing together amorphous phosphorus with half its weight of powdered zinc, and gently heating the mixture

in a hard glass tube through which a current of dry hydrogen or coal-gas passes. The tube and contents must be cooled in the current of gas. From the zinc phosphide so prepared phosphuretted hydrogen may be readily obtained by means of dilute sulphuric acid or by boiling with caustic potash. The gas is, however, the non-spontaneously combustible kind. The spontaneously combustible gas may be obtained by taking a larger quantity of zinc phosphide and dissolving it in warm dilute sulphuric acid.

Distinction between Phosphates and Arseniates

A. H. Allen remarks that it is well known that the difference in colour between silver phosphate and silver arseniate furnishes the most simple means of distinguishing between the two classes of salts. The presence of free nitric acid or ammonia interfering with the reaction, it is necessary to apply the test to a neutral solution, in which case many other salt radicles may be precipitated. If the phosphate or arseniate be first separated as the ammonio-magnesium salt, it is usual to dissolve this precipitate in nitric or acetic acid before adding silver nitrate. This is quite unnecessary, the characteristic yellow phosphate or brown arseniate being immediately produced on addition of silver nitrate to the crystalline precipitate. This modification renders the test more delicate as the reaction takes place in a neutral liquid. A few streaks on a test-tube show the reaction very distinctly, hardly changing colour if due to phosphate, but turning quite brown if caused by arseniate, in each case becoming soluble in ammonia. On this account the ammonio-magnesium salt must be washed free from ammonia, which would either prevent the reaction or lead to confusion by precipitating brown silver oxide. Acetic acid dissolves both silver phosphate and arseniate, the former far more readily than the latter. If, therefore, acetic acid be gradually added to a mixed precipitate of silver phosphate and arseniate, the phosphate dissolves first, and the brown colour of the arseniate becomes more apparent. If, after the addition of a moderate quantity of acetic acid, the liquid be filtered, the dissolved phosphate may often be detected by cautious neutralisation with ammonia, when the yellow silver phosphate is thrown down; but this reaction is uncertain, as both silver phosphate and arseniate are soluble in ammonium acetate, the phosphate more readily than the arseniate.

Estimation of Phosphoric Acid

1. By the Modified Tin Process (Reynoso's).—(*A*) This method depends upon the fact that, when metallic tin is added in excess to a solution of a phosphate in nitric acid, the stannic acid formed by the oxidation of the metal combines with the phosphoric acid and completely removes it from solution. On filtering, therefore, we at once separate the bases which remain in solution from the insoluble combination of

stannic and phosphoric acids. In order to estimate the amount of phosphoric acid contained in the tin oxide, the compound is dissolved in a small quantity of concentrated potash solution, when the two acids dissolve as metastannate and potassium phosphate; the liquid is now saturated with sulphuretted hydrogen, a small quantity of ammonium pentasulphide added, and, lastly, a slight excess of acetic acid. The tin sulphide is then separated by filtration; all the phosphoric acid is contained in the filtrate, and its amount may be estimated by the ordinary method as magnesium ammonio-phosphate. Two very good modifications of this method have been given.

(*B*) *Modification* 1.—According to the first the substance is dissolved in nitric acid. When there are any difficulties in getting it into solution, dissolve it first in any convenient reagent, then add excess of ammonia to the solution, which precipitates all the phosphoric acid, with most of the bases; well wash the precipitate; it will then be readily soluble in nitric acid.

If, for instance, a specimen of cast iron is being analysed, it must be dissolved in aqua regia; if a refractory mineral, it must be attacked by alkalies, &c.

The nitric solution having been obtained (which should be free from chlorides), throw into it an indefinite quantity of pure tin; about four or five times the supposed weight of the phosphoric acid present may be employed. This tin passing to the state of stannic acid, under the influence of the nitric acid, carries down with it all the phosphoric acid, as well as a great portion of the iron and a little aluminium; wash at first by decantation and then on a filter, and place on one side the nitric solution, which is free from tin, but contains all the bases minus a portion of the iron and aluminium. Then redissolve the precipitate in a small quantity of aqua regia, and, without troubling about the filaments of filter-paper, or the small portions of tin phosphate which may remain undissolved, supersaturate with ammonia, and then add an excess of ammonium sulphide. The stannic acid and tin phosphate immediately dissolve, leaving a black precipitate of iron sulphide containing aluminium; allow it to stand for an hour or two, and then filter, taking care to wash the precipitate with ammonium sulphide to remove the last traces of tin. It is then only necessary to add magnesium sulphate to the filtered liquid to obtain the characteristic precipitate of magnesium ammonio-phosphate. Collect this on a filter, wash it first with ammonium sulphide, then with ammoniacal water, and afterwards calcine in the ordinary manner.

The filter containing the iron sulphide and aluminium is redissolved in nitric acid, and the filtered liquid is added to the original solution of the bases, which may then be separated in the ordinary way.

This method is both simple and rapid; it enables one to estimate the phosphoric acid contained in the most complicated mixtures, and then admits of the accurate separation of the bases.

(*C*) *Modification* 2.—Obtain the phosphate in solution in nitric acid as described above. Concentrate the solution and add the strongest nitric acid (boiling at 86° C.). The nitric acid solution is now in the highest possible state of concentration: on throwing a small quantity of tin into this solution, the metal is rapidly oxidised to stannic acid, and the supernatant liquid remains perfectly clear. The preliminary heating of the solution is indispensable, since in the cold the metal is apt to become passive, when it completely resists the action of the acid. The precipitate is now dissolved in a small quantity of caustic potash, and saturated with sulphuretted hydrogen; on adding acetic acid in slight excess the tin sulphide is precipitated. The precipitate is then separated by means of the Bunsen filter-pump, and the whole of the phosphoric acid is contained in the filtrate. After concentrating the solution, and again filtering from a minute precipitate of tin sulphide, which invariably separates out (tin sulphide being slightly soluble in solutions containing sulphuretted hydrogen), the phosphoric acid may be precipitated as the magnesium-ammonio salt, and weighed as pyrophosphate.

The amount of tin need not exceed four times the weight of the phosphoric acid present. This, however, is the minimum quantity that can be used with safety.

2. Estimation of Phosphoric Acid by the Magnesium Process.—(*A*) The estimation of phosphoric acid in minerals containing fluorine, iron, and aluminium is a matter of considerable difficulty. After dissolving in mineral acids, most authorities advise that the acid solution should be brought to dryness before proceeding to separate the calcium. Some analysts, however, neglect this part of the process, from the impression that it has no influence on the estimation of the phosphoric acid, and that it is only necessary when the siliceous matter is required for a full analysis. T. R. Ogilvie has instituted several experiments to show that this impression is an erroneous one. From them the following are selected :—

(1) A gramme of Cambridge coprolites was dissolved in moderately strong hydrochloric acid, evaporated to dryness, the residue again dissolved in acid, the calcium separated with ammonium oxalate, citric acid added to hold up iron and aluminium, the solution made alkaline with ammonia, and the phosphoric acid precipitated with 'magnesia-mixture.' A perfectly granular precipitate was obtained, which, after standing for twelve hours, was washed, dried, ignited, and weighed, and found to be equivalent to 47·44 per cent. tricalcic phosphate.

(2) Another gramme of the same coprolites was treated in exactly the same way, with the exception that the acid solution was *not* brought to dryness. The magnesium ammonio-phosphate, as it gradually formed, presented the usual appearance; but, when stirred up after a few minutes, a white flocculent body was also observed. After standing for the usual time, the whole precipitate was collected,

washed, dried, ignited, and weighed, and gave 53·04 per cent. calcium phosphate.

(3) A third gramme was treated as in (2), with the difference that, after the addition of citric acid, the solution was made alkaline with ammonia, and allowed to stand. In a short time a white flocculent precipitate formed, which was filtered, washed, dried, ignited, and weighed.

To the clear ammoniacal filtrate, 'magnesia-mixture' was added; and a granular precipitate, free from any flocculent matter, was obtained, equivalent to 47·2 per cent. calcium phosphate. This closely corresponds with the result (viz. 47·44 per cent.) obtained in (1) after evaporating to dryness.

The flocculent precipitate got by ammonia weighed 4·05 per cent. Had it not been removed, it would have been taken as magnesium ammonio-phosphate, and, as such, been equivalent to 5·66 per cent. calcium phosphate; this, added to 47·2 per cent., gives 52·86 per cent., against 53·04 per cent. found in (2) by weighing the flocculent precipitate along with the magnesium ammonio-phosphate.

In these experiments, care was taken that the calcium was perfectly separated, and that sufficient citric acid was present to hold up iron and aluminium.

The precipitate which forms on the addition of ammonia to the citric acid solution when the material has not, at the outset of the process, been brought to dryness, consists of silica, alumina, and iron sesquioxide as silicate, and, when carefully washed, is free from phosphoric acid. In the case of sombrerite, some magnesium ammonio-phosphate would also come down, owing to the presence of a considerable quantity of magnesium in that mineral. But, with coprolites and other phosphatic minerals, which contain only minute quantities of magnesium, neither phosphoric acid nor magnesium is found, unless the flocculent precipitate is not filtered from the solution for a few hours.

All phosphatic minerals which contain fluorine, iron oxide, and alumina give this precipitate.

Those minerals containing fluorine, and only a trace of iron and aluminium, such as Canadian apatite and Spanish phosphorite, give no appreciable flocculent precipitate. A sample of sombrerite was also examined, but, as it was exceptionally free from iron and aluminium, it gave no flocculent precipitate.

It may be mentioned that, when coprolite, or other ferruginous phosphatic mineral, is moistened with sulphuric acid, gently heated, and the fluosilicic acid which forms driven off, then dissolved in hydrochloric acid, and the calcium removed without the solution being brought to dryness, no flocculent precipitate is obtained.

It would thus seem that, in the analysis of the majority of the phosphatic minerals at present in use by manure manufacturers,

special care must be taken to obtain a pure and perfectly granular precipitate of magnesium ammonio-phosphate, either by evaporating the acid solution to dryness, or by separating the precipitate which forms on the addition of ammonia to the solution containing citric acid; otherwise an erroneously high result is obtained.

(*B*) For the rapid estimation of phosphoric acid, magnesia, and lime, G. Ville proceeds as follows:—Attack in the cold 2 grammes of phosphate with 50 c.c. of hydrochloric acid or weak nitric acid, and filter it. Take 5 c.c. of this solution, add at first some citric acid, then ammonia in excess, and lastly precipitate by a solution of magnesium chloride, the liquid being maintained ammoniacal.

The phosphoric acid deposits in the form of magnesium ammonio-phosphate. By means of the exhausting filter (figs. 21, 22), separate it from the supernatant liquid, wash it with ammoniacal water, exhaust again, and finally estimate the precipitate by means of uranium acetate, according to Leconte's process.

Suppose we have to analyse calcium superphosphates of commerce. The necessity of distinguishing phosphoric acid which is in the soluble state from that which is in the insoluble state, requires two parallel attacks, one with distilled water and the other with weak nitric acid. The operation is always the same. Work on each liquid separately, as just pointed out in the case of natural phosphates.

A glance at the accompanying drawing of the apparatus that has so much expedited the work is sufficient to understand the arrangement and mode of action (figs. 21, 22).

An exhaustion is formed equal to some centimetres of mercury in the globe, D, by the help of a small hand-pump. The base of the cone,

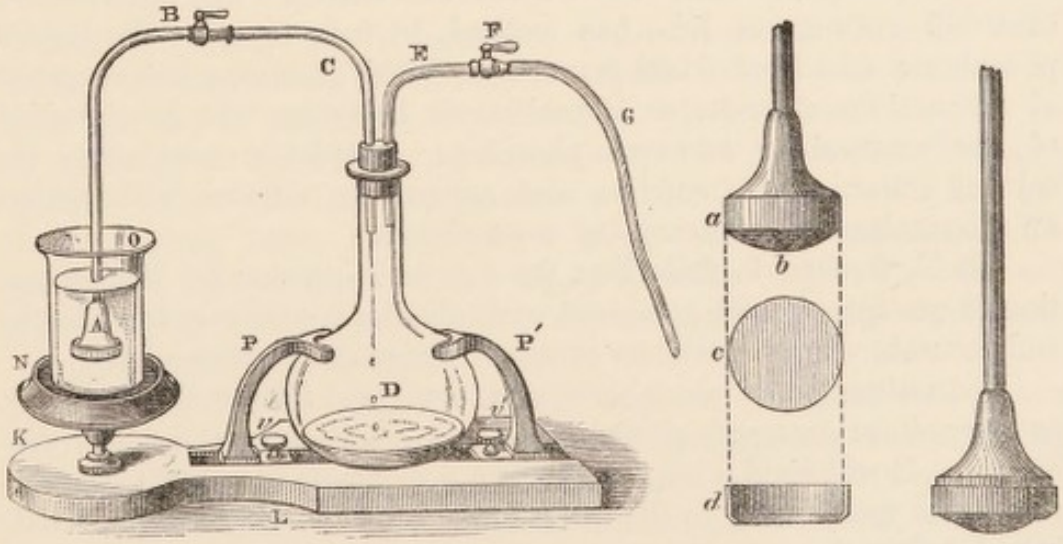


FIG. 21.

A, *a*, *b*, covered with one or two discs of blotting-paper *c*, held in place by a ring, *d*, fitting tightly by friction, works as a true filter, which acts under pressure.

Two forms of apparatus have been made, one of platinum (fig. 21), and the other of glass (fig. 22). The fragility of the latter is obviated by means of the consolidation arm, M, which firmly fixes the exhausting tube.

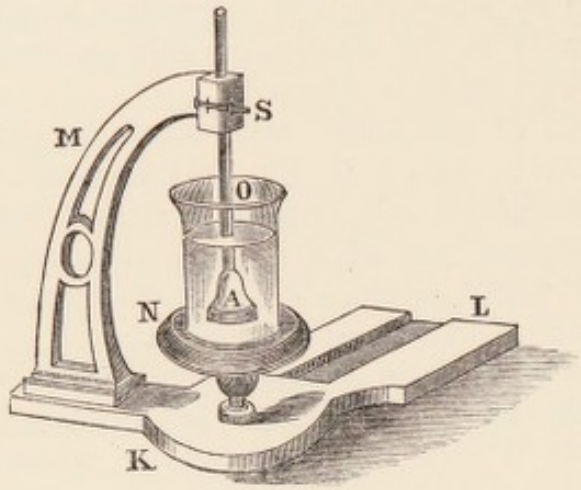


Fig. 22.

In order to render the precipitation almost instantaneous, it is necessary to operate on a moderate quantity of phosphate, and to employ an excess of magnesium chloride. With a small quantity of chloride the precipitation is slow, with an excess it is immediate. After waiting a quarter of an hour, we may proceed with the estimation of phosphoric acid, only the filtration takes a little longer; after an hour the result is perfect.

An excess of ammonium citrate holds in solution very appreciable quantities of magnesium ammonio-phosphate; the loss, however, which results from it is very slight. For 0·05 gramme of phosphoric acid, and after waiting eighteen hours, not less than 6·852 grammes of citric acid were required to retain in the solution 0·002 gramme of the phosphoric acid. When the quantity of citric acid employed is from 80 to 100 times that of the phosphoric acid, there is no loss. On the contrary, the presence of lime completely changes the results.

Calcium citrate dissolves nearly three times more magnesium ammonio-phosphate than does ammonium citrate. The intervention of 0·059 gramme of lime has sufficed, in fact, to raise the loss of phosphoric acid from 0·002 gramme to 0·006 gramme; but an excess of magnesium chloride, so efficacious in hastening the precipitation of the magnesium ammonio-phosphate, completely neutralises the solvent action of the calcium and ammonium citrates, and confers on the results both accuracy and concordance.

(*C*) T. R. Ogilvie finds that the magnesia process for the estimation of phosphoric acid combined with alkalies is perfectly trustworthy and accurate when a moderate excess of magnesia-mixture is used.

The estimation of phosphoric acid, combined fully with lime only, as magnesium ammonio-phosphate, is not satisfactory under any conditions. It will yield a low result when a moderate excess of magnesia-mixture is used, owing to the solvent action of the ammonium oxalate introduced in the act of removing the alkaline earth; or a high result when a greater quantity of magnesia-mixture is used.

The estimation of phosphoric acid, combined with lime and iron and alumina as magnesium ammonio-phosphate, is also unsatisfactory, owing to the combined action of ammonium oxalate and ammonium

citrate. High or low results may be got, according to the quantities of these salts and of magnesia-mixture present.

Precipitation in boiling solution, or reprecipitation, will not fully remedy the errors incident to the use of the reagents mentioned.

By the judicious use of the reagents the least error that may be anticipated in the estimation of calcium phosphates by this process is 1·27 per cent., and in the estimation of phosphates containing iron and alumina oxide 1·01 per cent., while, by the indiscriminate use of reagents, errors up to 10 per cent. or 12 per cent. may be introduced.

As to the special result of this investigation, Ogilvie condemns the use of this process in the analyses of phosphates containing iron and alumina, unless in cases in which the results are expected to be merely *closely approximate*. In all analyses that are to be the basis of money valuation or of scientific statements, the molybdate or other method should certainly precede precipitation with magnesia.

(*D*) Professor Tollens states that if a precipitate of magnesium ammonio-phosphate is contaminated with magnesium or calcium tri-phosphate, caustic lime, or magnesia, or the citrates of these bases, there is obtained on ignition a white mass, which, if covered with silver nitrate and heated quickly, turns yellow. This test should be especially applied when citric solutions of phosphates are directly precipitated with magnesia-mixture.

(*E*) Joulie uses the following modified magnesia process. He employs as a precipitating solution—

Citric acid	400 grammes
Magnesium carbonate	20 „
Distilled water	200 „

When the magnesium carbonate is quite dissolved, 500 cubic centimetres of ammonia at 22° Baumé are added. The liquid becomes hot, and the rest of the citric acid dissolves. It is allowed to cool, and is made up to the volume of a litre with distilled water, filtering if needful. The solution is permanent; it is decidedly acid, but only heats slightly when mixed with a large excess of ammonia. The precipitate thrown down by this liquid is redissolved on the filter with dilute nitric acid, reprecipitated with ammonia, collected and again washed, ignited and weighed.

(*F*) An equally accurate result may be obtained with greater speed by estimating the phosphoric acid contained in the precipitate volumetrically by means of a standard solution of uranium nitrate.

Dr. Carl Mohr remarks:—This method of treatment introduces into the solution too large a quantity of neutral ammoniacal salts, which are known to have a retarding effect on the appearance of the final reaction with potassium ferrocyanide. It is also known that large quantities of neutral calcium and alkaline salts have the same disturbing influence, rendering the results always too high. It is

hence of great importance, in estimations with uranium, to keep within the boundaries which were observed in standardising the solution. This state of affairs has led the author to obtain a double standard for his uranium solution : the one for solutions poor in lime, such as superphosphates, Mejillones' guano, &c. ; and the other for solutions rich in lime, like the marl phosphates. The differences are not very considerable, but still enough to have a noticeable effect in the result. Thus for superphosphates 1 c.c. of the uranium solution represented 0·0041 phosphoric acid, but for marl phosphates only 0·0039 gramme.

The author has undertaken to estimate, by a series of comparative experiments, the influence of combined ammonia in titrating magnesium ammonio-phosphate with uranium, and also to decide how far this ammonium compound has a retarding action upon the appearance of the final reaction. For this purpose he prepared a solution of pure calcium phosphate in dilute nitric acid. In one series of experiments portions of 10 c.c. of this solution were mixed with sodium acetate and titrated with uranium. In the second series the lime was thrown down with ammonium oxalate, and the phosphoric acid with magnesia. In both series equal quantities of uranium solution would be consumed if the ammonium compound had no disturbing influence.

In direct titration the average quantity of uranium solution consumed was 9·46 c.c. If the phosphoric acid was precipitated as magnesium ammonio-phosphate, dissolved and titrated, the average was 9·37.

These experiments prove that there is a sufficient agreement between the two processes if, in using the second or indirect method, the precaution is adopted of allowing the precipitate and filter to stand for some time in a warm place, so that the free ammonia of the washing-water may evaporate.

E. W. Parnell considers that the correction of 1 milligramme for every 54 c.c. of filtrate and washings is unnecessary, and that the two ammoniacal solutions should be raised to a boil before being mixed, to prevent an excess of the base from being carried down.

(*G*) The Committee of the British Association are of opinion that magnesium sulphate should be abandoned in favour of the chloride.

The volume of magnesia-mixture employed for the precipitation should only be in moderate excess of the amount necessary to completely precipitate the phosphate present.

The use of a large excess of the precipitate causes a more rapid separation of the double phosphate, but is attended with such a serious tendency to error that any advantage gained is more than counterbalanced. The precipitation should be conducted in the cold. The proportion of free ammonia in the liquid should be large.

If the above precautions are duly observed, and silica, fluorine, iron, and aluminium be previously removed, it will rarely be necessary to purify the precipitate by solution in acid and reprecipitation with

ammonia. In reprecipitating, some magnesia-mixture should be added, as its presence tends to reduce the solubility of the precipitate in the ammoniacal liquid.

In igniting the precipitate, the heat should be very gentle at first, and afterwards be raised as high as possible. If citric acid has been employed, the ignited precipitate is often discoloured. This may be remedied by cautious treatment in the crucible with strong nitric acid, followed by re-ignition.

If the precipitate of magnesium ammonio-phosphate be titrated by standard solution of uranium instead of being weighed, many of the above precautions are superfluous.

Concerning the usual method of estimating magnesium ammonio-phosphate by ignition as magnesium pyrophosphate, Dr. Broockmann remarks that it involves certain sources of error which cannot be avoided, even with the utmost care. Such are the double salts creeping up the sides of the beaker and of the funnel, so that it is not readily brought into the filter without loss; then there is loss in the form of dust on introduction into the crucible; and, thirdly, there are variations in the ash of the filter. To avoid these sources of error the author dissolves the washed precipitate direct from the filter, and any particles present in the beaker, in nitric acid, places the solution in a weighed crucible, evaporates to dryness, and ignites.

3. Estimation of Phosphoric Acid by the Uranium Process. In the analysis of manures, coprolites, bone-ash, and similar commercial substances, the magnesium process for estimating phosphoric acid is beset with so many difficulties that it is worth while to look for some other method by which the same end can be attained without the expenditure of so much time and trouble.

(*A*) Sutton strongly recommends the uranium process, which he considers to be equally accurate with the magnesium process, and far preferable to it in readiness of application and general convenience. One of the chief advantages connected with the use of uranium as a means of estimating phosphoric acid in calcium phosphates, &c., is that the presence of acids does not interfere with the result.

The metals which admit of this mode of estimation are, so far as present experiments have proved, potassium, sodium, calcium, magnesium, iron, and aluminium; the two latter only, however, with modifications of the process as applied to the former. These modifications are given further on.

In the presence of potassium, sodium, magnesium, calcium, and barium, the following course must be adopted :—

The substance is to be dissolved if possible in acetic acid; if, however, this cannot be done, a nitric, hydrochloric, or sulphuric acid solution is admissible, taking the precaution to avoid any great excess of acid; add ammonia in excess, and redissolve the precipitate in acetic acid; in the presence of mineral acids it is advisable to add ammonium

acetate as well as acetic acid. Lastly, add a solution of uranium acetate (best obtained by dissolving pure uranium ammonio-carbonate in acetic acid) and heat to boiling, by which means the phosphoric acid is completely separated as uranium and ammonium phosphate.

This precipitate is of a greenish-yellow colour and somewhat slimy in its nature; therefore in order to prevent the pores of the filter from being choked by it, it must be treated in the following manner:—After boiling, set aside on the sand-bath, and allow the precipitate to settle; when the supernatant liquid is clear, decant through the filter, pour water over the precipitate, and again boil for a few moments; decant as before, taking care that the precipitate has entirely subsided; repeat the process three or four times until the sliminess of the precipitate has given place to a feathery appearance, then pour it out upon the filter and complete the washing in the usual way.

(*B*) The above process may be hastened somewhat by adding to the liquid in which the precipitate is first suspended, after it has somewhat cooled, a few drops of chloroform; then vigorously stirring the liquid or boiling it up once or twice causes the precipitate to settle more rapidly.

The uranium and ammonium phosphate thus obtained is totally insoluble in water and acetic acid, but easily so in mineral acids; the addition, however, of a sufficient excess of ammonium acetate throws it down completely again on boiling. On burning the precipitate the ammonia is driven off, and a lemon-coloured phosphate of uranium sesquioxide is obtained. If, however, carbon or any reducing gas is present during the burning of the precipitate, it is partly reduced to phosphate of uranium protoxide, of a green colour; but on moistening it with nitric acid and again heating, the yellow colour of the higher oxide is reproduced.

It is therefore advisable in burning the precipitate to separate it from the filter, first burning the latter, then adding the former, and heating to redness until every trace of carbon is removed. As a precaution against partial reduction it is advisable in all cases to moisten the precipitate when cool with nitric acid, and again heat to redness. The burning may take place in an open platinum crucible, and as the precipitate is scarcely hygroscopic it may be weighed uncovered.

If it should be necessary to redissolve the precipitate in order to estimate the phosphoric acid afresh, the solution must be preceded by melting the precipitate with a considerable excess of sodium carbonate so as to convert the pyrophosphoric into tribasic phosphoric acid.

The composition of the uranium phosphate is as follows:—

		Per cent.
$2Ur_2O_3$	285·6	80·01
P_2O_5	71·0	19·99
	356·6	100·00

Therefore $\frac{1}{5}$ of the precipitate may be calculated as phosphoric acid.

This process has been used for the estimation of phosphoric acid in guanos, the so-called lime, bone-ash, coprolite, &c. superphosphates, in above a hundred analyses, and in many of them the results controlled by other methods, without one instance of inaccuracy or failure. In the more delicate process of urinary analysis it has been found equally reliable.

Special Precautions to be taken when Iron is present.—When a compound containing iron as well as phosphoric acid is submitted to analysis by the uranium process, the precipitate of uranium-phosphate invariably carries down a portion of iron with it. In this case the colour of the precipitate is altered to a dirty orange-yellow, and possesses a somewhat granular appearance. The quantity of iron depends in some measure upon the length of time the mixture has been kept at a boiling heat. If the boiling be continued for about twenty minutes, the iron is entirely removed from the precipitate, and the solution is coloured red by acetate of iron sesquioxide. The better way, however, is not to depend upon this mode of separation, but to reduce the iron sesquioxide to protoxide by means of uranium protochloride.

The compound is to be dissolved in the smallest possible quantity of hydrochloric acid (at most 1½ ounce) and the solution of uranium protochloride added in sufficient quantity to produce a distinct green colour, or until one drop of potassium sulphocyanide does not show a change to red. Now add ammonia in sufficient quantity to neutralise the free hydrochloric acid, making sure by throwing into the mixture a small piece of litmus-paper. Add a solution of uranium acetate and free acid, together with a few drops of acetate of uranium protoxide (obtained by precipitating the protochloride with ammonia and redissolving in warm acetic acid), to ensure the presence of sufficient protoxide, and heat to boiling.

The mixture must now possess a distinct greenish colour, not a dirty tinge, which shows the presence of undissolved uranium protoxide. Put aside until the precipitate has settled; when this has *completely* taken place, decant the supernatant liquid through the filter; pour hot water over the precipitate, adding some ammonium chloride, and boil again; repeat the operation once more, and the washing is complete; the precipitate may now be thrown upon the filter, dried, and burned as described at the commencement of this process.

Preparation of Uranium Protochloride.—It may not be amiss here to give the best method of preparing a solution of uranium protochloride, which promises to be a most serviceable reducing agent in analysis.

Uranium ammonio-carbonate is to be dissolved in about twice as much hydrochloric acid (diluted with an equal quantity of water) as is necessary for solution. A concentrated solution of platinum bichloride is added in the proportion of about 2 drops to each ounce of uranium-salt; fine shreds of copper are then to be added in excess,

and the mixture boiled for ten or fifteen minutes, or until the liquid assumes a distinct green colour, and the uranium sesquichloride is reduced to protochloride.

In order to remove the copper protochloride from the solution it is now to be boiled until, on adding a few drops to some water, an immediate precipitate is produced. Half an hour's boiling is generally sufficient to attain this end. The solution is then to be diluted pretty freely with water, and set aside to cool. When perfectly cold, the copper will in great measure be separated. Sulphuretted hydrogen, however, must be passed through the filtered solution till every trace of copper is precipitated and the liquid smells strongly of the acid.

The filtered liquid is now to be poured into a porcelain capsule, and evaporated at a boiling heat, adding some considerable quantity of ammonium chloride to prevent the precipitation of protoxide and uranium sulphide, which would otherwise be the case.

As the sulphuretted hydrogen is very difficult to remove, the evaporation must be carried on till the liquid corresponding to each ounce of the original uranium salt is reduced to about 3 ounces. It is absolutely necessary that every trace be removed. If at the end of the operation a precipitate has occurred, it may be dissolved in a little concentrated hydrochloric acid after the clear green liquid has been poured off, and the two solutions mixed and kept for use.

The solution so prepared contains ammonium chloride, which is of no consequence for the purpose here contemplated; neither is it any hindrance to the preparation of the pure crystals of uranium protochloride, as on adding excess of ammonia the uranium is precipitated and can be redissolved.

The value of this solution as a means of reducing iron sesquioxide to protoxide (and probably other higher oxides to lower) cannot be too highly estimated, for at ordinary temperatures it takes place speedily, but at boiling heat immediately: moreover, the change is visible to the eye, for the reddish colour of the solution gives place to green, and so long as this is the case the iron exists in the form of protoxide.

The delicacy of this reaction may be readily seen, if to a solution of iron sesquichloride a drop or two of potassium sulphocyanide be added, which produces a blood-red colour: add now a few drops of the uranium solution, and immediately the colour turns to green, showing that a reduction has taken place; this reaction may be made over and over again by adding first iron and then uranium.

(*C*) Concerning the uranium method A. Kitchin remarks that the chief points required are a sufficient amount of ammonium acetate, and not too much free acid present; if these precautions are adopted the precipitate settles in a few minutes. The washing is best done first by decantation, boiling up after each fresh addition of water, and lastly on the filter. After drying, the precipitate is strongly ignited

until the filter is consumed; then a little nitric acid added, evaporated to dryness, and finally gently ignited; the residue should be of a full yellow colour. If, in the final ignition, too much heat be applied, the uranium phosphate is reduced to a considerable extent, and turns a greenish colour; a second evaporation with nitric acid is then necessary.

(*D*) F. Jean dissolves the phosphatic matter in nitric acid, and the solution, separated by filtration from insoluble matter, is mixed with a slight excess of ammonia. Citric acid is then added, which dissolves the precipitate formed by the ammonia, and yields a perfectly clear and acid solution, which is boiled for some time with uranium acetate. The yellowish precipitate formed is collected on a filter, washed with boiling water, dried, ignited, and weighed. It contains 20·04 per cent. of phosphoric acid. The filtrate on examination with ammonium molybdate is found free from phosphoric acid.

(*E*) Dr. Carl Mohr formerly proposed a process for estimating phosphoric acid with uranium in presence of iron. He has now adopted a modification. In his original memoir he proposed to throw down the ferruginous solution of phosphate partially with uranium, and then to add so much potassium ferrocyanide as suffices for transforming the ferric phosphate. This transformation is often incomplete if but little iron oxide is present, as in animal charcoal and guano. It is therefore better to throw down the iron with potassium ferrocyanide before precipitating the phosphoric acid. Filtration is in either case unnecessary. Instead of precipitating the iron with pulverised potassium ferrocyanide, as directed in the author's first memoir, he prefers a 5-per-cent. solution, which is introduced into a small bulb-pipette drawn out below to a fine orifice. To regulate the outflow of the liquid a glass tap is adapted below the bulb.

When precipitating a ferruginous phosphatic solution it is needful to ascertain previously how many drops of the ferrocyanide solution are necessary. The solution is added carefully till a drop of the liquid gives a faint reddish or brown colouration. To a second portion there are added 1 or 2 drops fewer, and it is ascertained by a second test with uranium solution if the precipitation-point has been reached. It is necessary to count the drops exactly. In metallurgical or mining establishments where ores of the same class are always examined, a single estimation of the number of drops is sufficient to show how much ferrocyanide solution is always to be used for the precipitation of the iron.

4. **Estimation of Phosphoric Acid by the Bismuth Process.**—(*A*) Take 2 grammes of the very finely pulverised phosphorite; put the weighed mineral into a flask, or glass beaker, and pour over it about 7 c.c. of nitric acid free from chlorine, and of 1·25 sp. gr. Heat the vessel and its contents for about half an hour nearly to the boiling-point, dilute with pure distilled water and filter; add to the well-washed

filtrate as much water as will suffice to make up a quantity of 500 c.c. Take 100 c.c. of this liquid, representing 0·4 gramme of phosphorite; add another 100 c.c. of pure distilled water, heat to the boiling-point, and precipitate the hot liquid by the addition of a solution of bismuth nitrate prepared in the following manner:—

Take crystallised bismuth nitrate, dissolve in water; add as much nitric acid as is required to prevent precipitation on the addition of more water; make up the solution in such a manner as to obtain a litre of liquid containing 26 grammes of bismuth.

The precipitate, occasioned by the addition of the bismuth solution to the solution of phosphorite, is left standing till quite cold, and is then filtered off, the precipitate being washed with cold water. Next, the bismuth phosphate is dissolved, while on the filter, in a few drops of hydrochloric acid, and the solution is treated with ammonia and ammonium sulphide, and gently heated, until all the bismuth has been converted into sulphide. When this has been effected, the liquid is acidified with acetic acid, and heated to near the boiling-point; the precipitate is then collected on a filter, the last traces of sulphuretted hydrogen being eliminated by a few drops of chlorine water.

The phosphoric acid is estimated in the acetic acid solution by the uranium process.

(*B*) A. Adriaanzs gives the following modification of the bismuth process for estimating phosphoric acid in presence of iron and alumina. To the hydrochloric solution of the substance in which the phosphoric acid is to be estimated, sodium thiosulphate is added first, so as to reduce the iron peroxide to protoxide; next, bismuth nitrate is added, and the vessel containing the substances heated for about four hours on a water-bath. The precipitate which is formed is filtered off after twenty-four hours, and after having been well washed is dissolved in nitric acid. The hydrochloric and sulphuric acids present in this solution are next eliminated by means of silver nitrate and barium nitrate, while the phosphoric acid is afterwards thrown down by means of bismuth nitrate. The bismuth phosphate precipitate is collected on a filter, washed, and lastly dissolved in hydrochloric acid, and estimated as magnesium ammonio-phosphate in the presence of ammonium citrate. This process may even be employed when the substance contains fifty times more alumina than phosphoric acid; but if the proportion of alumina be very large, it is best to add to the substance a weighed quantity of pure sodium phosphate. If the iron happens to be present in very large excess, it is necessary to re-dissolve the first bismuth precipitate and reprecipitate it a second time.

5. Estimation of Phosphoric Acid by the Lead Process.—For the estimation of phosphoric acid in coprolite or sombrerite, which contains a considerable amount of iron and aluminium, besides calcium, magnesium, &c., Warington considers that very few of the

processes usually recommended for the estimation of phosphoric acid are here applicable. The molybdic acid method is inadmissible from the large amount of phosphoric acid to be estimated. The mercurial method fails owing to the presence of aluminium. The uranium method can be employed only if the iron be previously reduced by means of uranium protochloride. The tin method is free from all these objections, and is no doubt, when carefully conducted, an excellent one, but the time it takes up is considerable. The process which Warington prefers is given below.

The subject divides itself into two parts: the estimation of phosphoric acid and of the alkaline earths, and the estimation of iron and aluminium.

The nitric acid solution[1] of the mineral, previously freed from silica in the usual way, is treated cautiously with dilute ammonia to remove all unnecessary excess of acid; the clear liquid is then treated in one of two ways: either an excess of neutral lead acetate is added, or the solution is treated with lead nitrate, and digested with successive portions of finely powdered litharge till slightly alkaline, the liquid in this case being finally acidified with a few drops of acetic acid. The former plan is generally to be preferred, though the precipitate is considerably more bulky, as only a portion of the iron, and probably none of the aluminium, is in this case precipitated with the phosphoric acid.

The precipitated lead phosphate is warmed for some minutes to induce aggregation, and then thoroughly washed by decantation, the washings being filtered. The washing-water should be slightly warm, and contain a little ammonium acetate, otherwise the filtrate is apt to be turbid.

There are several ways of treating the precipitate. It may be dissolved in nitric acid (which for this purpose must not be too weak), the solution diluted and the lead precipitated by means of sulphuretted hydrogen; or the nitric solution may be treated with an excess of sulphuric acid and the lead precipitated as sulphate. The first plan is unexceptionable and yields excellent results; the necessary dilution entails, however, a subsequent concentration which occupies some time. If lead acetate has been used, the best plan for ordinary purposes is to treat the lead phosphate with oxalic acid and a few drops of potassium oxalate. The decomposition is rapid and complete; the lead oxalate may after a short time be separated by filtration. Oxalic acid does not perfectly decompose the densely aggregated precipitate obtained with lead nitrate and litharge. The action of sulphuric acid on the precipitate is incomplete, whether lead acetate or nitrate has

[1] When nitric acid alone is used to effect the solution of a coprolite, a trace of phosphoric acid is sometimes left with the silica; it is therefore safest to dissolve in hydrochloric acid, and after evaporation to dryness to redissolve with nitric acid.

been employed. Lead oxalate is nearly insoluble in oxalic acid; its solution, if treated with sulphuretted hydrogen water, appears only very slightly discoloured when looking through a depth of several inches.

The lead being separated, the solution now contains the whole of the phosphoric acid with a little iron; some citric acid is added and an excess of ammonia; the clear solution is finally treated with 'magnesia-mixture,' and the phosphoric acid separated in the usual way.

The calcium, magnesium, and alkalies are readily estimated in the original filtrate from the lead phosphate, the excess of lead being first precipitated by means of sulphuretted hydrogen. A little citric acid must be added before the solution is made ammoniacal for the estimation of the magnesium, to hold in solution the iron and aluminium. This method has the advantage of speed, and admits of the convenient estimation of all the bases except iron and aluminium. It is applicable to the analysis of all the phosphates employed in agriculture.

6. **Estimation of Phosphoric Acid by Means of Mercury.**—The nitric acid solution of the phosphate is evaporated to dryness with excess of metallic mercury, the residue collected and washed, mixed when dry with sodium carbonate, and very gradually heated to fusion. The fused mass is dissolved in water, neutralised with acid, and the phosphoric acid estimated as magnesium ammonio-phosphate. This method gives very accurate results.

7. **Estimation of Phosphoric Acid by Means of Iron.**—Dissolve the phosphate in acid, add to the solution iron perchloride, and then excess of sodium acetate. Boil for some time till the whole of the iron is precipitated. The whole of the phosphoric acid will come down with the iron.

If the substance under analysis is free from iron or aluminium, the iron perchloride should be added in known quantities from a standard solution. Upon now washing, drying, and weighing the precipitate, the excess of weight over that due to the iron sesquioxide present represents phosphoric acid.

If, however, iron or aluminium is present, the precipitate is dissolved in hydrochloric acid, citric acid is added, and the phosphoric acid precipitated by 'magnesia-mixture.' Were it not for the inconvenience of working with so large a bulk of iron precipitate, this process would leave little to be desired.

8. **Estimation of Phosphoric Acid by the Molybdic Acid Process.**—(*A*) To the nitric acid solution of the phosphate, add a large excess of solution of ammonium molybdate in nitric acid; a yellow precipitate of ammonium phospho-molybdate falls down, which is almost insoluble in acids. Allow the mixture to stand in a warm place for a day, filter, and wash with a dilute acid solution of ammonium molybdate. Dissolve the precipitate in ammonia, and to the

clear solution add 'magnesia-mixture.' This process is very accurate when small quantities of phosphoric acid have to be estimated in the presence of large quantities of iron or aluminium. No arsenic or silicic acid must be present, as it would precipitate with the molybdenum solution, and afterwards with the magnesia-mixture. According to Nuntzinger's analysis of ammonium phospho-molybdate, after drying at 212° F. it contains 3·577 per cent. of ammonium oxide, 3·962 per cent. of phosphoric acid, and 92·461 per cent. of molybdic acid.

(*B*) The following process has proved satisfactory in the experience of many years :—

From 25 to 50 c.c. of the solution of the phosphate, which may contain from 0·1 to 0·15 gramme phosphoric acid, are placed in a porcelain capsule with the addition of 100 to 150 c.c. molybdic solution. The mixture is heated on the water-bath, with occasional stirring, to about 80°, set aside for an hour, filtered through a plain filter, and the yellow precipitate (which need not be entirely rinsed on to the filter) is washed with dilute molybdic solution. The porcelain capsule is then placed under the funnel, the filter is pierced with a platinum wire, and the precipitate is washed into the capsule with dilute ammonia ($2\frac{1}{2}$ per cent.), washing the filter-paper well, dissolved, stirring with the glass rod, and the solution washed into a beaker with ammonia of the same strength, enough of which is added to make up a volume of 100 c.c. About 15 c.c. of magnesium chloride mixture are then gradually dropped in, constantly stirring. After the mixture has been set aside for two hours, covered with a glass plate, it is filtered through a plain filter, the weight of the ash being known, and the precipitate is washed with dilute ammonia of the same strength till a portion of the filtrate, after being acidulated with nitric acid, does not show the presence of chlorine with silver nitrate. The dried precipitate is separated from the filter, and placed in a porcelain crucible; the paper is charred but not incinerated, and the char placed in the crucible, which is heated first gently, then ignited strongly for ten minutes in a slanting position over a Bunsen burner, and finally exposed for five minutes to a blast-flame, cooled in the desiccator, dried, and weighed.

The first 6 or 8 c.c. of the magnesia-mixture should be added very cautiously.

The final ignition before the blast serves to volatilise any traces of molybdic acid which may have been precipitated.

(*C*) The molybdic process is used under the following conditions at the Halle Agricultural Station :—A quantity of the sample is taken containing from 0·1 to 0·2 gramme phosphoric acid. The bulk of the solution should be from 50 to 100 c.c. The molybdic solution is prepared by dissolving 150 grammes of ammonium molybdate in 1 litre of water, and pouring this into 1 litre of pure nitric acid. The quantity of the solution used should be such that for 1 part of phosphoric acid present there should be 50 parts of molybdic acid. Hence about

100 c.c. of the above solution are necessary for 0·1 gramme of phosphoric acid. A large excess of molybdic acid is not to be desired, since a certain quantity of free molybdic acid is almost always deposited, and does not readily redissolve in ammonia. For the complete precipitation of the phosphoric acid it is sufficient to allow the mixture to digest from four to six hours at 50° C. After cooling, the yellow precipitate is filtered, and washed with a mixture of the molybdic solution and water, equal parts. The yellow precipitate is dissolved on the filter with *hot* ammonia, 1 part of commercial ammonia to 3 parts of water. As little as possible is used, and the excess is neutralised with hydrochloric acid, which is added as long as the precipitate formed redissolves quickly. The liquid must then be cooled before adding the magnesia-mixture, as, if it is hot, basic magnesium salts are sometimes thrown down. The magnesia-mixture is made up with 110 grammes crystalline magnesium chloride, 140 ammonium chloride, 700 liquid ammonia, and 1300 water. To precipitate 0·1 gramme of phosphoric acid we require 10 c.c. of this mixture. After adding the magnesia-mixture, pour in $\frac{1}{3}$ of its volume of concentrated liquid ammonia. The total bulk of the liquid should not exceed 100 to 110 c.c. In three or four hours the precipitate is ready for filtration.

The precipitate is washed on the filter with dilute ammonia (3 : 1) until chlorine can no longer be detected in the filtrate. No subsequent correction is needful. When dry, the precipitate is removed from the filter (which is burnt separately). The flame must be feeble at first, and be gradually increased. It is finally ignited with the gas blowpipe.

(*D*) Drs. Stunkel and Wetzke and Professor Wagner have examined the conditions upon which the accuracy of the molybdic method depends, and give the following as the best means of carrying out this process :—From 20 to 25 c.c. of a solution of phosphate free from silica, and containing 0·1 to 0·2 gramme of phosphoric acid, are placed in a beaker, and mixed with so much solution of ammonium nitrate (see below), and so much molybdic solution, that the total liquid may contain 15 per cent. ammonium nitrate, and not less than 50 c.c. of molybdic solution per 0·1 gramme phosphoric acid. The contents of the beaker are heated to 80° or 90° in the water-bath, set aside for an hour, filtered, and the precipitate washed with dilute ammonium nitrate. The beaker is now set under the funnel, the filter pierced with a platinum wire, the precipitate rinsed into the beaker with ammonia at $2\frac{1}{2}$ per cent., washing the filter-paper well. It is then dissolved, stirred with a glass rod, and ultimately so much of the weak ammonia added as to make up the volume of the liquid to about 75 c.c. To 0·1 gramme of phosphoric acid 10 c.c. magnesia-mixture are dropped in, stirring continually ; the beaker is covered with a glass plate, and set aside for two hours. The precipitate is then filtered off, washed with ammonia at

2 per cent., and dried. The precipitate is introduced into a platinum crucible, putting in also the rolled-up filter; the crucible is covered and heated till the filter is carbonised. It is then placed in a slanting position in the flame of a Bunsen burner for ten minutes, and is afterwards ignited before the blast for five minutes, allowed to cool in the desiccator, and weighed.

The strength of the solutions to be employed is as follows :—

(1) *Molybdic Solution.*—150 grammes ammonium molybdate are dissolved in water, so as to make 1 litre, and poured into 1 litre nitric acid of sp. gr. 1·2.

(2) *Concentrated Solution Ammonium Nitrate.*—750 grammes ammonium nitrate dissolved in water to the bulk of 1 litre.

(3) *Dilute Solution Ammonium Nitrate.*—100 grammes ammonium nitrate dissolved in water to the bulk of 1 litre.

(4) *Magnesia-Mixture.*—55 grammes crystallised magnesium chloride and 70 grammes ammonium chloride are dissolved in 1 litre ammonia at $2\frac{1}{2}$ per cent.

The process differs in three points from that commonly followed :—

(1) The precipitation and washing of the molybdic precipitate is executed in presence of ammonium nitrate, for the practical purpose of economising time and materials.

(2) The authors rinse the precipitate from the perforated filter with ammonia at $2\frac{1}{2}$ per cent., and add the magnesia-mixture at once, while generally the precipitate is dissolved on the filter with heated concentrated ammonia and the ammoniacal liquid is neutralised with hydrochloric acid; the liquid, which is thus heated, is allowed to cool, then mixed with magnesia-mixture, and finally diluted to $\frac{1}{3}$ with ammonia. This modification of the common process is recommended for practical reasons.

(3) The magnesia-mixture is added drop by drop, and with continual stirring, while other instructions are silent on this head. These precautions are given because otherwise an impure precipitate and an excess of phosphoric acid are obtained.

(*E*) As regards the first point, E. Richters demonstrated several years ago that the separation of the molybdic precipitate, which is interfered with by the presence of much acid and certain salts, *e.g.* potassium and sodium sulphates, is greatly facilitated by the addition of ammonium nitrate. This recommendation is also given by Gilbert. The authors have found, in a special series of experiments, that a much smaller excess of molybdic solution suffices if ammonium nitrate is present.

They have also found experimentally that the application of a heat of 80° and a rest of an hour will suffice to effect the precipitation of all the phosphoric acid. If the temperature exceeds 90°, free molybdic acid separates out, which does not readily dissolve in ammonia, and is therefore troublesome.

The molybdic precipitate is insoluble both in dilute molybdic solution and in a 15-per-cent. solution of ammonium nitrate slightly acidulated with nitric acid. Hence this mixture may be safely used for washing the precipitate, even without the addition of molybdic solution. But the authors find, further, that a 10-per-cent. solution of ammonium nitrate gives satisfactory results even without acidulation with nitric acid, and this accordingly they recommend.

The reason for the direct addition of magnesia-mixture to the ammoniacal solution of the molybdic precipitate is as follows:— Simply rinsing the precipitate from the filter, and washing the paper with dilute ammonia, are much more easily and readily effected than dissolving the precipitate upon the filter with hot ammonia, followed up in the ordinary manner; in this way, also, too much ammonium chloride is often formed.

As regards the third point the authors have previously shown that a sudden addition of magnesia-mixture occasions an impure precipitate. A pure precipitate and an accurate result can be obtained only by a very gradual addition of the magnesia-mixture with constant stirring.

There remain only three questions:—

(1) In how far does the degree of concentration of the solution influence precipitation with magnesia-mixture? The experimental reply is that it may safely vary within wide limits.

(2) How long must the solution stand after the addition of the magnesia-mixture, before it can be filtered? The results of the authors, in accord with those of Abesser, Jani, and Märcker, show that it is not merely unnecessary to allow the mixture to stand twelve to twenty-four hours, as was formerly customary, but, on the average, more accurate results are obtained (supposing a quantity of phosphoric acid exceeding 0·1 milligramme) by filtering after about two hours.

(3) How far is the concentration of the ammonia used for washing the magnesia precipitate, of importance? The authors conclude that the solubility of the magnesia precipitate is so exceedingly small that there is no need to cut short the washing, as is almost always recommended.

(*F*) R. Finkener proposes the following method for the direct estimation of phosphoric acid from the weight of the phospho-molybdic precipitate. The following conditions must be observed in precipitation:—The solution must contain a sufficiency of free nitric acid. The molybdic solution added must be fourfold the volume of the phosphoric solution to be precipitated, and at least $\frac{1}{3}$ of the molybdic acid added must be in excess of the quantity required for combination with the phosphoric acid. In every 100 c.c. of the volume of liquid after the addition of the molybdic solution must be dissolved 25 grammes ammonium nitrate. The precipitate of ammonium molybdate is filtered after standing for twelve hours, and is washed with a 20-per-cent. solution of ammonium nitrate, to which at the beginning of the

washing $\frac{1}{30}$ of its bulk of nitric acid is added. After removal of the greater part of the ammonium nitrate by means of water the contents of the filter are rinsed into a porcelain crucible, the matter adhering to the paper is dissolved in hot dilute ammonia, the solution is concentrated by evaporation, an excess of nitric acid is added, the solution is poured into the porcelain crucible, the liquid is evaporated away, and the ammonium nitrate expelled by gently heating over a flame placed below a wire gauze. The volatilisation of the ammonium nitrate is found to be complete when a cold watch-glass placed over the crucible is not clouded. The ammonium phospho-molybdate is not decomposed if a needlessly high temperature is avoided. The residue is hygroscopic, and must be cooled in the desiccator over sulphuric acid, and quickly weighed in a covered crucible. The residue is said to contain 3·794 per cent. phosphoric acid.

9. (*G*) Dr. B. W. Gerland thus modifies the oxalic acid process :— The properly prepared solution of the weighed sample in hydrochloric or nitric acid is neutralised as much as possible without forming a permanent precipitate, heated to boiling, and oxalate added in small excess. If the dilution is already sufficient, ammonium oxalate may be added in crystals. Sodium (or ammonium) acetate is added in sufficient quantity to take up the free mineral acid, and the liquid is removed from the fire. The calcium oxalate settles rapidly as a heavy granular powder. The liquor, which appears clear while hot, becomes turbid on cooling, but after two hours' rest is again clear. The filtration of the calcium oxalate can now be proceeded with ; it requires very little time. The precipitate is free from iron and aluminium phosphates, which is readily proved by dissolving the calcined residuum in hydrochloric acid and adding ammonia, when no precipitate will be formed.

From the filtrate and wash-waters of the calcium oxalate iron and aluminium are to be separated. Ammonia alone does not effect it completely, boiling assists it, and the addition of bromine-water still more ; but, to make the separation complete, it is advisable to add ammonium sulphide, and allow the sample to stand in a warm place until the liquor has cleared itself, and assumed a bright yellow colour. It is then filtered with the known precautions. The precipitate is generally free from magnesia, particularly if ammonia was not added in too great excess, but contains, besides aluminium phosphate and iron sulphide, a not insignificant quantity of silica, even if the solution has been previously evaporated to dryness. Phosphoric acid retains silica with a tenacity similar to vanadic acid. For the analysis of the iron and aluminium precipitate, the molybdic acid method is the most convenient. Instead of using ammonium sulphide, the liquor may be treated with chlorine, or evaporated with sodium carbonate, and the residuum calcined for the destruction of the oxalic acid. The filtrate from the ammonium sulphide precipitate is to be concentrated,

and the magnesia precipitated with part of the phosphoric acid by ammonia. Lastly, the remaining phosphoric acid is separated by magnesia-mixture.

With these modifications the 'oxalic method' compares favourably in point of convenience with Sonnenschein's, and yields results no less accurate.

10. Estimation of Phosphoric Acid as Calcium Phosphate.—This is a very common method of approximately estimating the value of guano, and sometimes bone-ash. The results are never very exact, but the method is simple and speedy, and will frequently give all the information that is required. The phosphate is dissolved in acid, and to the clear solution ammonia in very slight excess is added; the precipitated calcium phosphate is collected and weighed. With guanos which contain calcium phosphate and alkaline salts the results are tolerably accurate, but in the case of bone-ash the precipitated calcium phosphate contains lime mechanically carried down. The results are quite untrustworthy in the case of coprolites, although this method is sometimes used in their valuation.

Estimation of 'Reduced' Phosphates in Calcium Superphosphate

(*A*) In the analysis of calcium superphosphate for agricultural purposes, the money value is generally based upon the amount of phosphate present which is soluble in water. But it frequently happens that on keeping, a process of 'retrogression,' or going back, takes place; so that while a sample of freshly prepared superphosphate may contain, say, 25 per cent. of soluble phosphate, the same sample after being kept for some time may contain only 22 or 23 per cent. It is impossible for the manufacturer to calculate the amount of this retrogression, and hence the discrepancies in the amount of soluble phosphate estimated by the seller and the buyer give rise to frequent disputes; and as from the nature of the action the seller's estimate must always be the highest, there is a tendency to throw discredit upon his analysis. The manufacturer considers it unjust that he should have expended time and money in producing soluble phosphate, which, owing to this retrograde action, is valued at only about one-third the price it ought to fetch; while the buyer, who measures the value of a superphosphate by the amount soluble in water, naturally objects to pay for more soluble phosphate than his analyst certifies is present.

To avoid these frequent disputes, it is becoming the custom to express the amount of this reduced phosphate in an analysis of superphosphate, and many methods have been proposed for the purpose of estimating it with accuracy. The point is to find some reagent which does not affect the undecomposed coprolite (that being the mineral now more especially considered); dilute acids, such as acetic, citric, and

oxalic (the latter least so), are objectionable on this account. The best plan is that in which ammonium oxalate is employed. The process is carried out in the following manner:—Take about 1½ gramme of superphosphate, extract the soluble part with cold water, and, afterwards, with boiling water; wash the insoluble residue on the filter into a beaker, boil for about half an hour with ammonium oxalate, and about 2 drops of oxalic acid, so as to have a slight acid reaction (this is done in order to keep the magnesium phosphate in solution). Then filter; the filtrate contains the calcium and magnesium phosphates, and, perhaps, a little iron and aluminium phosphate. To the filtrate add tartaric acid, ammonia, and the magnesia-mixture, weigh the precipitate, and estimate the phosphoric acid as $Ca_3(PO_4)_2$; wash the insoluble residue on the filter into a beaker, boil for about an hour with ammonium sulphide and a few drops of ammonia, filter, &c.; to the filtrate add the magnesia-mixture, and calculate the results in the same manner as the reduced calcium and magnesium phosphates.

Ammonium oxalate is used, as, being a perfectly neutral salt, it is altogether unlikely to decompose a perfectly mineralised substance like coprolite. As is well known, the decomposition of gelatinous calcium phosphate by ammonium oxalate is a quantitative reaction, which takes place at once, the only necessity for boiling being to assist the subsequent filtration. Boiling for ten minutes is sufficient to effect this object, while the oxalate does not, under these circumstances, attack the coprolite to any material extent.

(*B*) Sibson has tried the following experiments on this process:—25 grains of Cambridge coprolite are boiled with an equal weight of ammonium oxalate, in 2 ounces of water, for ten minutes, and filtered; the filtrate acidified with hydrochloric acid, and made alkaline with ammonia (merely to ensure the presence of ammonium chloride), and ammoniacal magnesium sulphate added. No precipitate will probably be obtained; but, *if it be obtained*, it is not conclusive of the presence of phosphoric acid; and great errors may be made if a precipitate in this place be accepted as magnesium and ammonium phosphate. After standing for two hours, the small precipitate is collected (which often resembles the phosphate closely, but consists of magnesium oxalate, which sometimes separates from a concentrated solution, and a little iron oxide) and redissolved in hydrochloric acid, citric acid added, and reprecipitated with ammonia. A precipitate, if now obtained, consists of magnesium and ammonium phosphate only, and, if burned and weighed as magnesium phosphate in the usual way, will be found to amount to less than 0·5 per cent., calculated as bone-earth. This was the case with coprolite ground as fine as it is possible to get it for analysis; but with coprolite in the state usually employed by manufacturers, no weighable quantity of magnesium phosphate is found after standing three hours; 0·5 per cent. of calcium phosphate is therefore

the utmost error that can be made by this process under proper management.

In the case of a superphosphate containing retrograde phosphate, and treated as above, after having first extracted the soluble phosphate by cold water, the magnesium phosphate calculated as bone-earth will represent the phosphate so reduced.

(*C*) Concerning the estimation of reduced or reverted phosphoric acid with ammonium citrate, Grupe and Tollens find that the calcium phosphates soluble in citrate are transformed into calcium citrate and ammonium phosphate, the former salt being soluble in an excess of the liquid. Not merely dicalcium, but to some extent tricalcium phosphate is dissolved if it has not been very strongly dried. Phosphoric acid in magnesium ammonio-phosphate cannot be estimated by this method. The solvent action of the citrate liquid is greater at 35° than at common temperatures. Three times the calculated quantity of magnesia-mixture gives approximately accurate results. Crispo pronounces the method in need of improvement, and shows that the presence of calcium carbonate or magnesia in any form renders the phosphoric acid, which has been dissolved on treatment with ammonium citrate, insoluble again. Thus there is often found less phosphoric acid soluble in the citrate liquid than in water.

(*D*) P. Chastaigne finds too low figures for the phosphoric acid in superphosphates in presence of magnesia. He proposes to extract first with water, and then to treat with ammonium citrate—a suggestion with which Petermann agrees. He wishes to confine the estimation of phosphoric acid soluble in water to dissolved guano and bone superphosphates. The Committee of the British Association on the Estimation of Phosphoric Acid in Commercial Products consider that any known method of estimating the reduced phosphates is purely arbitrary.

Separation of Phosphoric Acid from Aluminium

(*A*) To the acid solution of aluminium phosphate add caustic soda in excess, digest for some time at a gentle heat, and separate the clear liquid by decantation and filtration. To the solution add barium chloride cautiously, till no more precipitate of barium phosphate is produced, add sodium carbonate to remove the excess of barium, and lastly some more caustic soda; then warm and filter. The phosphoric acid will be in the precipitate as barium phosphate, together with barium carbonate, and the aluminium will remain in the filtrate, from which it may be separated in the usual way.

(*B*) Another excellent method of separating phosphoric acid from aluminium is to add to the solution tin bichloride, boil, and precipitate all the tin oxide in combination with phosphoric acid, by means of sodium sulphate. If iron sesquioxide is also present in the liquid, a certain quantity will be precipitated at the same time.

(*C*) Phosphoric acid may also be separated from aluminium by potassium silicate. To the acid solution containing aluminium phosphate add caustic soda in excess ; digest for some time and filter ; then add an excess of solution of potassium silicate, which occasions the formation of a bulky precipitate of aluminium silicate ; collect this on a filter and wash. Acidify the filtrate with hydrochloric acid and supersaturate with ammonia to precipitate as far as possible excess of silica. Filter off and concentrate the solution, and add 'magnesia-mixture.' This occasions the formation of a bulky precipitate, in part flocculent, in part crystalline. The whole is acidified with hydrochloric acid, which dissolves the crystalline and leaves the flocculent part of the precipitate. The liquid is filtered off, supersaturated with ammonia, and left for twenty-four hours. The magnesium ammonio-phosphate which separates is highly crystalline.

Separation of Phosphoric Acid from Chromium

Phosphoric acid in combination with chromium may easily be overlooked in following the method indicated in Will's tables, when chromic oxide and chromium phosphate are obtained simultaneously in solution with potash. On boiling this solution to precipitate the chromium, the phosphate is entirely decomposed, and not a trace of phosphoric acid is precipitated with the chromium oxide.

Separation of Phosphoric Acid from Bases in general

A good method for separating phosphoric acid from bases consists in dissolving the substance to be analysed in a small quantity of nitric acid, and adding to the solution, first silver nitrate, then silver carbonate, and well shaking. All the phosphoric acid then combines with the silver oxide, and is precipitated, while the bases remain in solution and may be freed from the excess of silver by means of hydrochloric acid.

Estimation of Phosphorus in Iron

(*A*) A. E. Haswell covers iron borings with a 7-per-cent. solution of ammonio-cupric chloride in a well-corked flask, which is kept cool by being set in cold water. After digestion for twelve hours, with occasional shaking, the solution of ferrous chloride, which should be nearly free from copper, is carefully decanted from the residue. The latter, containing, in addition to the spongy deposit of copper, all the negative elements of the iron, carbon, silicon, sulphur, and phosphorus, is repeatedly washed with distilled water. The turbid washing-waters are filtered, and the filter is dried and incinerated. The residue in the flask is oxidised by the gradual addition of strong nitric acid, and finally by the application of heat. When the reaction is over, the contents of the flask are rinsed into a capsule. The ash of

the filter is then added, the solution is evaporated to dryness in the water-bath to eliminate silica, the soluble portion is filtered from the carboniferous silica, and the latter is purified by fusion with potassium-sodium carbonate, and again separated with nitric acid. The phosphoric acid in the second filtrate from the silica is precipitated by molybdic solution, and this precipitate is added to the main phosphoric precipitate. The deep blue filtrate from the carbonaceous silica, which contains the main bulk of the phosphoric acid, is treated with molybdic solution in the usual manner. If the solution of molybdenum, prepared according to the formula of Lipowitz with ammonium nitrate, is used in presence of copper, the phosphoric acid is thrown down imperfectly or not at all.

(*B*) E. Agthe finds that the precipitation with molybdic acid is a delicate point, and that the following precautions conduce to the greatest accuracy. Operating as below, four hours are amply sufficient, and a more prolonged contact is often the cause of defective results. If the analyst is pressed for time he may even filter after one hour.

Five grammes of the sample are dissolved, 50 c.c. of the molybdic liquid are added, the mixture is stirred frequently and filtered after four hours.

Under these conditions the estimation is exact when the proportion of phosphorus does not exceed 0·11 to 0·15 per cent. Beyond this range the result becomes uncertain. For a proportion of 0·43 per cent. 50 c.c. of the molybdic solution are required, as this reagent must always be in excess. In place of 50 c.c., 75 or 100 c.c. of the molybdic solution are employed, which is still suitable for proportions of phosphorus of 0·7 and 0·8 per cent. If the percentage is still higher, only 1 or 2 grammes of the sample should be dissolved. The nitric acid should not be too concentrated or employed in excess, as it hinders complete precipitation. As far as possible the carbon should be burnt off, as the presence of this element renders the result too low.

If in the analysis of steel, white pig iron or manganiferous iron—in short, iron low in silica—the latter body is not separated, the result is too high. It is necessary, therefore, to filter before adding the molybdic acid, even in cases where no distinct precipitate of silica can be seen.

Before filtration the solution should be allowed to take the ordinary temperature of 15° to 20°, otherwise the filtrate will become turbid and deposit a slight precipitate. The author operates as follows:—He dissolves 5, 2, or 1 gramme of the sample, according to its supposed richness, in 50 c.c. of nitric acid; he then evaporates to dryness and heats rather strongly, and to eliminate the last traces of nitric acid he evaporates a second time with hydrochloric acid. The residue treated with concentrated hydrochloric acid is taken up in water, and the silica

which remains insoluble is separated by filtration. The liquid is evaporated again over a naked flame in a porcelain capsule as long as the ferric chloride which is deposited on the sides of the vessel redissolves on inclining the capsule, and the process is then continued on the water-bath to incipient solidification. This operation requires to be watched, for if there remains too much hydrochloric acid the results are too low; if, on the contrary, too much acid is driven off and hard crusts are formed, we do not obtain a clear solution with nitric acid.

After cooling, we add 35 c.c. of ammonia (0·96) and mix with the stirrer, so as to obtain a homogeneous paste, and add 75 c.c. nitric acid (1·12 to 1·2) and the whole is set on the water-bath. When the solution is complete the liquid is transferred into a precipitating glass, and from 50 to 180 c.c. of the molybdic solution are added and the whole is kept at a temperature of 50° to 80°, stirring frequently. After four hours it is cooled, filtered, and washed with dilute molybdic liquid. The author recommends the following proportions for the preparation of the molybdic solution:—115 grammes of molybdic acid are dissolved in 460 grammes ammonia (0·96), and made up with water to 1 litre. This solution is then poured into 1 litre of nitric acid at sp. gr. 1·2, and the mixture is allowed to stand for a day and filtered.

When the phosphomolybdic precipitate has been sufficiently washed it is dissolved in the smallest possible quantity of ammonia; the ammoniacal solution is neutralised with hydrochloric acid up to the point where the precipitate produced by this reagent is redissolved very slowly, and when cold it is mixed with 15 to 25 c.c. of magnesia-mixture, stirred well, and filtered after standing for six hours. The precipitate is washed with ammoniacal water, dried, calcined, and weighed.

The author prepares his magnesia-mixture as follows:—

Magnesium chloride	100
Ammonium chloride	200
Ammonia (sp. gr. 0·96)	400
Water	1000

It is well to ascertain that the mother-liquors from the ammonium phosphomolybdate, when mixed with ammonia slightly heated, do not give a further precipitate; in the contrary case the analysis would be inaccurate. It may, however, be completed by neutralising as far as possible with ammonia, adding molybdic liquid, and adding the second precipitate to the former.

(*C*) **Sir F. Abel's Process.**—Fifty grains of iron borings are acted on with warm nitrohydrochloric acid in a flask with a long neck, and after complete solution of the metal the contents of the flask are transferred to a porcelain basin and evaporated to dryness; the residue is moistened with concentrated hydrochloric acid and again evaporated, so as thoroughly to expel nitric acid. The residue is dissolved in

hydrochloric acid, the solution diluted, filtered, nearly neutralised with ammonium carbonate, and the iron in solution reduced to protoxide by the addition of ammonium sulphite to the gently heated liquid, and the subsequent careful addition of dilute sulphuric acid to expel excess of sulphurous acid. Ammonium acetate and a few drops of solution of iron sesquichloride are then added and the liquid boiled, when the phosphoric acid is precipitated as basic phosphate of iron sesquioxide with some basic acetate. The liquid is rapidly filtered, with as little exposure to air as possible, the precipitate is slightly washed, and dissolved in hydrochloric acid, the solution neutralised with ammonium carbonate, and a mixture of ammonia and ammonium sulphide added; it is then gently heated to ensure the conversion of the phosphate into iron sulphide. The latter is afterwards removed by filtration, washed with dilute ammonium sulphide, and the phosphoric acid is precipitated from the solution as magnesium ammonio-phosphate, and weighed as magnesium pyrophosphate.

(*D*) For the separation of phosphoric acid from ferric oxide and alumina, Dr. W. Flight boils the solution containing the alumina, iron, and phosphoric acid (which should not be very acid) for two or three hours with excess of sodium thiosulphate. All the alumina with a part of the phosphoric acid is precipitated, while the iron with the rest of the phosphoric acid remains in solution. From this solution the iron is at once precipitated by ammonium sulphide, and converted into ferric oxide, while the alumina and phosphoric acid in the precipitate are separated by treatment with excess of caustic soda and barium chloride, which precipitates the phosphoric acid in combination with the barium, while the alumina remains in solution. In washing the precipitate a few drops of soda solution must be added to the wash-water, as the phosphate is decomposed by pure water. This phosphate is then decomposed by sulphuric acid, and the phosphoric acid estimated in the usual way.

In the analysis of native iron and aluminium phosphates the following precautions are suggested:—1. The total water (=loss by ignition) should be estimated by igniting the whole or a large portion of the sample previously crushed as rapidly as possible to the size of peas, but not on any account ground. 2. The only method suitable for the estimation of phosphoric acid is the ammonium molybdate process, soluble silica having been previously removed.

(*E*) For the estimation of alumina and iron in phosphates, A. Esilmann proposes a process founded on the fact that, in the presence of an excess of sodium thiosulphate and acetic acid, alumina phosphate precipitates in the tribasic form of constant composition at the boiling temperature. The precipitate is mixed with sulphur, easily washed, and on ignition the sulphur burns off, leaving pure phosphate, 122·5 parts of which are equal to 51·5 parts of alumina. Of course the presence of excess of phosphoric acid must be ensured. All our

present methods involve the previous separation of the phosphoric acid, necessitating in most cases operating on very small quantities and delicate working; but the one under notice is applicable whatever be the quantities of phosphoric acid, iron, lime, or magnesia present. This process is, in fact, most commonly used for estimating small quantities of alumina in presence of large proportions of phosphoric acid, where the molybdic method proposed by Ogilvie would be almost impracticable.

One defect of it is the invariable precipitation of traces of iron with the aluminium phosphate; but the following test-results, performed under very varying circumstances, show that its accuracy thereby is not materially impaired. The solution ought to be dilute and not very hot, and should contain a tolerable amount of free acid. An excess of sodium thiosulphate is added, then acetic acid in liberal excess. Ten or fifteen minutes are allowed for the complete deoxidation of the iron, and then the solution is boiled for about the same length of time. The filtration and washing of the precipitate are effected hot and rapidly, and after drying, the precipitate is ignited in a porcelain crucible.

The iron can be estimated in the filtrate from the aluminium phosphate after decomposition of the thiosulphate by boiling with excess of hydrochloric acid; but it is better to employ a separate portion for that object. For reducing the peroxide by metallic zinc or tin protochloride an excess of ammonium sulphide is employed; the excess is decomposed by hydrochloric acid, and the sulphuretted hydrogen is easily and completely driven off by ebullition. This plan is more expeditious than when zinc is used, and more accurate than the tin method.

Separation of Phosphoric Acid from Silica and Fluorine

(*A*) In the estimation of silica in fluoriferous phosphates, especially apatite and phosphorite, losses are often experienced when the separation of silica is effected by digesting or evaporating the sample with concentrated hydrochloric or nitric acid, as considerable quantities of silicofluoric gas are volatilised. This loss is avoided or brought to a minimum if the calcium phosphate and fluoride is dissolved by gently heating in strongly diluted hydrochloric acid, the solution separated from silica by decantation, and the latter substance afterwards perfectly freed from ferric oxide by digestion in concentrated hydrochloric acid.

(*B*) Dr. Gilbert digests 2 grammes of powdered apatite in a platinum capsule with 50 c.c. of dilute hydrochloric acid (1 part acid at sp. gr. 1·12 with 10 parts of water) for ten minutes on the water-bath, decants the solution through a filter, treats the residue once more in the same manner, and finally dissolves the last traces of iron by heating with concentrated hydrochloric acid, and collecting the silica upon the filter which has been already used. The fluorine present

in phosphorite was calculated from the lime, and was as a check estimated by Penfield's method. For this purpose 5 grammes of finely ground phosphorite were mixed in a platinum crucible with 10 grammes of powdered quartz, the mixture ignited, placed in the apparatus along with 50 c.c. of concentrated sulphuric acid and distilled. The alcoholic solution of potassium chloride was placed, not in a U-tube, but in a Bunsen washing-bottle containing a little mercury, into which the delivery tube dipped. A second washing-bottle, containing a similar solution, was connected as a matter of precaution, but the decomposition was completely effected in the first. The liberated silica was equally diffused in the liquid. Professor E. W. Atkinson has refuted the assertion that the presence of silica does not interfere with the estimation of phosphoric acid by the molybdic method.

Preparation of Phosphorous Acid

Phosphorous acid is a useful reducing agent, and has been recommended in previous chapters as one of the reagents to be employed in the separation of certain metals from one another. It is prepared in a sufficiently pure state for this purpose as follows:—Introduce a number of separate sticks of phosphorus into glass tubes an inch long, open above and below, but drawn out funnel-shaped at the bottom, these tubes being arranged in a funnel, and the funnel inserted into a bottle which stands in a dish containing water. The whole arrangement is covered with a bell-jar, but in such a manner as to give access to the external air, which, however, should not be very warm. The acid which collects in the bottle is equal to about three times the weight of the phosphorus consumed. It is a mixture of about 1 atom of phosphorous acid and 4 atoms of phosphoric acid.

Detection of Phosphorous Acid

For detecting phosphorous acid in phosphoric acid Dr. Reickher adds a slight excess of mercuric chloride, and heats to 80°.

Estimation of Phosphorous Acid

Prinzhorn and Precht find that phosphorous acid can be very conveniently and accurately estimated by means of mercuric chloride. The phosphite is dissolved in hydrochloric acid, an excess of the chloride is added, and the whole is heated in the water-bath till mercurous chloride is rapidly and completely deposited, for which about two hours are requisite. When the filtrate no longer becomes turbid, even when boiling over the open flame, the deposit is collected upon a tared filter, dried at 100°, and weighed. If the filtrate is then freed from mercury by the passage of sulphuretted hydrogen, and from other bases

which interfere with the estimation of phosphoric acid, the latter may be thrown down with magnesia-mixture, thus furnishing a way of checking the result.

NITROGEN

Estimation of Nitrogen by Weight

In those analyses of nitrates or nitrites in which it is only desired to estimate the nitrogen, Dr. Wolcott Gibbs recommends the following modification, which may be employed with advantage :—

A hard glass tube about six inches in length is sealed at one end, and its volume estimated by filling it with mercury and pouring this into a graduated vessel. The tube is to be carefully dried and weighed with a good cork ; it is then to be filled with finely divided metallic copper, prepared by the reduction of the oxide, so as to enable the operator to judge of the quantity necessary. The salt to be analysed is then weighed and mixed with the metallic copper, either in a mortar or with a mixing-wire in the tube, and the tube with its contents and cork is again weighed. The weight of the copper employed is thus known, and its volume may then be found by dividing this weight by the density of metallic copper. A weighed calcium-chloride tube is then adjusted as in organic analysis, and the combustion tube is heated in the usual manner. When the combustion is finished, the open end of the calcium-chloride tube is sealed with the blowpipe flame, and the combustion-tube allowed to become perfectly cold. The chloride tube is then removed and weighed, and the combustion-tube also weighed with its cork. The increasing weight of the calcium-chloride tube gives the amount of moisture in the copper and the water in the salt analysed. The loss of weight in the combustion-tube gives the nitrogen in the salt after correction for the oxygen in the tube, for the moisture in the copper, and for the water in the salt. The correction for the oxygen in the combustion absorbed by the copper is easily found, with a sufficiently close approximation, by subtracting the volume of the copper from that of the tube, finding the weight of the residual air, taking one-fifth of this as oxygen, and considering the whole of this oxygen as absorbed by the copper. A piece of asbestos may be placed between the copper and the cork with advantage ; but this renders an additional correction necessary.

In two analyses executed by this method—in the first, a sample of pure saltpetre gave 13·86 per cent. nitrogen, theory requiring 13·86 per cent. ; in the second, a specimen of the commercial salt gave 13·7 per cent. nitrogen, while the same salt analysed by Simpson's method, in which the volume of the nitrogen is estimated, also gave 13·7 per cent. The whole analysis, with the weighings, may easily be executed by one person in an hour and a half. It is easy to see that this method applies to all inorganic nitrates and nitrites, whether hydrated

or anhydrous, but that it cannot be employed in the case of organic or ammoniacal salts. In the analysis of inorganic nitrates or nitrites by Simpson's method, it is not necessary to use mercury oxide to prevent the formation of nitrogen binoxide. In all such cases it will be found sufficient to mix the salt with pure metallic copper. In this manner the dimensions of the combustion-tube may be greatly diminished. It is also advantageous to exhaust the air from the combustion-tube before disengaging carbonic acid from the manganese carbonate. By alternately pumping and filling the tube with carbonic acid, the air may be completely expelled before the combustion commences. It is also better to draw the tube out before a blowpipe, as it is difficult to make the cork and indiarubber connector perfectly tight. With a little practice the drawing out is easily effected even with the hardest combustion-tubes.

Detection of Nitric Acid

(*A*) The following test, proposed by Blunt, for the presence of nitrates in a drinking water is a little more delicate than the common one with ferrous sulphate; it depends on the reducing action exercised by sodium amalgam on nitric acid.

When a moderately concentrated solution of potassium nitrate is poured over a sodium amalgam containing about $\frac{1}{2}$ per cent. of the metal, there is no evolution of hydrogen, and on pouring off the supernatant liquid after some minutes, and applying the Nessler test, a considerable quantity of ammonia may be detected. A solution of pure potassium nitrate, containing $\frac{1}{50}$ grain of the salt, gives a just perceptible colouration with the Nessler test after standing over a $\frac{1}{2}$ per cent. amalgam for about twelve hours; $\frac{1}{25}$ grain of the salt gives a marked reaction. Several attempts have been made to adapt the above test to the estimation of small quantities of nitric acid; they have at present, however, been unsuccessful, through the impossibility of pushing the reaction to completion. It is possible, however, that a system of comparative testing analogous to that at present adopted in the case of ammonia may lead to some results. As an example of the mode of applying the test qualitatively to a drinking water, the following account may be given of an actual experiment:—

To 2 oz. of a water known to contain a trace of nitrates was added about 100 grains of a solution of potassium hydrate containing $\frac{1}{12}$ of its weight of alkali; the whole was then evaporated nearly to dryness; thus any ammonia already existing in the water would be expelled. The residue was exhausted with distilled water which gave no reaction with the Nessler test, and the quantity of the solution made up to 200 grain measures, which were afterwards divided into two equal portions. One was at once tested with ferrous sulphate solution and sulphuric acid; a very faint brown colouration appeared at the point of junction of the layers of liquid, increasing considerably after a few hours.

The second portion was introduced into a carefully cleaned test-tube, with about 200 grains of ½ per cent. sodium amalgam; the tube was lightly corked to check, as far as possible, diffusion of the ammonia formed, but not so tightly as to prevent the egress of the hydrogen, which in dilute solutions of a nitrate is always evolved from the amalgam. The whole was left for about twelve hours; the liquid was then rinsed with successive portions of pure distilled water into a glass cylinder about 6 inches high and 1 inch wide, and the quantity was made up with distilled water to about 1000 grains. On adding about 15 grain measures of the Nessler test, a very strong colouration, accompanied by incipient precipitation, at once appeared. It is to be remarked that the liquid must always be decanted from the amalgam before applying the Nessler test, as the presence of nascent hydrogen appears to interfere with the action of the latter.

(*B*) F. Bucherer gives a process which he states will detect $\frac{1}{100000}$ of a nitrate in aqueous solution. It is founded on the action of nitrous vapours on potassium iodide; the potassium is oxidised by the oxygen of the nitrous vapours, which are thereby reduced to the state of binoxide, and iodine is set at liberty. For the test to be conclusive, any chlorine or bromine must have been separated from the liquid. The author places 8 or 10 grammes of the liquid to be tested in a tube 6 or 8 inches long, introduces a few copper turnings, and 3 or 4 drops of strong sulphuric acid. Then boil for a moment and nearly fill up the tube with water; now add a few drops of a solution of potassium iodide. If the liquid contains any nitrate the iodine is set at liberty, and on adding a small quantity of carbon disulphide and shaking vigorously, the sulphide will dissolve the iodine and float on the surface of the liquid, taking a violet or deep red colour, according to the quantity of iodine displaced.

To detect free nitric acid operate as above, but omit the sulphuric acid. To detect a nitrite use the same method with the omission of the copper.

Electrolytic Determination of Nitric Acid in Nitrates

(*A*) Classen has shown that the action of the current transforms the nitric acid into ammonia. If the solution of an alkaline nitrate acidified with dilute sulphuric acid is exposed to the action of the current, no ammonia is formed.

(*B*) Luckow has observed that a reduction of nitric acid always ensues if there exists simultaneously a metallic salt in solution, which is decomposed by the current with precipitation of the metal. Copper salts are the most suitable.

(*C*) G. Vortmann has ascertained the conditions for the quantitative determination of nitric acid in nitrates. The solution of the nitrate is mixed with a sufficient quantity of copper sulphate (*e.g.* in the analysis of potassium nitrate, with half as much crystalline copper sulphate as

there was potassium nitrate employed), acidified with dilute sulphuric acid, and electrolysed in the cold with a current of 1 or 2 c.c. detonating gas. After the reduction has taken place the liquid is decanted, and the ammonia distilled off as usual, with the addition of soda-lye, and determined volumetrically in the receiver. There was used $\frac{1}{5}$ normal sulphuric acid and ammonia. In order to determine the effective value of the sulphuric acid decompose a weighed quantity of crystalline copper sulphate (0·5 gramme) electrolytically, and titrate with ammonia the sulphuric acid thus set free. Vortmann decomposed 0·4876 gramme of copper sulphate ($CuSO_4.5H_2O$), and consumed, for neutralising the sulphuric acid set free, 19·6 c.c. ammonia, equivalent to $\frac{1}{5}$ normal sulphuric acid. One c.c. of the latter combines, therefore, with 0·0028017 gramme nitrogen in the state of ammonia.

Estimation of Nitric Acid by the Oxidation of an Iron Proto-salt

(*A*) This is commonly known as Pelouze's method. The weighed nitrate is boiled, out of contact with air, with a solution of iron protochloride and an excess of hydrochloric acid. Under these conditions the nitric acid splits up on the one hand into oxygen, which converts the iron proto-salt into a per-salt, and on the other into a lower oxide of nitrogen, which escapes. The requirements of this process are, firstly, that the decomposition of the nitrate shall take place in an atmosphere of which oxygen does not form a part, and, secondly, that such decomposition shall be complete.

In the ordinary mode of conducting this process the operation takes place in a retort, through which a current of hydrogen is passed. Attached to the stem of the retort is a U-tube, containing a little water, which serves as a lute to prevent access of air.

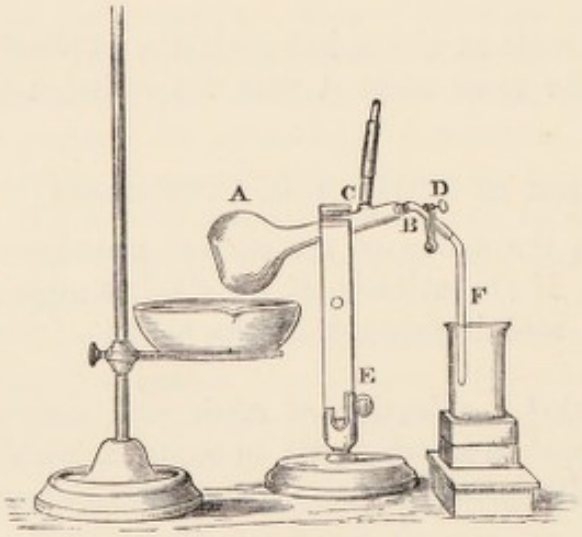


Fig. 23.

(*B*) Holland has modified this arrangement so that the operation is conducted *in vacuo*, and at its expiration the solution is boiled to expel the nitric oxide, thus avoiding the necessity of employing either hydrogen or carbonic acid.

In the accompanying sketch, A is a long-necked assay flask drawn out at B so as to form a shoulder, over which is passed a piece of indiarubber tube, D, about 6 centimetres long, the other end terminating in a glass tube,

F, drawn off so as to leave only a small orifice. On the elastic connector D is placed a screw compression-clamp. At C, a distance of 3 centimetres from the shoulder, is cemented with the blowpipe a piece of glass tube about 2 centimetres long, surmounted by one of rubber tubing rather more than twice that length. The elastic tubes must be securely attached to the glass by binding with wire. After binding, it is as well to turn the end of the connector back and smear the surface with fused caoutchouc, and then replace it. The wooden clamp E gives support to the flask; the rest of the arrangement requires no explanation.

The analysis of a nitrate is conducted as follows:—A small funnel is inserted into the elastic tube at C, the clamp at D being for the time open; after the introduction of the solution, followed by a little water, which washes all into the flask, the funnel is removed, and the former placed in the inclined position it occupies in the figure. The contents are now made to boil so as to expel all air and reduce the volume of the liquid to about 4 or 5 c.c. When this point is reached, a piece of glass rod is inserted into the elastic tube at C, which causes the water vapour to find egress through F.

Into the small beaker is put 50 c.c., more or less, of a previously boiled solution of iron protosulphate in hydrochloric acid. (The amount of iron already existing as a per-salt must be known.)

The boiling is still continued for a moment to ensure perfect expulsion of air from F, the lamp is then removed, and the caoutchouc connector slightly compressed with the first finger and thumb of the left hand. As the flask cools, the solution of iron is drawn into it; when the whole has nearly receded the elastic tube is tightly compressed with the fingers, while the sides of the beakers are washed with a jet of boiled water, which is also allowed to pass into the flask. The washing may be repeated, taking care not to dilute more than necessary or admit air. While F is still full of water, the elastic connector previously compressed with the fingers is now securely closed with the clamp, the screw of which is worked with the right hand. Provided the clamp is a good one, F will remain full of water during the subsequent digestion of the flask.

After heating at 100° C. for half an hour, the flask is removed from the water-bath and cautiously heated with a small flame, the fingers at the time resting on the elastic connector at the point nearest the shoulder; as soon as the tube is felt to expand, owing to the pressure from within, the lamp is removed and the screw clamp released, the fingers maintaining a secure hold of the tube, the gas flame is again replaced, and when the pressure on the tube is again felt, this latter is released altogether, thus admitting of the escape of the nitric oxide through F, which should be below the surface of the water in the beaker while these manipulations are performed. The contents of the flask are now boiled until the nitric oxide is entirely expelled and the

solution of iron shows only the brown colour of the perchloride. At the completion of the operation the beaker is first removed, and then the lamp.

It now only remains to transfer the solution of iron to a suitable vessel, and estimate the perchloride with tin chloride in the usual way, or with copper subchloride (see page 209).

The process is easy of execution, and gives satisfactory results. The points requiring attention are that the apparatus should be capable of retaining a sufficiently perfect vacuum during the operation; this condition is fulfilled by the use of a suitable elastic tube and clamps. What is known as French tubing serves the purpose well: its sides are thick, and its material free from metallic oxides.

It is advisable when making the digestion at 100° to place the flask in cold water, which is afterwards raised to the boiling-point; if, on the other hand, the flask is heated at once, a violent bumping ensues, and portions of the liquid are projected into the tube at c.

(*C*) Schlœsing employs the following process:—The nitrate mixed with ferrous chloride and hydrochloric acid is introduced into a very small tubulated retort, the extremity of which dips under mercury. The air is expelled by a stream of carbonic acid. The retort is then boiled for eight minutes, and the gas evolved collected in a small jar containing caustic potash. This nitric oxide is converted into nitric acid by treatment with water and oxygen, and finally titrated with alkali. The method fails, however, with extremely small quantities of nitrates and in the presence of certain kinds of organic matter. The prejudicial effect of the organic matter is removed to some extent by boiling the contents of the retort to dryness, but with very small quantities of nitric acid the results are still too low. The author has been able to estimate 98 to 100 per cent. of the nitrogen, even when half a milligramme of nitrogen as nitre was used. Perfect exclusion of oxygen from the apparatus is essential. This is effected by mixing the hydrochloric acid used in the carbonic acid generator with cuprous chloride, and protecting its surface with a layer of oil. The carbonic acid is always kept under pressure, so that any leak must be outwards. The nitric oxide is estimated by gas analysis, preference being given to absorption over caustic potash, after successive treatments with oxygen and pyrogallol. In the introduction of the oxygen a gas delivery-tube invented by Professor Bischof was found of great service. It consists of a test-tube, with a minute perforation about half an inch from the mouth. The tube, being filled with gas, has its mouth closed by an indiarubber cork, through which passes a short glass tube with a fine orifice. On tilting the tube under mercury, with the perforation downwards, minute bubbles of gas rise from the perforated stopper closing its mouth, and thus the quantity added can be regulated with great accuracy.

(*D*) J. Boyd Kinnear reduces nitric nitrogen to ammonia by the

action of zinc in a very dilute acid solution. The point of dilution may for practical purposes be taken as 1 of nitrogen (nitric) in 5000 of water, though the reaction will often be found perfect in solutions of twice or three times this strength. The necessary proportions of zinc and acid are indicated by the equation (supposing potassium nitrate and sulphuric acid to be employed)

$$2KNO_3+8Zn+11H_2SO_4=8ZnSO_4+2HKSO_4+(NH_4)_2SO_4+6H_2O.$$

But it is advisable to use at least a half more of sulphuric acid than is required by the formula, and the larger the surface of zinc the more quickly is the reaction completed. Hydrochloric acid answers as well, and iron might be substituted for zinc but for its liability to contain occluded nitrogen. When only a slight excess of acid is used the action is slow and the evolution of hydrogen trifling, but by employing a moderate excess of acid and nearly filling the vessel with granulated zinc, the evolution of gas is rapid, much heat is produced, and the conversion into ammonia is often complete in ten minutes. In all cases the process must be stopped by pouring off the acid liquid and washing the zinc before the acid is fully saturated.

Besides rapidity and simplicity another advantage is that in many cases the resulting ammonia may be at once estimated in an aliquot portion by the Nessler process. For this purpose care must be taken that the zinc and sulphuric acid are both pure, and that substances which give coloured iodides are absent. Lime and iron, which most frequently occur in ordinary analyses, may be previously precipitated by oxalic acid and potash. When the quantity of zinc dissolved is small, the addition of the Nessler solution causes no precipitate; but when it does, the zinc may be first precipitated and redissolved by solution of potash. Very rapid and often sufficiently accurate estimations may thus be arrived at; but of course other methods of estimating the ammonia are equally available.

The reaction between the nascent hydrogen and the nitrates and nitrites appears to be quite without effect on organic nitrogen, so much so that the nitric acid in urea nitrate may be thus estimated without the urea being decomposed. The advantage of this in examinations of juices of plants, water, and manures, need not be pointed out. When the quantity of the material available is small, it is also an advantage that the same solution may serve for the successive estimations, first of the ammonia already formed, next (directly or by difference) of the nitric nitrogen, next of so-called 'albuminoid ammonia,' and lastly, by combustion, of the total nitrogen, without risk of results of each process overlapping the other and thus giving too high a result.

Estimation of Nitric Acid in Commercial Nitrates

F. Jean recommends the following procedure :—Into a small glass flask holding about 200 c.c. introduce a concentrated and very acid solution of ferrous chloride. The flask is closed with an indiarubber stopper pierced with holes, through which pass a delivery-tube under a leaden shelf in a tank of water lined with lead, and a very short tube, to which is fixed a small funnel by means of a flexible caoutchouc tube, the communication with the flask being intercepted by means of a Mohr's spring clip or a small glass tap. The trough being filled with water, the ferrous chloride is raised to a boil, and, as soon as the sound made by the condensation of the acid on the water of the trough announces that a vacuum has been made in the flask, a gas-jar filled with water is placed over the opening in the shelf. The jar should be of the capacity of 200 c.c. graduated in tenths. Then pour into the funnel 5 c.c. of a solution of sodium nitrate, formed by dissolving in a litre of water 66 grammes of pure sodium nitrate recently melted at a low temperature. The solution of ferrous chloride being kept at a boil, the solution of nitre is allowed to enter the flask drop by drop, taking care not to empty the funnel completely. 2 to 3 c.c. of distilled water are then placed in the funnel and allowed to enter the flask, and finally the funnel and the tube are rinsed with 5 to 10 c.c. of fuming hydrochloric acid. The nitrogen binoxide produced by the decomposition of the sodium nitrate enters the graduated jar, and as soon as the sound announcing the presence of a vacuum in the flask is heard, the graduated jar is withdrawn and allowed to stand on a support in the trough. This first operation gives the volume of gas obtained from a known weight of nitre, without its being needful to take account of the corrections for temperature, pressure, &c. Into the flask are then introduced 5 c.c. of a solution of the nitre in question in 100 c.c. of distilled water, and the salt is decomposed. This solution is made by dissolving 6·6 grammes in the same manner as the foregoing, and the nitrogen binoxide is collected in a second graduated jar. The two jars are kept till they have acquired the same temperature and the respective volumes of gas produced are read off, care being taken to keep them immersed so that the water may stand at the same level within and without. The volume of gas produced by a given weight being thus known, the proportion of real nitre existing in the sample under examination is readily calculated.

Estimation of Nitric Acid when in the Free State

Nitric acid dissolved in water is most easily estimated by acidimetric processes. It has been proposed to evaporate the acid liquid with a given weight of lead oxide; but lead oxide forms with nitric acid various insoluble basic combinations, which retain a certain

quantity of water at 160°, and attract atmospheric carbonic acid. Lead oxide may be advantageously replaced by baryta water and barium carbonate.

Estimation of Nitric Acid when Combined with Heavy Metals

The nitrates of metals precipitable by sulphuretted hydrogen being first decomposed by this reagent, the nitric acid can be estimated in the liquid by baryta, the excess of sulphuretted hydrogen being previously eliminated by copper sulphate. Barium sulphide does not well take the place of sulphuretted hydrogen; there is a risk of the formation of thiosulphates, which might interfere with the estimation.

Estimation of Nitric Acid when Combined with any Base

(*A*) Nitric acid in combination may be estimated by distilling with dilute sulphuric acid, and estimating the nitric acid in the distillate. Two litres of the solution are boiled down to about 200 c.c., and during evaporation pure potassium permanganate is added (the object of which is to convert nitrites into nitrates), until a permanent pink colour is obtained. The concentrated liquid is filtered, pure sulphuric acid added, and distilled into a flask containing barium carbonate suspended in water. The distillation is interrupted when sulphuric acid begins to go over. The contents of the receiver are filtered, and in the filtrate which contains barium nitrate and chloride the barium is estimated in the usual manner. The amount of chlorine being known from a separate experiment, all data are given for the calculation of the quantity of nitric acid present in the 2000 c.c. of water.

(*B*) The error caused by the oxidation of ammonia to nitrous and nitric acid is inappreciable.

Instead of collecting the nitric acid in barium carbonate, a standard caustic alkaline solution may be employed. A very good method consists in distilling nitrates with sulphuric acid diluted with twice its volume of water. The operation is conducted at a temperature not above 70° or 80° C. in a retort with the neck drawn out and bent so that by means of an indiarubber tube it may be connected with a little receiver with three bulbs, containing a known volume of a standard solution of soda or potash. The distillation must be continued for three or four hours to obtain 1 or 2 grammes of nitrate. The distillation may be effected by a water-bath in a vacuum, either by means of an air-pump, or by expelling the air from the apparatus by boiling, and then closing hermetically. If the nitrate is mixed with chloride, a solution of silver sulphate or moist silver oxide is added previous to distillation.

Estimation of Nitric Acid by Fusion or Calcination

(*A*) Nitric acid may be estimated by difference in some salts decomposable by calcination, unless the production of a higher oxide of the base may occur. Nitric acid may be driven off by sulphuric acid, the weight of the sulphate being deducted from that of the nitrate.

Nitrates with strong bases are transformed into chlorides by calcination with ammonium chloride.

(*B*) Nitrates may also be decomposed by fusion with borax, or, better still, with potassium bichromate. The crucible is weighed with the alkaline nitrate, and heated sufficiently to melt the nitrate; potassium bichromate is added after cooling (2·25 of bichromate for 1 of nitrate); the whole is gently heated and weighed. The crucible is then gradually heated to dull red heat, and weighed after cooling. The difference gives the weight of nitric acid. Neither chloride nor sulphates are decomposed under these conditions.

Detection of Nitrous Acid

(*A*) Thomas M. Chatard has reviewed all the tests given for this acid, comparing their relative degrees of delicacy, with the following results:—For testing, a very dilute solution of Fischer's salt,

$$(Co_2 6NO_2 + 6(KNO_2) + 2Aq),$$

which contained $\frac{1}{200000}$ part by weight of nitrous acid, was employed.

Schönbein's test with a weak solution of indigo decolourised by potassic sulphide failed to give accurate results. Besides, there are many substances which would have the same action upon the decolourised indigo as the nitrous acid.

C. D. Braun's test with cobaltous chloride and potassic cyanide gave no reaction with so dilute a solution, even when several cubic centimetres were taken, the reaction only appearing when a comparatively strong solution of the nitrite was used.

Hadow's reaction, in which a nitrite, when heated with prussic acid, is detected by an alkaline sulphide, gave good results only when the nitrous acid was present in larger quantities, not being delicate enough to give a reaction with the standard solution of nitrite employed.

A modification of this test suggested itself, in which the nitroprussic acid is thus produced. To the solution suspected to contain the acid, potassium ferrocyanide and acetic acid are added, and the whole boiled. The solution is allowed to cool, and ammonium sulphide added. If nitrous acid was originally present, the characteristic blue reaction will appear. 10 c.c. of the test solution gave the reaction, but it failed with a smaller quantity.

The problem was finally solved by another reaction—namely, the

production of phenol from aniline by means of nitrous acid. Evaporate the test liquid nearly to dryness, then rub it with a few drops of a strong solution of aniline sulphate. If nitrous acid is present, the odour of phenol will immediately result. This test is remarkably delicate, 1 c.c. of the test solution giving a perfectly distinct reaction. Nor can nitrous be confounded with nitric acid, as this last produces no phenol, but merely a yellow colour, which of itself, as is well known, is of value as a test for that acid.

(*B*) Dr. A. Jorissen proposes the following test for nitrous acid :—

Dissolve 0·01 gramme magenta in 100 c.c. glacial acetic acid, place 2 c.c. of this solution in a small porcelain capsule, and add a trace of solid potassium nitrite. The liquid turns successively violet, blue, green, and finally yellow. Nitrates are without action upon the reagent. If there be added to the test liquid free mineral acids, the mixture takes finally a yellow colour, but this is due to the formation of a tri-acid rosaniline salt, and the characteristic red colour of rosaniline can be reproduced by the addition of water. When the change of colour has been occasioned by nitrous acid, the original colour cannot be restored by the addition of water, but the liquid remains yellow.

To detect a nitrite in a liquid, it is concentrated, or by preference evaporated to dryness. When cold a suitable quantity of the reagent is added, when the characteristic play of colours is produced if a nitrite be present. The evaporation to dryness serves to render the reaction more sensitive, as it succeeds better the more concentrated the acetic acid.

In searching for minute traces of nitrous acid the quantity of magenta dissolved in the glacial acid may be proportionately decreased by, *e.g.*, mixing 1 c.c. of the reagent as described above with 9 c.c. of glacial acetic acid.

This new reagent may be used for the detection of nitrous acid in natural waters by Fresenius's method of distilling with glacial acetic acid. For this purpose 1 c.c. of a solution of 0·5 gramme potassium nitrite in 1 litre of water is added to 100 c.c. of water. This liquid, which contains 0·0005 gramme of the nitrite, is mixed with acetic acid and introduced into a small retort connected with a receiver containing a mixture of 9 c.c. glacial acetic acid and 1 c.c. of the test liquid (the solution of 0·01 gramme magenta in 160 c.c. glacial acetic acid). A few drops of the distillate suffice to produce the above-described change of colours in the receiver.

Estimation of Nitrites

1. When a Considerable Quantity is Present.—(*A*) In this case the following processes devised by Tichborne will be found very successful. The first process is based upon the reduction of chromic acid to chromic oxide by nitrous acid. In analysing a specimen of

commercial sodium nitrite, the mode of procedure is as follows :— If the sample contains sodium carbonate, a weighed quantity, say 2 grammes, is dissolved in a rather considerable quantity of water, and the carbonate present estimated by a standard solution of sulphuric acid, carefully avoiding an excess. To hit the exact point of saturation, soak a piece of good litmus-paper in the solution after the addition of each quantity of acid from the burette, and on drying it the exact state of the solution is perceived. A convenient indicator of the point of saturation in this case will be found in a solution of starch and potassium iodide contained in a test-tube ; one drop of the solution of nitrite added after each addition of acid will, when the carbonate is all decomposed, strike a blue shade on falling through the starch solution. After noting the amount of carbonate, the solution is in a fit condition for the estimation of the nitrite ; the remainder may practically be noted as nitrate. Three grammes of pure potassium bichromate for every 2 grammes of nitrite taken are dissolved with a little water in a flask fitted with a well-ground stopper ; an excess of sulphuric acid is then added, and the flask is placed in a vessel containing a freezing-mixture of sodium sulphate and hydrochloric acid. The solution of the nitrite may be placed also in the same bath for a few minutes previously to being poured on the surface of the chromic acid without mixing ; the stopper is then inserted, the flask taken out of the freezing-mixture, inverted, and left to regain the ordinary temperature of the room ; in the course of half an hour or an hour the flask will contain a mixture of chromic acid and chromic salt, the chromic oxide representing the nitrite in the sample.

In precipitating the chromic oxide a precaution is necessary. If there is any considerable excess of chromic acid left, which is generally the case when examining commercial samples, the ordinary method of precipitating with ammonia will not do, as a brown precipitate of a chromium peroxide, not decomposable by ammonia, is thrown down, although the substance is instantly decomposed, upon boiling, by a solution of potash into chromic oxide and chromic acid. It is therefore necessary to nearly neutralise with potash, and finish off with a few drops of ammonia, and boil until all trace of the latter substance is gone ; but if accidentally too much potash is added, a few drops of ammonium chloride and boiling for a few minutes will rectify the mistake. If the operation has been correctly performed, it will be indicated by the colour. The dark brown colour instantly disappears on boiling, the precipitate taking the bright green of chromic oxide, while the solution becomes a bright yellow.

The chromic oxide is washed, but for accurate results it retains the potassium chloride too tenaciously to ignite and weigh directly. It is better to redissolve the washed hydrated chromic oxide in dilute hydrochloric acid, and to reprecipitate with ammonia in the usual manner. This gives the most exact results ; but there are quicker methods.

Thus, the hydrated chromic oxide might be washed and converted into chromic acid by Chancel's method (by lead peroxide) and estimated volumetrically.

Chromic oxide found $\times 1{\cdot}354$=sodium nitrite.

The second process is based upon the first, that both nitrites and nitrates of the alkalies are converted into chlorides upon ignition with ammonium chloride.

Pure sodium nitrite gives 84·78 per cent. of sodium chloride, while sodium nitrate gives only 68·82. From these data it is therefore easy to calculate the percentage, as anything under 84·78 indicates the presence of nitrate.

It must be borne in mind that if the specimen contains carbonate, this would give the percentage of nitrite too high. As 100 parts of carbonate would give 110·37 parts of sodium chloride after ignition, therefore it will be necessary to deduct an equivalent quantity of sodium chloride from the results before calculating them. A weighed quantity of the nitrite is intimately mixed with powdered ammonium chloride, and introduced into a platinum crucible; a gentle heat is applied, until the whole of the excess of sal-ammoniac and other gaseous bodies are volatilised. The residue is dissolved in water, and the sodium chloride estimated volumetrically with a silver solution.

After a deduction for any sodium carbonate present, the calculation may be made thus :—

$$\frac{(\mathrm{NaCl}-68{\cdot}82)+100}{15{\cdot}96}=x,$$

x being the percentage of sodium nitrite. The sodium chloride left, minus the percentage of nitrate, divided by the difference (15·96), will give the percentage of nitrite, or *vice versa* :—

$$\frac{(84{\cdot}78-\mathrm{NaCl})+100}{15{\cdot}96}=x,$$

x being in this case sodium nitrate; ammonium nitrite in solution is resolved on boiling into nitrogen and water.

2. When Minute Quantities only are Present.—(*A*) Nitrites have the property of liberating iodine from an acidified solution of potassium iodide. Dr. Angus Smith asserts that an amount of nitrous acid, so small as 1 in $3\frac{1}{4}$ millions of water, may easily be discovered in this manner.

(*B*) P. Holland has made use of this qualitative test for the purpose of quantitative estimation, the colouration imparted by the free iodine being taken as the measure of the nitrous acid present. For a 'colorimetric' standard, solution of iodine in potassium iodide is taken; about 4 grammes are dissolved in excess of iodide, and made up to the volume of a litre. In the next place it is necessary to prepare a pure salt of nitrous acid; for this purpose commercial potassium

nitrite is precipitated with silver nitrate, the resultant silver salt washed by decantation, recrystallised, and dried *in vacuo*.

To 0·3276 gramme of the silver salt, dissolved by heat in water, is added a slight excess of pure sodium chloride, and the liquid, when cold, made up to the volume of 1000 c.c.; therefore 10 c.c.=1 milligramme of nitrous acid.

The iodine solution is titrated as follows :—A permanganate burette divided into tenths of a c.c., and fitted with a float, is filled with it. Two narrow white glass jars are placed on a white slab; on each is marked the point at which a volume of 200 c.c. of water stands. Into one, A, is put an amount of the standard nitrite equal to 1 milligramme of nitrous acid, together with 6 c.c. of potassium iodide (1 to 10 of water), then distilled water nearly to the mark, and lastly, dilute sulphuric acid. The whole is to be mixed and allowed to stand until the colour is fully developed; when that point is reached, the second jar, containing an amount of potassium iodide and acid equal to that in A, is filled to within a short distance of the volume mark with water, and placed under the burette; the iodine solution is then cautiously delivered into it, until the depth of colour is judged to be equal in intensity to that in A. The iodine solution should be of such a strength that 10 c.c. have a colouring power equal to that possessed by 1 milligramme of nitrous acid in the presence of potassium iodide in a volume of 200 c.c. of water. It is unadvisable, when making the comparison, to add the standard nitrite from a burette to an acidified solution of potassium iodide, for an obvious reason. It may, however, be suggested that a definite quantity of nitrite should be added, together with iodide, to the water in the jar, and lastly the acid. Such a method is tedious, in that it would be necessary to make several assays before attaining the desired shade.

The following estimations of nitrous acid have been made in this manner :—An amount equal to 1 milligramme was evaporated with a litre of spring water to the volume of 100 c.c., the residue was filtered into the cylinder, and the filter washed; when cold some potassium iodide was added, then distilled water to within $\frac{1}{4}$ inch of the mark, and lastly dilute sulphuric acid. After thoroughly mixing, the contents of the cylinder were left undisturbed for the colour to become fully developed; when that stage arrived it was found that 11·5 was the number of c.c. of iodine requisite to impart the same colour to an equal volume of water. Ten c.c. only should have been required; the excess, therefore, of 1·5 c.c. is the measure of the nitrous acid in the water employed.

The process is not suitable when the quantity of nitrous acid is large; while it ranges below and up to 1 milligramme concordant results can be obtained.

Some precautions are necessary in certain cases. Sulphuretted hydrogen and sulphides must be removed if present; the former escapes

during the evaporation of the water; the latter may be decomposed by a metallic oxide. Organic colouring matter can be precipitated by means of calcium chloride, sodium carbonate, and a few drops of potassium hydrate, as suggested by Sir E. Frankland. Kaolin could, perhaps, be employed for the purpose.

(*C*) For estimating the nitrous acid in the Gay-Lussac column, Kolb gives the following process:—1 gramme of pure dry potassium permanganate corresponds to 0·6 gramme nitrous acid, and converts it into 0·85 gramme anhydrous nitric acid. The permanganate must not be dropped into the acid, but the acid under examination must be dropped into a known volume of permanganate until the latter is decolourised. Cold dilute nitric acid has no action upon permanganate. Kolb operates upon 0·5 gramme of permanganate in solution, and the volume of acid employed to decolourise it shows the amount of nitrous acid contained. To the liquid is now added a known volume of the normal solution of iron, and the whole is boiled to expel hyponitric acid. Dilute with boiled water, stopper the flask, and when completely cool, titrate with normal permanganate. We obtain thus an amount of nitric acid, from which it is necessary to deduct that furnished by the former operation, and which has been calculated into nitric acid. The difference shows the real quantity of nitric acid existing in the volume of liquid used, in the first place, to decolourise the 0·5 gramme of permanganate. Suppose, for example, that it was needful to use 10 c.c. of the sample of acid to decolourise the 0·5 gramme of permanganate. These 10 c.c. contain 0·3 gramme of nitrous acid. If, in the second place, it is found by means of the normal solution of iron that the same 10 c.c. of acid contain 0·572 of nitrous acid, from this quantity we must deduct 0·425, the equivalent in nitric acid of the 0·3 of nitrous acid. There remains 0·147 of nitric acid for the 10 c.c. of acid operated upon, or in 100 parts—

Nitrous acid . . .	3·00
Nitric acid . . .	1·47

(*D*) For estimating the nitrogen compounds in the acids from the Gay-Lussac column and the Glover tower, and also in chamber acid, G. E. Davis remarks that if arsenious acid is present in the vitriol, the process of examination by either the chloride of lime or the permanganate method or the bichromate method would be incorrect, seeing that arsenic acid would be produced from the arsenious compound, and the amount of the deoxidation would be reckoned as nitrous acid.

The methods of oxidation alluded to can only be exact, or approximately so, when the arsenic compounds are in a state of peroxidation, and the vitriol is free from organic matter and iron proto-salts, and also when the nitrogen oxides are all in the same degree of oxidation, and that degree positively known. It is therefore certain that none of

the oxidation methods can be used for estimating with certainty the amount of nitrogen compounds in ordinary pyrites vitriol, and only under certain conditions is it permissible to use an oxidation process for the estimation of the nitrogen compounds in brimstone vitriol.

(*E*) G. E. Davis proposes the following modification of a process devised by Walter Crum:—1 c.c. of the vitriol is measured very accurately by means of a fine pipette, and introduced into Frankland's stopcock-tube, standing over mercury. By opening the stopcock the vitriol is allowed to run in, and the cup is washed out with pure strong vitriol which is also run into the tube. The bottom is now closed with the thumb, and the vitriol agitated with the mercury in such a manner that an unbroken column of mercury always remains between the vitriol and the thumb. The reaction is complete in less than five minutes, and the tube being graduated, the mercury is levelled, and the volume of gas read off. For technical purposes this volume will be found accurate enough, but in cases where extreme accuracy is required, the tube must be left to itself for several hours, the temperature and pressure noted, and the necessary corrections made.

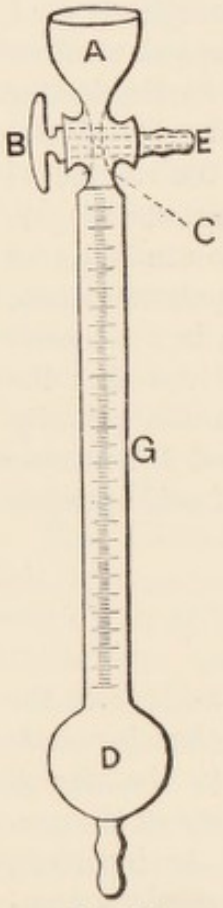


Fig. 24.

The mercury reduces the whole of the nitrogen oxides to nitric oxide, and the presence of any other compound found in vitriol has no influence on this test. The only precaution to be taken is to have the vitriol in the tube strong enough.

For working out this process Davis has devised a convenient and economical mercurial trough, which is supplied by Messrs. Mottershead of Manchester.

(*F*) Another apparatus for the purpose, known as Tennant's nitrometer, is here figured:—B is a three-way stopcock, having a passage between the tube C and the cup A, and between C and the waste-pipe E. G is a tube graduated to 30 c.c. in fifths. A piece of caoutchouc tubing is fixed to the outlet of the globe D, and carried to a bottle or reservoir for mercury, whence the graduated tube may be filled.

A measured quantity of the acid to be tested is then introduced into the cup A, and, by lowering the mercury reservoir and opening the stopcock, allowed to pass into the graduated tube. The stopcock is then closed, and the column of acid vigorously shaken till its reaction on the mercury is completed.

CHAPTER XI

IODINE, BROMINE, CHLORINE, FLUORINE

IODINE

Preparation of Pure Iodine

The impurities to be looked for in iodine are moisture, hydriodic acid, bromine, chlorine, and cyanogen iodide. A number of processes have been suggested for obtaining a product free from these contaminations, but they all either are very elaborate, demanding no inconsiderable sacrifice of time, or, like the simple resublimation of iodine with potassium iodide, are inefficient. Lancelot W. Andrews [1] has experimented on the reaction between fused potassium pyrochromate and potassium iodide, which occurs in accordance with the equation

$$5K_2Cr_2O_7 + 6KI = 8K_2CrO_4 + Cr_2O_3 + 6I,$$

and it offers a simple method for obtaining pure iodine directly from the impure iodide. A preliminary experiment showed that by fusing a mixture of 29·5 grammes of potassium pyrochromate with 20 grammes of potassium iodide, practically the whole of the iodine was obtained in the free state. No iodine was set free on fusing a mixture of normal potassium chromate and iodide. A mixture of potassium bromide (6 molecules) with pyrochromate (5 molecules) furnished, on fusion, a trace of free bromine; but when to the same mixture a little normal potassium chromate had been added, no bromine was set free.

The following are the necessary steps in the preparation of pure iodine by this method :—

Pulverise potassium iodide with 1·4 times its weight of potassium pyrochromate, each salt having been previously separately fused to ensure perfect dryness. Introduce the thoroughly incorporated mixture into a wide tube, closed at one end, and heat to about 200° in a current of dry air to expel any moisture which may have been taken up during the pulverisation. Place a plug of dry glass-wool over the mixture, and wipe out carefully the interior of the tube above the plug with absorbent cotton secured to a glass rod. Slip over the open end of the tube a

[1] *Chemical News*, July 15, 1904.

second short one, fitting it as snugly as possible. Fix the tube at an angle with the horizontal, and heat the powder gradually with a small flame, using if necessary a screen of asbestos board. Having sublimed the iodine into the upper part of the tube, cut off the latter, when cold, at a point 2 or 3 centimetres above the glass-wool plug, or, if smaller amounts are being operated on, the tube can be melted off at the place indicated.

Assay of Commercial Iodine

The methods generally adopted, based on the well-known reactions of sulphurous acid or sodium thiosulphate, yield excellent results in experienced hands, but are attended with many sources of error owing to the rapid alterations in the standard solutions. Mohr's method, based on the use of sodium arsenite, is much more accurate, and with the modifications introduced by A. Bobierre, leaves little to be desired on the score of accuracy or speed.

Make a concentrated solution of potassium iodide, which should remain unchanged for a certain series of experiments; this is to dissolve the iodine which is to be tested. The standard solution of sodium arsenite is obtained by dissolving 4·95 grammes of arsenious acid with 14·5 grammes of crystallised sodium carbonate, and diluting the aqueous liquid to 1 litre. This solution should decolourise an iodised liquid containing 12·688 grammes of iodine per litre. But supposing that the arsenious liquid may not have this reducing power, the test will be none the less exact, as at the time of performing it the relation of a given weight of pure iodine to the arsenite will also be estimated. A somewhat concentrated solution of sodium bicarbonate is also to be prepared.

The analysis is best effected in a small stoppered flask. Into this are put 10 c.c. of the sodium arsenite, to which must be added 5 c.c. of alkaline bicarbonate solution; the whole then receives a further addition of about 4 c.c. of perfectly colourless benzol.

Weigh a certain quantity of pure iodine between two watch-glasses; dissolve this in the concentrated solution of potassium iodide prepared beforehand, and which must be of the same strength in all the various estimations which may be made; with this coloured solution fill a flask containing 100 c.c., shake it, and pour the contents into a graduated burette.

On allowing the iodised solution to fall into the arsenite drop by drop, and stirring it quickly, the brown colour will be seen to disappear instantaneously; but scarcely will all the arsenite have been changed to arseniate, when the addition of iodine will produce a double reaction: in the first place, the benzol will turn red; secondly, the aqueous liquid, which was perfectly colourless at the beginning of the operation, assumes a very sensibly yellowish tinge. The significant character of

this is the more surprising when we remember the very small quantity of iodine which causes it.

A second experiment is now to be performed upon the iodine to be estimated, and the same weight being used, its standard is at once shown, since the volume of solution requisite to destroy the alkaline arsenite is in inverse proportion to the quantity of real iodine to be estimated.

Detection of Minute Quantities of Iodine

(*A*) Make a mixture of water, 100 grammes; starch, 1 gramme; potassium nitrite, 1 gramme: boil this for five minutes; it will then keep for years without deterioration. When required for use, take 10 c.c., and add to it one drop of hydrochloric acid. Take a piece as large as a pin's head of the dry salt to be tested for iodine, place it in a clean porcelain capsule, and add a drop of the test liquid. When no iodine is present, no colouration ensues; but the least trace of iodine gives rise to the formation of a well-defined blue colour.

(*B*) Carey Lea makes use of the oxidising properties of chromic acid to liberate iodine from its hydrogen and metallic combinations and thereby bring about the starch reaction.

If, for example, we take an extremely dilute solution of potassium iodide, such that the addition of nitric acid and starch produces no perceptible effect, the further addition of a single drop of very dilute solution of potassium bichromate will instantly bring about the characteristic reaction. When hydrochloric acid is substituted for nitric, the effect of the bichromate is still more marked. The test has, then, the full delicacy at least of the chlorine test, with this great advantage, that an excess of the reagent does not prevent the reaction. As to the delicacy of this test, the following observations have been made:— With solutions of potassium iodide up to $\frac{1}{100000}$ the precipitate is abundant, becoming less blue and more tawny as the dilution increases. Beyond this point the distinctness rapidly falls off. The indications are observable at $\frac{1}{400000}$. With a solution of $\frac{1}{800000}$ it is doubtful whether any effect is evident. The experiment can be made in two ways, according to the result desired.

In employing the reagent in the search for iodine, add the starch to the liquid to be tested, stir it up, add a drop of dilute solution of potassium bichromate, enough to communicate a pale yellow colour, and finally add a few drops of hydrochloric acid. The test is then the production of the characteristic precipitate, or in case of great dilution, approaching to a half-millionth, merely the tawny shade given to the solution.

If a very great excess of acid is used, and too much bichromate taken, the starch may be made to reduce the bichromate. Even this, however, cannot deceive, for a bluish-green solution is thereby produced, whereas the indications of iodide are in the order of their

strength—blue precipitate, tawny precipitate, tawny solution. Unless in the case of very exceptional dilution above spoken of, a well-marked blue precipitate is always obtained.

(*C*) The method of estimating iodine by the thiosulphate process is best conducted as follows :—

Prepare a normal standard solution containing, for each litre of water, about 40 grammes of sodium thiosulphate, so that 50 c.c. of this solution will completely decolourise 1 gramme of iodine.

Then take 10 c.c. of the iodised liquid to be tested, diluted with water if it be very concentrated or rich in iodine ; then add carefully, after it has been acidulated with hydrochloric acid, some drops of hyponitric acid. When it becomes yellow, shake it with benzol or petroleum, which will immediately turn rose or violet. Separate the iodised benzol from the acid liquid, and repeat the operation until the solvent liquid ceases to become coloured.

Collect the iodised benzol resulting from these treatments, and wash it with distilled water, which will remove all traces of chlorated or bromated compounds without removing any appreciable quantity of iodine. Then, with constant stirring, add, by means of a burette graduated to tenths of a c.c., the standard thiosulphate liquid until all colour is destroyed ; each half cubic centimetre of the normal liquid will correspond to 1 centigramme of iodine contained in the liquids assayed.

It is always necessary to desulphurise solutions containing sulphides, sulphites, or thiosulphates, by boiling them with nitric, sulphuric, or hydrochloric acid.

To ascertain the purity of commercial iodines, dissolve about 50 centigrammes in diluted alcohol, and operate as above.

To ascertain the quantity of iodine in dry or wet sea-plants, cut them into small pieces ; dry them, place them in a porcelain capsule and cover them with alcohol ; set fire to the alcohol, carefully stir the mass with a glass rod, and the carbon will be obtained without loss of iodine ; then well wash the latter, and act on the solution as above described.

Detection of Small Quantities of Iodine in Sea-water, &c.

(*A*) The liquid to be tested is placed in a test-tube along with carbon disulphide, and a very few drops of dilute sulphuric acid. Hereupon the vapour of red fuming nitric acid is allowed to fall for a moment into the tube. After strong agitation, the carbon disulphide is coloured rose if the slightest trace of iodine is present.

(*B*) A. Chatin points out certain causes of failure in the detection of minute quantities of iodine in potable waters, &c. It is needful to precipitate the soluble calcium and magnesium salts with an excess of pure potassium carbonate. The iodine being thus fixed will be

found in the residue after evaporation, which is slightly ignited to destroy organic matter. The liquid must be separated by decantation from the earthy carbonates, which will be deposited during the first quarter of the evaporation. Towards the end of this process the heat must be diminished to avoid any loss of the soluble residue by spirting. This last point is important, as the iodide is among the last drops evaporated. The excess of carbonate remaining after the precipitation of the calcio-magnesium salts should be the larger the more organic matter is present. We may ascertain that this excess has been sufficient, either by the residue appearing colourless after calcination, or by the circumstance that although coloured it forms a paste if treated with alcohol at 90 per cent. If the alkaline carbonate has been insufficient, the residue will be divided in the alcohol, like a powder; the iodine then escapes in great part or entirely during calcination. The alkaline residue left on the evaporation of the water must be treated three times with alcohol, and the solutions are mixed together in a capsule capable of holding at least four times the quantity. Before proceeding to evaporate, which must be done at a low temperature, the alcohol is mixed with about half its volume of pure distilled water. The water should have been distilled after an admixture with potassium carbonate. Frequent agitation is useful. Slight calcination is again needed to destroy a certain quantity of organic matter which has escaped the former ignition, and the presence of which would mask the character of traces of iodine. The residue at the bottom of the capsule should be colourless and scarcely perceptible. If it is very appreciable in quantity too much alkaline salt is present, and it must be redissolved in alcohol. The last condition is that this residue must be dissolved in a minimum of water, 2 drops, or even a single drop, which must be led over the bottom of the capsule with a glass rod, so as to dissolve all the iodide present. With the end of the stirrer this liquid is divided into three or four portions, one of them—which will give the most distinct reaction—being left in the bottom of the capsule, the others being placed on fragments of porcelain. One of these little drops is mixed with palladium chloride; the others, having first received a trace of recently made starch-paste, are carefully touched, the one with nitric acid, the other with commercial sulphuric acid; chlorine water only gives the blue colouration if the quantities are more considerable. A common cause of failure is the use of chlorine water, and of too dilute solutions. Earths, ores, metals, sulphur, &c., are first finely divided, and then boiled in a solution of potassium carbonate, which is then treated as above. It is well to make blank experiments in researches of this kind.

(*C*) Sergius Kern recommends that palladium salts should be very carefully used in analysis for the detection of iodine, because in presence of potassium ferrocyanide or potassium ferricyanide the iodine is not detected, and cannot be separated from bromine or chlorine by

palladium chloride. So as gold salts also give, with potassium ferrocyanide, a green colouration, this reagent may give faulty results, as it was remarked that palladium salts give the same colouration.

If palladium salts are used as a reagent for iodine, the preliminary analysis must be very carefully executed, in order to be quite convinced of the absence of double potassium ferrocyanides and other cyanides. In presence of alkaline sulphocyanides iodine is not precipitated by palladium nitrate or chloride.

Estimation of Iodine in Organic Liquids

(*A*) There are met with in commerce mother-liquors which are utilised for the manufacture of iodine, and containing, besides this metalloid, sensible quantities of alkaline arseniates and arsenites, as well as organic matter. These liquids occur in the manufacture of aniline colours, and their value depends upon the amount of iodine they contain. The following is the best process to adopt for estimating this :— 10 grammes of liquid are treated with 2 grammes of concentrated solution of caustic potash ; the mixture is then evaporated to dryness under a chimney with a good draught, or in the open air, on account of the cacodylic products occasionally evolved ; it is ultimately ignited. The aqueous solution of the residue is diluted with water and treated with a mixture of sulphuric and hyponitric acids. The iodine is separated by agitating with carbon disulphide, and this carbon disulphide solution agitated with water until the washings no longer affect litmus-paper ; when this is attained, a titration of the iodine present is made with sodium thiosulphate or arsenite.

(*B*) To estimate the iodine contained in organic hydriodates, Kraut proposes that their solution be digested for some time with a known weight of recently precipitated silver chloride ; the chlorine is replaced by iodine, and from the increase in weight of the silver chloride the amount of iodine may be calculated. This method has the advantage of not altering the substance beyond removing its iodine, which is replaced by chlorine.

(*C*) Reinige describes a very interesting method for the estimation of iodine, viz. by means of potassium permanganate. Two equivalents of the latter and 1 equivalent of potassium iodide produce 1 of potassium iodate, 2 of free potash, and 4 of manganese peroxide. The decomposition is assisted by boiling the solution, and if the latter is very dilute, a little potassium carbonate is added to induce the commencement of the reaction. As bromine and chlorine are not in the least acted upon under the same circumstances, this reaction is, perhaps, the most convenient for the estimation of iodine. The latter must be combined with potassium, and the solution rendered nearly neutral, but still slightly alkaline. It is heated till it boils gently, and a solution of 2·5 grammes potassium permanganate in 497·5 grammes

water is gradually added, removing the beaker from the lamp each time for a few moments, to allow the precipitated peroxide to deposit, but heating it again to the boiling-point before adding another portion of permanganate. When the solution, after the precipitate has subsided, shows a distinctly reddish tint, all potassium iodide is decomposed. The small excess of permanganate is estimated by sodium thiosulphate, and the remainder shows exactly 2 milligrammes of iodine for each c.c. of the permanganate solution used. The results are very accurate.

BROMINE

Detection of Bromine

The best solvent for bromine just displaced by chlorine is carbon disulphide, a substance long used in France for detecting iodine. Fresenius, who has verified this fact with his usual care, insists on the necessity of avoiding excess of chlorine, and of employing carbon disulphide free from sulphurous and sulphuric acid.

His preference for carbon disulphide over ether and chloroform is founded on a series of direct experiments with standard solutions containing various proportions of bromides. Solutions containing only $\frac{1}{30000}$ of bromine in the state of potassium bromide, when treated with the requisite quantity of chlorine, do not communicate the least colour to ether or chloroform, while carbon disulphide acquires a decided yellow tint. Moreover, being heavier than water, it sinks to the bottom of the liquid with the bromine it has dissolved, and there remains.

If the bromide is accompanied by an iodide, the iodine must be previously eliminated by adding a little hyponitric acid and a drop of carbon disulphide, which takes away the displaced iodine. After this the separation of the bromine may be proceeded with.

Detection of Bromides in Potassium Iodide

Dr. E. van Melckebeke finds that if to a saturated solution of potassium bromide a small quantity of pure potassium iodide is added it will completely dissolve, but if the iodide is contaminated with potassium bromide this impurity will remain undissolved; 100 parts of water (distilled), at 16°, dissolves 140·1 parts of potassium iodide, and the same quantity of water, at the same temperature, dissolves 63·39 of potassium bromide: 100 parts of water saturated with bromine dissolve only 13·15 parts of potassium iodide, and if more of that salt be added bromide is precipitated. As the solution of the salts in water causes a very sensible lowering of temperature, for testing, the author recommends to dissolve pure potassium bromide in warm water, to let this solution cool, and decant from the crystalline deposit. To 10 c.c.

of this solution 10 drops of water are added in a test-tube, and afterwards in small quantities, and, constantly shaking, 1 gramme of the suspected iodide in coarse powder; if free from bromide it will dissolve almost instantly, while if bromide is present it will remain undissolved.

Solution of Bromine as a Reagent

L. de Koninck has for three years successfully used the solution of bromine in a 10-per-cent. solution of potassium bromide. The author recommends it for the precipitation of manganese from an acetic solution, for the conversion of arsenious into arsenic acid, and for the detection of nickel in presence of cobalt in a potassium cyanide solution.

Detection of Chlorine, Iodine, and Bromine in Organic Matter

C. Neubauer introduces a little copper oxide into the loop of a platinum wire, and heats till it adheres. It is then dipped into the substance, or a little of the latter if dry is sprinkled upon it. The loop is then brought into the flame of a gas-burner moderately opened, near the lower and inner margin of the flame. The carbon burns first, and the flame becomes luminous, followed by the characteristic blue or green colour.

Estimation of Bromine and Iodine in the Presence of Chlorine

(*A*) This process is of special use for the assay of mother-liquors from saltpetre and kelp. A measured quantity of the liquor is introduced into a long tube with 20 alkalimeter measures of carbon disulphide; and nitrous sulphuric acid (prepared by passing nitrous acid through sulphuric acid) is added, drop by drop, till iodine ceases to be liberated. The tube is inverted several times after the addition of each drop of acid, in order that the iodine may at once be dissolved by the carbon disulphide, to which it gives a violet colour, varying in intensity with the amount of iodine in solution. The quantity of the iodine is estimated by comparing the degree of the colour with that which results when a standard solution of potassium iodide is used in the same way. The delicacy of the reaction is such that 0·01 gramme will communicate a distinct rose tint to the carbon disulphide. When the amount of iodine exceeds 0·2 gramme of iodine in the quantity operated on, a difficulty occurs, as the violet colour becomes so deep that the various shades cannot be distinguished with accuracy. When all the iodine is separated by the carbon disulphide, the solution containing the bromine is introduced into another tube, and the bromine is liberated by chlorine water in the usual way, and taken up by a fresh quantity of carbon disulphide. In this case, an orange colour is

the result, and the amount of bromine may be estimated by comparing the colour with that resulting when a solution of potassium bromide is used of known strength.

(*B*) Colour tests being always liable to much uncertainty in their indications if any great accuracy is desired, the following process may be found preferable. It is devised by Tatlock, and is based upon the wide difference between the equivalents of iodine, bromine, and chlorine. The mode of procedure depends upon the displacement of iodine by bromine, and of iodine and bromine by chlorine.

The solution containing the iodide, bromide, and chloride, preferably in combination with an alkali metal, is divided into three equal portions. To the one, solution of silver nitrate is added in excess, to precipitate the whole of the iodine, bromine, and chlorine. The liquid is then feebly acidified with pure nitric acid, warmed, and agitated till the precipitate settles. This is collected on a small weighed filter, washed with hot water, dried as far as possible at 100° C., removed from the filter, dried perfectly by heating to incipient fusion, and weighed, the weight of the small portion adhering to the filter being added, and the weight of the whole noted as

$$AgI + AgBr + AgCl.$$

Another portion of the solution is transferred to a small basin, and a quantity of pure bromine water added. The mixture is then carefully evaporated on an open water-bath, more bromine water being added from time to time, till the escaping vapours no longer turn starch-paper blue on a fresh addition—showing that all the liberated iodine has escaped. To ensure excess, a little more bromine water is added, and the solution evaporated to complete dryness. The dry residue is then drenched with water, and the result heated till again dry; this operation is repeated two or three times, to ensure the complete expulsion of any hydrobromic acid that may have been present in the bromine water. The residue, which now consists solely of alkaline bromide and chloride, is dissolved in water, silver nitrate added in excess, the solution acidified, and the precipitate collected and weighed in the usual way. It is noted as

$$AgBr + AgBr + AgCl.$$

The last portion of the solution is brought into a small basin, and a quantity of strong chlorine water added, to effect the liberation of the iodine and bromine. The mixture is then evaporated till all colour is gone, and some more chlorine water added. If the solution remains colourless, the whole of the iodine and bromine has been expelled, and the alkali metal will exist entirely as chloride. The solution is then brought completely to dryness, after which it is evaporated with a few drops of water two or three times, to expel any hydrochloric or hydrobromic acid. The dry residue is dissolved in water, the solution

acidified with pure nitric acid, silver nitrate added in excess as before, and the silver chloride collected as usual. Its weight is noted as

$$AgCl + AgCl + AgCl.$$

It is obvious that we have now data from which we can calculate the amounts of iodine, bromine, and chlorine present; for, as the equivalent of bromine is less than that of iodine, in the proportion of 80 to 127, the second precipitate, in which the iodine is replaced by bromine, must weigh proportionately less than the first; and, as the equivalent of chlorine is less than that of either iodine or bromine, in the ratio of 35·5 to 127 in the one case, and to 80 in the other, the last precipitate must weigh still less than the second, and we can thus, from the observed differences, deduce the exact quantities of the three elements present.

Example :—

1. AgI + AgBr + AgCl weighed 15·57
2. AgBr + AgBr + AgCl „ 14·69
3. AgCl + AgCl + AgCl „ 12·20

Then—

I.		II.		Observed difference.
15·57	−	14·69	=	0·88

Loss for 1 equiv. I.		Observed loss.		1 equiv. I.		I present.
47	:	0·88	::	127	:	2·378

I.		III.		Observed difference.
15·57	−	12·20	=	3·37

But, as a portion of this loss is caused by the replacement of iodine by chlorine, namely—

Equiv. of I.		Loss in replacing 1 equiv. I by Cl.		I found.		Loss accounted for by I present.
127	:	91·5	::	2·378	:	1·713

Observed loss.		Loss accounted for by I present.		Difference for Br.
3·37	−	1·713	=	1·657

Loss for 1 equiv. Br.		Observed loss on account of Br.		1 equiv. Br.		Br found.
44·5	:	1·657	::	80	:	2·978

Then, as the proportions of iodine and bromine are already known, it will be an easy matter to calculate them to iodide and silver bromide, and deduct their weight from precipitate 1, calculating the remainder (silver chloride) to chlorine, thus :—

I.		AgI.		I present.		AgI.
127	:	235	::	2·378	:	4·400

And—

Br.		AgBr.		Br present.		AgBr.
80	:	188	::	2·978	:	6·998

Then—

AgI	4·400
AgBr	6·998
	11·398

Then—

15·57 − 11·398 = 4·172

Then—

AgCl.		Cl.		AgCl.		Cl.
143·5	:	35·5	::	4·172	:	1·032

There were, therefore, present in the solution—

Iodine	2·378
Bromine	2·978
Chlorine	1·032

The bromine water may be easily obtained free from chlorine by distilling potassium bromide in solution with less potassium bichromate than is necessary to expel the whole of the bromine, using, of course, a little hydrochloric acid.

(*C*) *Application of the foregoing Method to the Analysis of Kelp.*—It is quite obvious that this process cannot be directly applied to substances containing iodine, bromine, and chlorine, in very different proportions, and consequently it cannot be used for the estimation of these elements in kelp immediately. The following method of treatment will be found to equalise as nearly as necessary the proportions of the three :—

2000 grammes of the kelp are digested in hot water, the solution allowed to settle, and the clear liquor filtered. The residue is boiled two or three times with water, the liquid being filtered in each case, and the residue finally brought on a filter and washed with boiling water. The filtrates and washings are neutralised as nearly as possible with hydrochloric acid, and chlorine gas passed into the solution till the latter becomes of a distinct orange colour, due to the liberation of iodine and bromine.

The liquid is then shaken up with about $\frac{1}{4}$ of its bulk of carbon disulphide, which takes up the liberated iodine and bromine, and carries them in solution to the bottom of the vessel, provided the sp. gr. of the kelp solution be not higher than that of the carbon disulphide. When this is not the case, the solution of kelp may be diluted till the carbon disulphide sinks.

The bottom liquid, containing the iodine and bromine, is then drawn off by a fine syphon, and shaken up with an equal volume of water and some zinc filings. The solution is soon decolourised, on account of the formation of zinc iodide and zinc bromide, which pass into the water; and we have thus an aqueous solution of the two latter salts above, and colourless carbon disulphide at the bottom. The latter is drawn off by a syphon, and restored to the kelp solution, to which

some more chlorine water is added; and, if a further quantity of iodine and bromine be liberated, the above operations are repeated till the liquor is quite exhausted.

It now only remains to evaporate the solution of zinc salts, divide into three equal portions, and determine iodine, bromine, and chlorine, as before described.

Detection of Bromides in the Presence of Chlorides

When gold chloride is added to a faintly acid solution of an alkaline bromide, a colouration is produced ranging from dark orange red to light straw colour according to the strength of the solution. Iodides must not be present; chlorides, however, do not interfere. The best mode of proceeding is as follows:—Remove the iodides, if present, by means of palladium, and after getting rid of excess of palladium by sulphuretted hydrogen, concentrate the solution to about 25 c.c. Select two test-tubes of the same size and shape and colour of glass; into one pour the solution suspected to contain bromine, and into the other pour pure water containing a trace of potassium chloride. Add to each tube one drop of hydrochloric acid, and one drop of gold chloride solution. On now comparing the two tubes, particularly in the direction of their length, a yellow colour will be observed in the tube containing the bromide, which will be rendered very manifest by comparison with the other tube.

The mixed chloride and bromide should be brought to the state of alkaline salts if necessary, by precipitating with silver nitrate, thoroughly washing and fusing with *potassium* carbonate. If sodium carbonate is used for this purpose the subsequent reaction with the gold test is not so decided.

Detection of Chloride in Potassium Bromide

(*A*) The bromide to be examined is first tested for iodine. For this purpose a small quantity of the salt is dissolved in water in a test-tube, and an equal volume of carbon disulphide added. Upon the addition of a few drops of bromine water, the carbon disulphide becomes coloured violet, under the influence of iodine, if this be present. When the test shows the presence of iodine, it is necessary to remove the whole of this element from the sample. This is effected by dissolving about 10 grammes of the salt in distilled water, adding bromine water until violet vapours are no longer visible upon boiling, and then testing for iodine in the manner first described. Afterwards the solution is evaporated to dryness to remove the excess of bromine, and thus is obtained a potassium bromide free from iodide, but which may contain chloride.

The remainder of the process depends upon the fact that a given weight of potassium chloride requires, for complete precipitation, a

much greater amount of a standard solution of silver nitrate than the same weight of potassium bromide. While the bromide for the complete precipitation of 1 gramme requires 1·428 gramme of silver nitrate, 1 gramme of the chloride requires 2·278 grammes. A standard solution of silver nitrate is first prepared by dissolving 10 grammes of the pure salt in a litre of water, each 0·1 c.c. corresponding to 1 milligramme of silver nitrate; 1 gramme of the bromide to be examined, freed as above from iodine, is dissolved in 100 c.c. of distilled water; 10 c.c. of this solution, representing 0·1 gramme of potassium bromide, would require, if pure, 14·2 c.c. of the silver solution; potassium chloride would require 22·7 c.c.

(*B*) Baudrimont has proposed a method of making the final reaction more delicate, by adding a few drops of solution of potassium chromate to the bromide examined; the silver nitrate added at first combines with the whole of the bromine and chlorine in preference, and the complete precipitation is marked by the production of the red precipitate of silver chromate. It is obvious that the bromide contains more or less chloride, according as the number of burette divisions (divided into $\frac{1}{10}$ c.c.) of the silver salt required exceeds 142. With a salt containing $\frac{1}{10}$ of its weight of potassium chloride 151 divisions are required, and with a mixture of equal weights of chloride and bromide, 185.

The same method may be employed to recognise the degree of purity of several compounds. Operating as before—that is to say, dissolving 1 gramme of the material to be examined in 100 c.c. of distilled water, and taking 10 c.c. of the solution—the following numbers of $\frac{1}{10}$ c.c. divisions required will show the purity for at least a considerable number of salts:—102 for pure potassium iodide, 257 for potassium cyanide, 246 for dry potassium carbonate, 290 for sodium chloride, 119 for sodium carbonate + 10 equivalents of water, 47 for sodium phosphate + 24 equivalents of water, and 54 for sodium arseniate + 14 equivalents of water.

Detection of Iodine in Potassium Bromide

(*A*) When potassium bromide is suspected to be adulterated, or mixed with potassium iodide, place a few grains of the salt in question on paper previously impregnated with starch-paste, moisten it, and admit a small quantity of chlorine gas, whereby the iodine is set free and the paper coloured blue.

(*B*) A better test is the use of bromine water added to the salt after it has been placed in benzol; if the latter becomes red-coloured, iodine is present.

CHLORINE

Estimation of Chlorine with the aid of Gooch's Method of Filtration

(*A*) David Lindo remarks that it is generally considered that chlorine can be estimated with great exactness by the gravimetric method.

Silver chloride being slightly soluble in water, especially in hot water, a small minus error may occur if the latter is employed to wash with, but this can be prevented by adding a little silver nitrate to the water, as recommended by J. P. Cooke.[1]

On the other hand, the precipitate retains occluded matters with great force. Error from not completely removing these often more than compensates for slight loss occasioned by the use of hot water alone, or merely acidulated with nitric acid, or by the manipulations necessary when paper filters are employed.

According to Fresenius,[2] we can, with great care, always obtain by this method 99·9 to 100·1 for 100 parts of chlorine taken. It is presumed Fresenius means when using paper filters, in which case the time required to make an estimate is generally six hours.

The limits of error here laid down are often reached when paper filters are employed, and no silver nitrate added to the wash-water.

Though sufficiently near for most purposes, greater accuracy in chlorine estimates may sometimes be desired. By adopting Gooch's method of filtration and Cooke's suggestion, with a few other simple precautions, a much higher degree of accuracy can be attained with less manipulation and expenditure of time than by the usual method.

Method :—Weigh the solution in a light glass-stoppered bottle, and turn it into a deep porcelain capsule, about $4\frac{1}{2}$ ounces capacity, provided with a well-formed lip and handle. Rinse the bottle with 25 c.c. distilled water. Add solution of silver nitrate in about the proportion of 25 c.c. to 0·5 gramme potassium chloride, and 2 c.c. pure nitric acid, sp. gr. 1·2. Heat to boiling-point, and keep at this temperature for some minutes without allowing violent ebullition, and with constant stirring, until the precipitate assumes the granular form. Allow to cool somewhat, and then pass the liquid through asbestos in a Gooch crucible. Wash the precipitate by decantation with 200 c.c. of very hot water, to which has been added 8 c.c. nitric acid and 2 c.c. dilute solution of silver nitrate containing 1 gramme of the salt in 100 c.c. of water. The washing by decantation is performed by adding the hot mixture in small quantities at a time, and stirring up the precipitate well with a thin glass rod after each addition. The pump is kept in

[1] *Chemical News*, vol. xliv. p. 235.

[2] *Quantitative Analysis*, Seventh Edition, p. 170.

action all the time, but to keep out dust during the washing, the cover is only removed from the crucible when the liquid is to be added.

Put the capsule and precipitate aside, return the washings once through the asbestos so as to obtain them quite clear, remove them from the filter, and set aside to recover excess of silver. Rinse the receiver and complete the washing of the precipitate with about 200 c.c. of cold water. Half of this is used to wash by decantation, and the remainder to transfer the precipitate to the crucible with the aid of a trimmed feather. Finish washing in the crucible, the lumps of silver chloride being broken down with the glass rod. Remove the second filtrate from the receiver, and pass about 20 c.c. of alcohol at 98 per cent. through the precipitate. Dry at 140° to 150°. Exposure for half an hour is found more than sufficient, at this temperature, to dry the precipitate thoroughly.

(*B*) In the volumetric estimation of chlorine, with a standard solution of silver and potassium chromate as an indicator, Professor A. R. Leeds points out that the chromate employed is more or less contaminated with alkaline chlorides. Hence it is necessary to estimate the number of tenths of a c.c. of the silver solution which correspond to the number of drops used of the particular chromate solution.

Detection of Chlorides in the Presence of Bromides

The only difficulty concerning halogen salts in general qualitative analysis is the detection of a small quantity of a chloride in the presence of a bromide.

Chapman Jones[1] uses ammonium bicarbonate for dissolving silver chloride in the presence of bromide. If a cold saturated solution of ammonium bicarbonate is poured over silver chloride on a filter-paper, the extract will give a distinct turbidity on acidification with nitric acid. Silver bromide similarly treated gives no turbidity.

By allowing the silver salts to remain in contact with the reagent for a few minutes with occasional agitation, the chloride will give a greater turbidity on acidification, while the treatment of the bromide may be continued sometimes even for half an hour before it begins to give a positive result.

If a turbidity is obtained on acidification of the extract, and it is doubtful whether it is due to silver chloride or bromide, its identity may be established in the following way:—The turbid liquid is divided into two parts; to one is added a slight excess of the bicarbonate solution, and to the other an equal quantity of water. If the turbidity is due to silver chloride, the ammonium salt will redissolve it in a few seconds. If it is due to the bromide, it will remain unaffected for several minutes, if not an hour or more. The part diluted with water is for comparison

[1] *Chemical News*, May 13, 1904.

with the other, as it is difficult to bear in mind the appearance of a turbid liquid, and to duly allow for its dilution.

It is desirable that the ammonium bicarbonate solution be not old, or it will probably have lost some carbonic acid. A boiling solution of sesquicarbonate of ammonia has been used before for dissolving out silver chloride from the bromide, but in this case some of the bromide is always dissolved.

Separation of Chlorine from Bromine

It is possible to effect the separation of chlorine from bromine in a complete manner by the action of ammonium persulphate. This substance decomposes the bromides, setting the bromine at liberty without affecting the chlorides, if the solution is sufficiently dilute.

R. Engel [1] effects the separation as follows :—Dissolve from 1 gramme to 2 grammes of the mixture of alkaline chloride and bromide in from 150 to 200 cubic centimetres of water, and add to the solution from 3 to 5 grammes of ammonium persulphate. The mixture is heated to 70° or 80°, and a current of air is passed into the liquid which carries away all the bromine. The operation requires about an hour, and the separation is theoretically perfect.

The bromine is collected in a dilute solution of sulphurous acid, and it is determined either in the state of silver bromide or after destroying the excess of sulphurous acid and neutralising the liquid, by standard silver nitrate, using potassium chromate as an indicator.

It is better to collect the bromine in a dilute solution of sulphurous acid rather than in a solution of potassium iodide, because the decomposition of ammonium persulphate by heat liberates oxygen containing traces of ozone, or perhaps persulphuric anhydride, according to Berthelot, which react upon potassium iodide. The quantity of iodine liberated in an hour under this influence may reach to 0·006 or 0·007 gramme.

Ammonium persulphate may likewise serve for separating the iodine of the iodides in presence of chlorides and bromides. In the cold, and in presence of sodium acetate, all the iodine of the iodides is precipitated by the persulphate without setting free the smallest trace of bromine or of chlorine. But the iodine cannot be separated by heat, as there is formed, in fact, in heat a certain quantity of iodic acid. Operate therefore in the cold, separating the iodine by means of carbon disulphide, and titrating with sodium thiosulphate.

Detection and Estimation of Chlorine in Presence of Bromine and Iodine

G. Vortmann has discovered a method by means of which even small quantities of chlorine along with the other halogens can be easily

[1] *Chemical News*, July 20, 1894.

and quickly detected. It depends on the different behaviour of the chlorides, bromides, and iodides with manganese and lead peroxides in the presence of acetic acid.

Iodides are partially decomposed by the above-mentioned peroxides, even in neutral solutions, and if they are boiled with the addition of acetic acid the iodine is completely eliminated. Lead peroxide oxidises a part of the iodine to iodic acid, but with manganese peroxide no iodic acid is formed.

In a neutral solution bromides are not decomposed either by manganese or lead peroxide. In an acetic solution the lead peroxide only acts; bromine escapes; but bromic acid is formed only if bromides are present in considerable quantities. Manganese peroxide has no action in the acetic solution, even on prolonged heating.

Chlorides are not attacked by either of the peroxides in presence of acetic acid. In testing for chlorides in presence of bromides or iodides it is sufficient to boil the substance in an acetic solution with lead peroxide till the liquid on settling is colourless and has not the slightest odour of bromine or iodine. The bromine and a part of the iodine escape as such; the remainder of the iodine remains as lead iodate along with the excess of the lead peroxide. On filtering and washing the precipitate, all the chlorine is found in the filtrate free from bromine and iodine. In this manner the chlorine may be estimated quantitatively. If the quantity of chlorine accompanying the iodine is considerable, manganese peroxide is preferable to lead peroxide, as otherwise the liquid must be largely diluted with water to prevent lead chloride from depositing. In estimating large quantities of chlorine in presence of bromine, it is well to add along with the lead peroxide some potassium sulphate so that all the chlorine may be found in the filtrate combined with potassium.

In order to expel the liberated bromine and iodine more rapidly a moderate current of air may be passed through the solution on the water-bath.

Detection and Estimation of Iodine in Presence of Bromine and Chlorine

E. Donath remarks that while potassium bichromate occasions in solutions of potassium iodide no separation of iodine, this result is at once produced by chromic acid. An estimation of the liberated iodine is not possible on account of the action of the excess of chromic acid upon sodium thiosulphate. The iodide of starch is precipitated by solutions of chromic acid as an almost black precipitate. Hence, starch-paste cannot serve as an indicator. The iodine is therefore distilled off, and is estimated in the distillate by means of sodium thiosulphate. The alkaline bromides and chlorides are not decomposed by concentrated solutions of chromic acid at common temperatures, and

the chlorides not even on boiling. Dilute solutions of chromic acid decompose the bromides only to a very small extent at the boiling heat, but the proportion increases with increasing concentration. The method is therefore suitable for accurate estimations of iodine in the presence of chlorine, but not when it occurs along with bromine. The solution of chromic acid employed contains from 2½ to 3 per cent., and is freed from traces of sulphuric acid by boiling with pure barium chromate.

Estimation of Chlorine in Bleaching Powder

(*A*) The commercial estimation of bleaching powder only extends to the estimation of the hypochlorite contained therein; the result being, however, calculated as so much per cent. of 'available chlorine.' Of the numerous methods proposed for the estimation of the hypochlorite, the one usually employed in the trade is that depending on the amount of ferrous salt oxidised by a given weight of bleaching powder. It frequently happens, however, that instead of a perfectly pure ferrous salt (such as the ammonio-sulphate precipitated by alcohol), the ordinary iron protosulphate of the druggists is used, discoloured crystals being of course rejected. The substance is, however, rarely pure, and hence errors are frequently introduced, less chlorine being required to peroxidise a given weight of impure than of pure substance. Again, some analysts neglect to add an acid to the ferrous solution used, and hence the precipitated ferric hydrate is liable to carry down perceptible quantities of ferrous hydrate, again making the apparent amount of chlorine required less than that really requisite. When acid is added, an error is liable to be introduced by the peroxidation of part of the iron by chlorine compounds derived from chlorate that may be present. Direct experiments have shown that acid ferrous solutions are perceptibly oxidised by the presence of chlorate in small quantities in the course of a very few minutes, even at the ordinary temperature, although the peroxidation due to the whole of the chlorate is not manifest until after standing some time at 20° C., or till after heating to ebullition. Lastly, the equivalent of chlorine is frequently taken to be 36 instead of 35·46 (Stas). All these sources of error tend to make the percentage of chlorine found higher than that really present; accordingly it often occurs that analyses of the same sample by different analysts differ by 1, 2, or 3 per cent. of available chlorine. This error becomes of serious importance, it frequently happening that the analysts employed by the seller and purchaser differ in their reports, thus causing much annoyance, and possibly the rejection of the goods as not being of contract strength.

(*B*) As regards the error introduced by the presence of chlorate in the sample analysed, Dr. C. R. A. Wright has made many careful experiments on the subject, which have yielded the following results:—

1. Acid ferrous solutions are peroxidised by the addition of a chlorate, at a rate depending on the strength of the solutions, the amount of free acid and the temperature, the reaction taking place completely after heating to ebullition for a minute, and almost as completely after standing for upwards of half an hour at 20° C., time being, however, required for any temperature short of ebullition.

2. Acid solutions of arsenious acid, where a large excess of free acid is present, are scarcely affected by chlorate at 20° C. until after standing some hours; the reaction ensues completely on heating to ebullition for a minute, and completely in a few minutes' heating on a water-bath.

3. Alkaline solutions of arsenious acid (containing sodium carbonate and free carbonic acid) are wholly unaffected by chlorate, either cold or boiling, even after several hours.

4. Acid solutions of potassium iodide (free from iodate). Iodine begins to separate even at 20° C. in a very few moments on addition of very little chlorate, and after some time much separates. Heated to 100° on the water-bath, the whole of the chlorate becomes completely decomposed, after five minutes, in presence of sufficient free acid.

5. Alkaline solutions of potassium iodide are unaffected by chlorates even on long standing or long boiling.

Where the hypochlorite contained in a sample of bleaching powder, which may also contain chlorate, is to be estimated, the only safe and convenient method is that of Penot, *i.e.* by the use of an alkaline solution of arsenious acid. When the chlorate likewise is to be estimated, it may be expeditiously done by heating the sample with a known quantity of the same arsenite solution, and addition of hydrochloric acid; from the difference between the quantities of arsenite peroxidised in the two instances the chlorate is readily known. Dr. Wright has found the bleaching powder of commerce to contain several units per cent. of calcium chlorate, even when newly made; in older samples the chlorate has been occasionally found to represent as much as 10 per cent. of available chlorine, or fully $\frac{1}{4}$ of the amount originally present; thus indicating overheating either in the process of manufacture or subsequently.

(*C*) Two grammes of the bleaching powder to be tested are well mixed with water, and the liquid so obtained mixed with a solution of iron protochloride freshly made by dissolving 0·6 gramme of pure iron wire in pure hydrochloric acid. Pure hydrochloric acid in excess is next added, and the liquid boiled in a flask, after previous addition of a piece of rather thick, perfectly clean, and polished sheet copper, of a weight of about 4 grammes. The boiling is continued until the colour of the liquid, at first darkish, has become bright green; the copper is then removed from the flask, washed with distilled water, dried, and weighed. A loss in the weight of copper of 63·4 parts (=2Cu) is equal to 35·5 parts of chlorine in the bleaching powder. This method is

based on the fact that, under the conditions described, the chlorine of the bleaching powder first changes the iron protochloride into perchloride, which in its turn is again reduced to protochloride by the metallic copper, whereby some of the latter becomes dissolved. Every 2 equivalents of copper dissolved in this way are equal to 1 equivalent of chlorine in the bleaching powder.

Estimation of Chlorate in Bleaching Chlorides

E. Dreyfus bases a process on the property of cupric oxide, in a strongly hydrochloric solution, of being reduced to cuprous oxide by the action of stannous chloride at a boil. The end of the operation is marked by the decolouration of the liquid, which from yellow becomes colourless. For the process are required :—

1. A solution of copper made by dissolving copper sulphate in distilled water, so as to make up a litre, of which 10 c.c. represent about 0·1 gramme of metallic copper.

2. An acid solution of stannous chloride made by dissolving 15 grammes of this body in 200 c.c. of hydrochloric acid, and making up to a litre with distilled water.

3. A solution of potassium chlorate. 5·917 grammes of this salt are dissolved in a litre of distilled water. Ten c.c. of this liquid are exactly equal to 0·05 gramme calcium chlorate.

To find the value of the cupric solution in comparison with that of potassium chlorate, 10 c.c. of the solution of copper (0·1 gramme of copper) are poured into a flask or a conical colourless glass holding 150 c.c., and 50 c.c. of hydrochloric acid are then added. The mixture is heated to an incipient boil, and titrated with the standard liquid till decolourised. To the colourless liquid are added 5 c.c. of the potassium chlorate, which oxidise a corresponding quantity of cuprous chloride. This quantity is estimated again by titrating with stannous chloride. By this titration is found the relation between the cupric and the chlorate solutions. When this relation is once found it does not vary as long as the solution lasts.

Preparation of the Sample of Chloride of Lime.—Ten grammes are stirred up in 100 c.c. of water and saturated with ammonia, which is added by small quantities till there is a slight excess. It is then boiled till the odour disappears, and the liquid, with the precipitate, is poured into a flask marked at 500 c.c. The liquid is allowed to settle, depositing a precipitate which contains a little ferric oxide.

The introduction of a little potash into the chloride after it has been saturated with ammonia much facilitates the settlement of the deposit. When the solution of the chloride is thus prepared we proceed to titrate ; 10 c.c. of the cupric solution are raised to a boil with 50 c.c. of hydrochloric acid, and titrated to decolouration with the stannous chloride. Then 50 c.c. of the solution of settled chloride are

added; the mixture is boiled, and the copper which has been oxidised is titrated again. This method is applicable also to liquid chlorides.

Detection of Arsenic in Hydrochloric Acid

Take a thoroughly clean and dry test-tube, of not too narrow a bore; put into it as much pure tin protochloride as can be placed on the point of a knife; next add from 4 to 6 c.c. of the hydrochloric acid to be tested; add, after this, gradually from 2 to 3 c.c. of pure concentrated sulphuric acid, taking care to move the test-tube very gently. If a white precipitate ensues, the addition of a few drops of the hydrochloric acid will be required to restore the liquid to perfect limpidity. If no arsenic is present, the liquid remains clear and colourless, even after standing for a time; but if only a trace of arsenic is present, the liquid becomes at first yellowish, next brownish coloured, and at last the metallic arsenic is deposited as a deep greyish-brown flocculent substance. Even with only $\frac{1}{500000}$ part of arsenious acid a colouration ensues. It is essential that when the sulphuric acid is added the liquid should become hot; if, therefore, that acid is too dilute to cause heating, the test-tube and contents should be warmed over a spirit-flame.

Purification of Hydrochloric Acid from Arsenic

(*A*) 1. *Preparation of Weak Acid.*—In the preparation of weak acid it is only necessary to boil the commercial arseniferous acid in a flat-bottomed dish until the acid is reduced to two-thirds of its original volume. By allowing the hydrochloric gas to escape without collecting it, all the arsenic is taken with it in the form of terchloride, and the liquid remaining in the dish is no longer arseniferous; 8 litres of commercial acid, treated in this way, furnish in less than three hours 2 litres of acid free from arsenic.

2. *Preparation of Fuming Acid.*—Into a flat-bottomed flask of 6 litres capacity, first pour 3 litres of the arseniferous acid, and add 0·3 gramme of powdered potassium chlorate (0·1 gramme per litre). Then adapt to the mouth of the flask a cork pierced with two holes, into one of which fit a straight and strong safety-tube; and into the other a larger tube, of the diameter used in organic analyses, 0·5 metre long, and serving, so to speak, as a vertical elongation. This lengthened tube should be very little tapered at its lower part; fill it with about 100 grammes of red copper turnings well beaten down to within 0·07 metre of its upper orifice, and then fill almost up with asbestos or broken glass. Pass the greater part of this tube through the neck of the flask, so that as much as possible of the surface may be heated by the hydrochloric vapour. Then furnish the upper part of the elongated tube with a tube to carry the gas into a receiver. In traversing the column of copper the acid gas is deprived of its chlorine,

and arrives in a pure state in the water destined to dissolve it. The mode of operation is very easily comprehended. By boiling the acid the transformation of the arsenic chloride into fixed arsenic acid is completed by the decomposition of potassium chlorate; the excess of chlorine is taken with the moist hydrochloric gas into the copper, which most readily absorbs it, in preference to the acid, for which its affinity is much less. The copper chloride returns to the flask in the form of a solution, while the gaseous hydrochloric acid condenses in the distilled water. But as it is important that there should always be in the boiling acid a slight excess of chlorine, to prevent the reduction of the arsenic acid, a constant current of hydrochloric acid, to each litre of which 0·1 gramme of potassium chlorate has been added, should arrive through the safety-tube (which should not dip more than from 3 to 5 c.c. into the liquid) so as always to maintain a small excess of chlorine, and at the same time to replenish the flask with hydrochloric acid to be purified. Generally the proportion of liquid acid thus added should be greater than is required for distillation, otherwise there might be an insufficiency of chlorine. When the experiment has been successfully performed the hydrochloric acid contains neither arsenic nor chlorine.

By this apparatus pure hydrochloric acid may be constantly obtained without any sensible loss of acid, and the process may thus be applied commercially.

(*B*) Into the crude acid to be purified pass a current of sulphuretted hydrogen until all the arsenic is precipitated. Separate the arsenic sulphide either by subsidence and decantation, or by filtering it through a funnel packed with asbestos. Remove the excess of sulphuretted hydrogen from the filtered liquid by the addition of a concentrated solution of iron sesquichloride, which destroys the sulphuretted hydrogen, being reduced to protochloride. Finally, rectify the acid from fixed matters.

Purification of Hydrochloric Acid from Arsenic

In the estimation of arsenic by the Marsh-Berzelius test, the use of hydrochloric acid is admittedly preferable to that of sulphuric acid. It is, however, practically impossible to purchase hydrochloric acid really free from arsenic, and it is therefore necessary to remove the last traces of arsenic from it in the laboratory.

L. T. Thorne and E. H. Jeffers[1] remove the whole of the arsenic by means of a modification of the well-known Reinsch test for arsenic in the following manner:—

The hydrochloric acid to be purified is diluted with water till its specific gravity is about 1·10, then raised to the boiling-point, and a piece of fine copper gauze introduced. The gauze should be of about

[1] *Chemical News*, May 30, 1902.

100 meshes to the inch, and of as pure copper as possible. When a couple of litres of liquid are being dealt with, the gauze should be about 4 inches square and coiled very loosely (about 1½ to 2 turns) round a long glass rod flattened at the end, as in this way it can be readily introduced and removed, besides being brought into better contact with the liquid. The whole is then kept just boiling for an hour. By this time the gauze will have become more or less blackened, and should be replaced by a second piece and the digestion continued for another hour. If this piece is also blackened, a third is used, and so on, until the gauze remains perfectly bright after about an hour's digestion. With moderately good acid, two, or at most three, pieces of gauze are sufficient. The gauze is then removed, and the acid at once transferred to a retort and distilled with a fresh piece of gauze. It is advisable, as a precaution, to reject the first 20 per cent. of the distillate, though even this is very rarely contaminated if the digestion is carefully carried out, and from 100 to 200 cubic centimetres should be left behind in the retort. The method is simple and requires but little attention, and it is not necessary to use the purest acid; even good muriatic acid, 'commercially free from arsenic,' may be satisfactorily employed. The acid obtained is the constant boiling-point acid, which is about the most suitable strength for use in the Marsh-Berzelius test.

The gauze must, of course, be gently ignited before being used, and should not be introduced until the acid is just beginning to boil. It is also preferable not to allow the digested liquid to cool in contact with the air before transferring to the retort, as the copper gauze would be much attacked and its efficiency for the present purpose considerably lessened by the consequent oxidation.

Detection of Free Hydrochloric Acid in Solutions of Ferric Chloride

Professor Nicola Rease finds that a solution of ordinary phenol treated with ferric chloride takes an amethyst colouration, turning to a brown. But if a drop of hydrochloric acid is added to the solution, the liquid either assumes no colouration at all or takes a greenish tint. He proceeds as follows:—1 gramme of the crystalline phenol of commerce is heated in 100 c.c. of pure water. He then pours 1 c.c. of the liquid ferric chloride into 50 c.c. of pure water. This solution being in a small test-beaker set on a sheet of white paper, the solution of phenol is added drop by drop. The first drop, if the solution is slightly acid, produces a fugitive colouration, but if it is strongly acid no colour appears. On continuing to add the phenol solution the colour becomes permanent and gradually darkens. From the volume of the phenol solution consumed an approximate idea of the quantity of acid present may be formed.

Detection of Hydrochloric Acid by Sulphuric Acid and Acid Potassium Chromate

H. W. Wiley finds that this well-known test is more conveniently applied in the following way than by distillation in a retort as usually directed. Two small beakers are taken, of different sizes, the smaller of which will fit into the larger, leaving a space of 2 or 3 centimetres between the two bottoms. The chloride and chromate are well rubbed together, and placed in the larger beaker, care being taken that none of the particles touch the sides of the vessel. A ew drops of oil of vitriol are added, and the smaller beaker then put in place. A lump of ice and if necessary a little salt are then placed in the inner beaker. The chlorochromic acid is given off at a very gentle heat much below the boiling-point, and is readily condensed on the cold surface of the beaker. If there is more than a mere trace of chloride, a watch-glass can be substituted for the smaller beaker.

After the reaction has ceased the inner beaker is removed. With a stirring-rod a very little oil of vitriol is placed on a white porcelain surface, and near it a minute crystal of strychnine. The end of the stirring rod is then moistened with the chlorochromic acid and brought into contact with the sulphuric acid and strychnine. The colour test for strychnine is developed with even greater brilliancy than with potassium chromate: the merest trace of a chloride is most unmistakably revealed by this test. If bromides are present, they do not at all interfere with the above reaction. Bromine itself with strychnine and sulphuric acid gives no play of colours. Bromides, moreover, when present, can usually be detected at the same time with the chlorides. The bromine formed is readily condensed, and either forms distinct globules or imparts a deeper colour to the chlorochromic acid. With iodides the case is quite different. In many cases no trace of chlorochromic acid has been found, when both chlorides and iodides were present. At other times, the iodine which is set free seems to be dissolved in the chlorochromic acid. In such cases, on adding ammonia to the reddish-yellow distillate, the whole turns black, from the formation of nitrogen iodide.

Valuation of Potassium Chlorate

After having proved the absence of heavy metals, those of the alkaline earths, and sodium, a certain quantity of the chlorate to be valued is dissolved in water. Some dilute sulphuric acid is then added to the solution, and a piece of zinc is placed in the mixture. The nascent hydrogen immediately transforms the dilute chloric acid into hydrochloric acid. In about half an hour the undissolved zinc is withdrawn from the liquor, the sulphuric acid is precipitated by barium nitrate, and the zinc and excess of barium by means of sodium

carbonate. The hydrochloric acid in the filtered solution is then estimated volumetrically by a standard solution of silver nitrate. A convenient solution is made by dissolving 1·387 gramme of silver nitrate in a litre of water, each c.c. of which solution will correspond to 1 milligramme of potassium chlorate.

If the chlorate contains chloride, the chlorine is first precipitated by silver nitrate, any excess of silver being removed from the filtered solution by sulphuretted hydrogen. The liquor filtered from the silver sulphide may then be treated with zinc and sulphuric acid, as described above.

FLUORINE

Detection of Fluorine in Water

Treat the solid residue of a large quantity of the water with an excess of concentrated sulphuric acid, and pass the gaseous products into slightly ammoniacal water. If fluorine is present in the water, gelatinous silica is precipitated in the liquid, resulting from the decomposition of the silicon fluoride which was disengaged from the residue.

Estimation of Fluorine

(*A*) For estimating fluorine in compounds easily attacked by sulphuric acid proceed as follows:—Cover the platinum capsule in which the decomposition takes place with a funnel, resting with the capsule on a platinum basin, on which it is fastened with wet plaster; ascertain the weight of the funnel and the composition of the glass of which it is made. Heat the whole until most of the sulphuric acid has been expelled; then raise the funnel, wash it carefully, dry and weigh it; the decrease in its weight is owing to a portion of the glass having been attacked; and as its composition was first ascertained, the weight of silica which has been attacked may be calculated from the decrease in weight, and, consequently, the quantity of hydrofluoric acid which has been disengaged. This method has given very satisfactory results with triplite of Limoges, and with zivieselite and other analogous phosphates of Schlaggenwald. With calcium fluoride and cryolite too little fluorine is found, because the decomposition of these minerals is complete only when the mixture is properly shaken, which is difficult with the apparatus described above. The same funnel may be used many times, and is even better after it has been corroded.

If the substance to be analysed contains silica, the quantity must be ascertained and added to that of the glass attacked, to obtain the weight of fluorine.

(*B*) Place the substance to be analysed in a rather deep platinum crucible, and cover it with 3 or 4 times its weight of silica; add a few drops of sulphuric acid, and heat gently for half an hour; then

gradually increase the heat until most of the sulphuric acid is expelled. Then treat the whole with hydrochloric acid, add some water, and leave it to deposit; collect the deposit, calcine, and weigh it, and the loss of silica will indicate the amount of fluorine contained in the substance analysed (38 of fluorine correspond to 30 of silica).

(*C*) For the estimation of fluorine, Professor A. Liversidge decomposes the fluoride by concentrated sulphuric acid in presence of silica, and passes the silicon fluoride formed into ammonia, the quantity of silica carried over being then estimated and the fluorine calculated therefrom. The powdered mineral is introduced into a platinum retort together with the needful quantity of sulphuric acid and finely divided silica. It is heated first in the water-bath and then at 160° C., the gaseous silicon fluoride formed being decomposed by passing it through a solution of ammonia. The last traces of the gas are carried over by drawing a current of air through the apparatus. The ammonia solution is gently evaporated in a platinum dish till the gelatinous silica passes entirely into solution, and it can then be precipitated as potassium silicofluoride by the addition of potassium chloride and alcohol.

(*D*) Chapman gives the following processes for the estimation of fluorine, especially applicable to commercial phosphates. The method depends on the fact that acid ammonium acetate (*i.e.* ammonia more than neutralised by acetic acid) precipitates calcium fluoride, but not calcium phosphate, from solution in acids. 2·5 grammes are ignited in a platinum crucible for a short time (this ignition prevents ferric and aluminium phosphates from dissolving in dilute hydrochloric acid), transferred to a mortar, and ground up with repeated small quantities of 10 per cent. hydrochloric acid, filtered, and washed.

The filtrate and washings are made up to 250 c.c. 100 c.c. of this are taken and added to the acid ammonium acetate, the calcium fluoride is precipitated, and calcium phosphate remains in solution.

The calcium fluoride is filtered off, washed, dried, ignited, and weighed as usual.

If the substance be not ignited, the calcium fluoride comes down mixed with ferric and aluminium phosphates, from which the amount of calcium fluoride can be obtained by subtracting the amount of ferric and aluminium phosphates.

This second method is not so accurate, as, even without ignition, all the ferric and aluminium phosphates do not dissolve up.

Volumetric Estimation of Fluorine

S. L. Penfield has made the well-known reaction

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$$

the basis of a volumetric estimation of fluorine, estimating the quantity of hydrofluosilicic acid formed from a given weight of fluoride by means of a standard alkali solution.

It is impossible to titrate the hydrofluosilicic acid directly, because as soon as an alkaline reaction is reached the silicofluoride is decomposed and a further acid reaction is indicated, which change goes on slowly. But when barium chloride and an equal volume of alcohol are added to the solution, barium silicofluoride is precipitated from the solution, and an equivalent amount of hydrochloric acid is liberated, which can be titrated; by this means, using litmus as an indicator, very satisfactory results have been obtained, but the turbidity caused by the barium silicofluoride interferes with the change of colour of the litmus.

It has been found that potassium chloride possesses some advantages over barium chloride. On adding potassium chloride and an equal volume of alcohol, potassium silicofluoride is precipitated from the solution, and an equivalent of hydrochloric acid is liberated, but the potassium silicofluoride is a very transparent precipitate, and does not interfere with the change of colour of the indicators.

It is necessary that alcohol shall make up at least one-half the volume of the liquid to be titrated, so as to precipitate the potassium silicofluoride as completely as possible.

The apparatus needed is very simple, and consists of a gasometer of 10 or more litres capacity, a few flasks of about 150 c.c. capacity, a few large plain U-tubes 18 centimetres long and $2\frac{1}{2}$ centimetres diameter, made without any narrowing in the bend, and a heavy iron plate supported properly, so that it may be heated with a lamp.

The fluoride is weighed out accurately into one of the flasks; unless it is a silicate, 10 grammes of powdered and ignited quartz are added, with 2 or 3 pieces of quartz about the size of kidney-beans. These last facilitate mixing up the powder when the flask is shaken. The contents of the flask are then drenched with from 30 to 40 c.c. of sulphuric acid which has been previously heated and allowed to cool. The flask is tightly closed with a doubly perforated cork; from the gasometer dry air is passed into the flask by means of a glass tube which reaches nearly to the bottom. The silicon fluoride mixed with air passes from the decomposing flask first through a small U-tube, made from ordinary glass tubing, 5 millimetres in diameter, and kept cool by being placed in a beaker of cold water, then into one of the large U-tubes intended for decomposing the silicon fluoride and absorbing the hydrofluosilicic acid. The U-tube contains a solution of potassium chloride mixed with an equal volume of alcohol; the escaping gas is made to bubble through this, and to ensure complete decomposition a second smaller U-tube is attached to the first: the first tube absorbs nearly all the acid, the second contains only traces. The decomposing flask is supported on the iron plate; by its side is placed a second flask containing sulphuric acid and a thermometer supported so that its bulb dips into the acid; the lamp heating the plate is placed midway between the flasks, and the heat is regulated so that the temperature of the acid remains between 150° and 160° C.

The decomposition is continued two hours in ordinary cases, and during that time a continuous current of air is forced through the apparatus, amounting to from 5 to 6 litres for the two hours, while the contents of the decomposing flask are frequently agitated by shaking.

After the decomposition and aspiration are completed, the contents of the U-tubes are titrated. For this purpose they may be transferred to a beaker, the tubes being rinsed with alcohol and water, or better, the acid may be titrated directly in the U-tubes. In order that the alcohol may make up one-half the volume of the liquid after the titration is completed, add a few c.c. of alcohol before titrating, or where 15 or more c.c. are to be added use a standard alkali one-half of whose volume is alcohol. As the separated silicic acid sticks to the sides of the U-tube, it is necessary to have prepared a glass rod bent a little at one end to scrape off and break up this silica.

A simple dry U-tube between the decomposing flask and absorbing tube is sufficient to condense any sulphuric acid that may go over from the heated acid.

When the fluorine is to be estimated in a mineral containing chlorine, as in the case of an apatite, substitute for the empty U-tube one filled with fragments of pumice impregnated with perfectly anhydrous copper sulphate. This will intercept any hydrochloric acid, and will also serve to condense any sulphuric acid vapour that may go over from the heated acid. The calculation is very simple. Each equivalent of sodium carbonate equals 1 equivalent of hydrofluosilicic acid or 6 of fluorine.

The qualitative search for fluorine in substances free from silica is easily made, with small quantities of matter, in a platinum crucible furnished with a lid with a small circular hole pierced in the centre, above which a disc of glass is placed.

CHAPTER XII

CARBON, BORON, SILICON

CARBON

Assay of Animal Charcoal

THE points of greatest importance in an analysis of animal charcoal are the carbon, the carbonates, and the iron; the decolouriser, the neutraliser, and the destroyer. Under certain circumstances sulphates may be included, and in the case of unused charcoal the salts soluble in water should also be carefully estimated. The amount of phosphates is comparatively unimportant. The following is the process recommended by Dr. Wallace; it was frequently verified during the progress of the author's work on Beet-root Sugar and the chemistry of sugar-refining.[1]

Carbon.—Five grammes of animal charcoal are dried at 220° F. in a hot-air bath or paraffin-bath; the loss of weight gives the moisture, which, subtracted from the loss by calcination, furnishes the proportion of carbon.

Calcium Carbonate.—This can be quickly and accurately estimated by well-known processes.

Iron.—After some little practice the iron can be safely estimated by Penny's process, using a very dilute solution of bichromate. The iron is always in a state of protoxide, faint traces of peroxide excepted, owing to the reducing action of the carbon in the re-burning.

Soluble Salts.—Fifty grammes of animal black are weighed and thrown into a little stoppered flask containing about 50 c.c. of distilled water; this is well shaken for a few minutes, and then filtered. The insoluble residue is re-digested in a fresh quantity of water; and this is repeated several times, so as to eliminate the whole of the soluble salts. The filtered liquid is evaporated over the sand-bath in a little porcelain capsule; the dry residue is weighed, and its weight gives the proportion of soluble salts. These salts consist of alkaline chlorides, sulphates, and carbonates; they also contain traces of calcium sulphate and sulphide.

[1] *The Manufacture of Beet-root Sugar in England and Ireland*, by William Crookes. London: Longman & Co., 1870.

Estimation of the Decolourising Power of Animal Charcoal

In these estimations the object is to carry out the operation in such a manner as to obtain, as nearly as possible, the same results on the small scale in the laboratory as in the manufacturing operations; and it is because many little precautionary measures which tend towards the attainment of that equality are usually omitted in the laboratory that such conflicting and apparently inexplicable results are recorded.

Arnot gives the following precautions to be observed so as to obtain trustworthy results :—

1. It must be decided what the results are to express: whether the relative decolourative power of equal bulks or equal weights of the charcoals, irrespective of size and proportion of grain, of the chars uniformly freed from dust, say by a 50-mesh sieve; or of equal weights of equal grains.

2. According as either of these alternatives is decided upon, the various samples must be thoroughly and intimately mixed, and, if necessary, brought to a uniform dryness and temperature. It is always safest to have them thoroughly dry, and at the temperature of the surrounding air.

3. The various samples are next to be put into glass tubes (tin may be used, but they preclude observations of a very important kind) provided with perforated false bottoms, covered with layers of cloth, and with taps capable of being accurately regulated. The tubes ought to be about 2 inches wide and 2 feet long, as nearly of the same diameter as possible. The best method of filling them is by passing the charcoal through a funnel, keeping the spout of the funnel moving constantly in a circular direction, so as to have the large and small grains equally diffused throughout. To allow the charcoal to run down either at one side, or, to a less degree, in the middle, is to cause to a certainty a separation of the larger grains from the smaller, and thus to create channels through which the liquor has too easy access.

4. See that no one tube is touched or shaken more than the others, after the charcoal has been put in.

5. Sufficient brown sugar liquor, of say 24° B., must be prepared, either by diluting raw filtered liquor from the sugar-house to that gravity, or by dissolving as much of an average quality of raw material as will make sufficient liquor for the whole experiment. In the case of preparing it on the small scale, albumin must be liberally used, and the liquor passed through paper filters—coarse French paper answers best. The albumin should not be added till all the sugar has been dissolved, and the temperature at, say, 160° F. An equal quantity of the prepared liquor, as nearly 180° F. as possible, must now be poured uniformly upon the charcoal in each tube.

The rapidity with which the liquor passes through the charcoal in each case may be noted. Care must be taken to have the top of the charcoal always covered with liquor, and the taps below open. As soon as the liquor begins to drop at the taps they are closed.

6. The tubes being fully charged with liquor (there should be as much left on the top of the charcoal as will serve to force out the liquor in the charcoal), they are put into a cistern of water at 140° F., the water in which will rise to about 1 inch from the mouths of the tubes; the time is noted, and the cisterns, which ought to be felted, are covered.

7. At the end of not less than one hour (longer than one hour is sometimes advantageous, particularly if the raw liquor was very brown) the tubes are withdrawn, placed in their stands, and about 2 ounces of liquor run off each; this may be rejected, as the portion between the false bottom and taps is often turbid, and in addition has not been in contact with the charcoal for a sufficient length of time. The remainder of the liquor, *i.e.* so much as has actually been in contact with the charcoal, may now be run off in three successive quantities for comparison. The results may be compared with any set of standard colours, and recorded accordingly.

8. If these results are not sufficiently conclusive, a further quantity of raw liquor may be run on each tube, and the whole transferred as before to the water-bath, which, if felted, will still be hot enough. The second quantity of liquor will be run off with the same precautions as the first, and the results will show the relative *persistency* of the charcoal under trial.

If the taps are large the liquor will be likely to run off too rapidly, and, in that case, they had better be partially and uniformly closed. If it is found that the liquor runs through one sample particularly slowly, and through another particularly fast, it is quite admissible to assist the one by suction, and to check the other by closing the taps; but this should not be done unless in extreme cases, and the fact of having so assisted or retarded the process should always be noted.

It is scarcely necessary to mention the several points wherein the foregoing differs from the course generally pursued in testing charcoal, and yet it may be useful briefly to indicate some of these. Too little care is usually bestowed upon the selection and preparation of the samples. The tubes are, as a rule, too small: the charcoal cannot be run so uniformly into small tubes as large ones. The samples once charged with liquor are not always kept warm: it is essential that they should be. Some charcoals act powerfully at low temperatures, while others require a considerable amount of heat to bring out their maximum decolourative power. Care must, however, be taken that the temperature employed does not exceed that attained on the large scale in the refining process. One sample of charcoal, known to be of very inferior decolourative power on the working scale, persistently gave

results, by the usual method of testing in the laboratory, equal to the very finest charcoal obtainable, but when kept at an elevated temperature, along with the finer samples, in the manner indicated above, its inferiority was at once manifest. The facts in this case were that the inferior charcoal readily yielded *all* its decolourative power at the low temperature, while the finer samples required the influence of heat to call their whole power into action.

Volumetric Estimation of Carbonic Acid in Animal Charcoal.—Dr. Scheibler has devised a very good instrument which is adapted for the estimation of the quantity of carbonic acid contained in native carbonates, as well as in artificial products, and has been specially contrived for the purpose of readily estimating the quantity of carbonic acid contained in animal charcoal. The principle upon which the apparatus is founded is simply this—that the quantity of carbonic acid contained in calcium carbonate can, according to well-known stœchiometrical rules, be used as a measure of the quantity of that salt itself; and instead of estimating, as has been usually the case, the quantity of carbonic acid by weight, this apparatus admits of its estimation by volume. It is by this means possible to perform, in a few minutes, operations which would otherwise take hours to accomplish. The analytical results obtained by means of this apparatus are very correct, provided care be taken to use the needful precautions.

The apparatus is shown in the annexed woodcut, and consists of the following parts:—The glass vessel A, serving for the decomposition of the material to be tested for carbonic acid, which, for that purpose, is treated with dilute hydrochloric acid; this acid is contained, previous to the beginning of the experiment, in the gutta-percha vessel S. The glass stopper of A is perforated, and through it firmly passes a glass tube, to which is fastened the indiarubber tube *r*, by means of which communication is opened with a three-necked tubulated bottle, B. The central neck of this bottle contains a glass tube firmly fixed, which is in communication, on the one hand, with A, by means of the flexible indiarubber tube already alluded to, and on the other hand, *inside* of B, with a very thin indiarubber bladder (similar, as regards thinness, to the very light and well-known inflated indiarubber balloons sold as toys). The neck, *q*, of the vessel B is shut off during the experiment by means of a piece of indiarubber tubing, kept firmly closed with a spring clamp; the only use of this neck of the bottle B, arranged as described, is to give access of atmospheric air to the interior of the bottle if required. The other opening is in communication with the measuring-apparatus, C, a very accurate cylindrical glass tube of 150 c.c. capacity, divided into 0·5 c.c.; the lower portion of this tube C is in communication with the tube D, serving the purpose of controlling the pressure of the gas; the lower part of this tube D ends in a glass tube of smaller diameter, to which is fastened the india-

rubber tube *p*, leading to E, but the communication between these parts of the apparatus is closed, as seen at *p*, by means of a spring clamp. E is a water reservoir, and on removal of the clamp at *p*, the water contained in C and D runs off towards E; when it is desired to force the water contained in E into C and D, this can readily be done by blowing with the mouth into V, and opening the clamp at *p*.

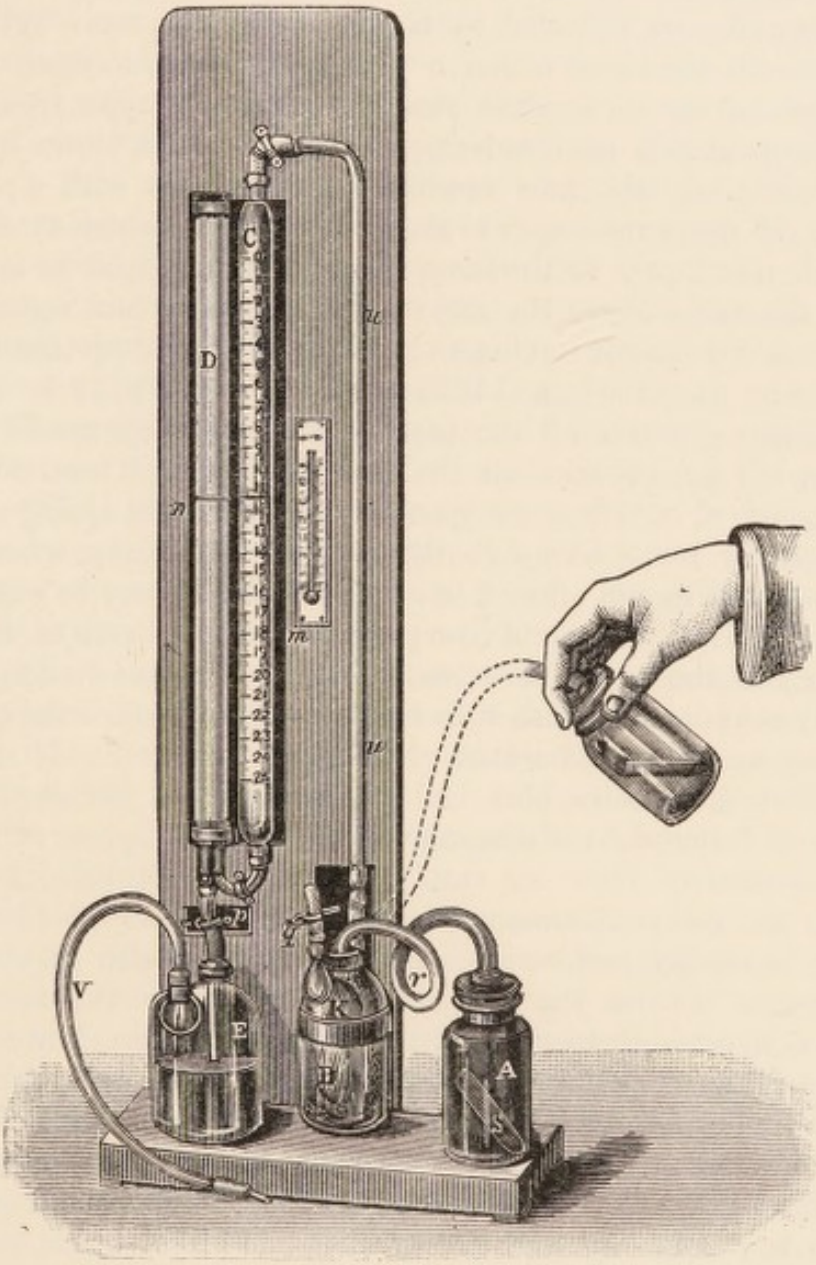


FIG. 25.

The following apparatus and reagents are also necessary:—A small and very accurate weight for weighing off the substances to be tested; a thermometer; hydrochloric acid; a solution of ammonium carbonate; and several small porcelain basins.

The main portion of the apparatus above described, with the exception, however, of the vessel A, is properly fixed by means of brass

fittings to a wooden board, as represented in the woodcut. The filling of the apparatus with water is very readily effected by pouring it through a suitable funnel placed in the open end of tube D, care being taken to remove, or at least to unfasten, the spring clamp at *p*; in this manner the water runs into E, which should be almost entirely filled. Distilled water should be used for this purpose, as the filling only requires to be done once, the water always remaining in E as long as the apparatus is intended to be kept ready for use. When it is required to fill the tubes C and D with water, so as to reach the zero of the scale of the instrument, remove the glass stopper from A; the spring clamp at *p* is next unfastened, the air is then blown by means of the mouth into the tube V, which communicates with E; by this operation the water rises up into the tubes C and D, which thus become filled with that liquid to the same height. Care should be taken not to force the water above the zero of the scale at C, and especial care should be taken against forcing so much of the liquid up that it would run over into the tube *u*, and thence find its way to B, as in this case a total disconnection of all the parts of the apparatus would become necessary. If by any accident the water should have been forced up above the zero at C, before the operator had closed the spring clamp at *p*, this is easily remedied by gently opening that clamp, whereby the water is allowed to run off to E in such quantity as may be required to adjust the level of the liquid in C precisely with the zero of the scale. The filling of the tube C with water has the effect of forcing the air previously contained in that tube into B, where it causes the compression of the very thin indiarubber ball placed within B. If it should happen that this indiarubber ball has not become sufficiently compressed and flattened, it is necessary to unfasten the spring clamp at *q*, and to cautiously blow air into B, through the tube *q*, by which operation the complete exhaustion of the indiarubber bladder placed within B is readily performed. This operation is also required only once, because during the subsequent experiments the indiarubber bladder K is emptied spontaneously. It may happen, however, that while the filling of the tubes D and C with water is being proceeded with, the indiarubber bladder K has become fully exhausted of air before the water in C reaches the zero of the scale; in that case the level of the water in the tubes D and C will not be the same, but will be higher in D. It is evident, however, that this slight defect can be at once remedied by momentarily unfastening the spring clamp at *q*.

The apparatus should be placed so as to be out of reach of direct sunlight, and should also be protected against artificial heat and sudden changes of temperature; the instrument is best placed near a north window, so as to afford sufficient light for reading off the height of the water in the tubes.

Hydrochloric Acid.—The acid required for the decomposition of the animal charcoal is poured into the vessels for use during

experiments. This acid need not be pure ; the crude acid of commerce answers the purpose, provided it be diluted to a specific gravity of 1·12 at 17° C. For practical purposes it is sufficient to mix 2 parts by bulk of water with 1 part by bulk of commercial hydrochloric acid.

Ammonium Carbonate.—In order to prepare the solution of this salt of the necessary strength, 1 part by weight of the ordinary ammonium carbonate of commerce is dissolved in 4 parts of water, and to this 1 part of liquid ammonia is added. The salt is first coarsely pulverised and immediately after placed in a bottle provided with a well-fitting glass stopper ; the mixture of water and ammonia is next poured over the salt, and the solution of the salt promoted by frequently shaking the bottle. This solution of ammonium carbonate is used for the purpose of converting into calcium carbonate any caustic lime which might be present in the materials to be submitted to analysis.

Mode of Operating.—(*A*) It is of the greatest importance that a good average sample, really representing the entire bulk of animal charcoal, be taken for investigation. This can be readily obtained by taking small samples, say a few ounces, from the filter (in sugar works) or from a cask, at various depths of the vessels containing the material, or, better still, if there be room, the charcoal should be placed in a heap on a large sheet of stout canvas, and well mixed together, and samples taken from various parts of the heap. These, if wet (as will be the case with charcoal just removed from the filters), should be dried by suitable means, and afterwards the whole sample should be coarsely ground and thoroughly mixed, and a portion taken for the purpose of being ground up to a very finely divided powder, to serve the purpose of weighing a sample from. It is essential that the charcoal should be ground to a very fine powder, because this greatly promotes the decomposition by the acid.

There is supplied with the apparatus a metallic weight to serve as normal weight. This weight is placed in one of the pans of the balance (any balance, provided it be sensitive to from $\frac{1}{8}$ to $\frac{1}{10}$ of a grain, will answer the purpose) ; in the same pan a small porcelain basin is placed, and equilibrium is restored by means of small lead shot. As soon as the equilibrium is attained the normal or standard weight is removed from the pan of the balance, and there is placed in the small porcelain capsule remaining in the pan as much of the sample of bone-black to be tested as is required to restore the equilibrium. When several experiments have to be made consecutively, it is better to arrange beforehand the joint tare weight of the normal weight and of a watch-glass of suitable size, and to weigh off upon the latter the several samples.

(*B*) Dr. Scheibler recommends the transference of these weighed quantities to a porcelain capsule, because, according to his plan, the samples, *after* having been weighed, have to be thoroughly moistened with the solution of ammonium carbonate already referred to, in order to convert any caustic lime which might happen to be present in the

material into calcium carbonate; but it is a decided improvement to moisten gently with the solution of ammonium carbonate a sufficient quantity of the sample to be tested previous to weighing, to dry it, and to employ at last, for a few moments, a stronger heat short of redness (an air or fusible metal bath, heated to 240° C.), so as to obviate the chance of either an excess of ammonium carbonate or of water being present, while, at the same time, the decomposition of the calcium carbonate is guarded against. After the samples are quite cold, they are to be transferred to the flask or bottle A. Recent researches have shown that animal charcoal which has been once used for filtering purposes in sugar works no longer contains caustic lime, and the treatment with ammonium carbonate can therefore be dispensed with in that case, and need only be employed with samples freshly made.

(*C*) The experiment for the estimation of the carbonic acid is carried out in the following manner:—First, the water in the tube C is made to stand exactly at the zero (0) of the scale; next, the weighed sample of the bone-black to be tested is transferred, with great care and without loss, to the bottom of the bottle A, which should be perfectly dry inside and quite clean. This having been done, the gutta-percha vessels, which should also be previously well cleaned, is filled with the hydrochloric acid above referred to, to within from $\frac{1}{2}$ to $\frac{3}{4}$ inch from the top, care being taken not to drop any hydrochloric acid on the outside of the vessel; the gutta-percha vessel is next placed within the bottle A in a slanting direction, as shown in the woodcut; after this the glass stopper is replaced at A, care being taken to slightly grease it and the inside of the neck of A, so as to secure a better air-tight fitting. The closing of A will (if all parts of the apparatus are properly tight) have the effect of slightly lowering the level of the water in C below the zero of the scale, while the water will rise just as much higher in D; by loosening, for a moment, the spring clamp at *q*, the normal height is properly restored. The operator should very carefully guard against handling or touching A after it has been once closed, because, by so doing, the warmth of his hand will cause the expansion of the air in A, and thereby affect the proper action of the apparatus. In order to cause the hydrochloric acid contained in the gutta-percha vessel placed inside A to run on to the animal charcoal, placed on the bottom of A, as described, the flask or bottle A is held by the neck, as shown in the woodcut. As soon as the acid comes into contact with the animal charcoal, the evolution of carbonic acid begins, and simultaneously the expansion of the very thin indiarubber bladder K, while the water in the tube C sinks, and correspondingly rises in D. While the bottle A is held in the right hand, as already indicated, and gently moved about so as to promote as much as possible the contact between the acid and the charcoal, the left hand is employed to gently open the spring clamp *p*, in such a manner as to run off towards E just as much water as is required to keep the level in the tubes C and D at the same height.

Both these manipulations should be continued as long as any sinking of the level of the water in C is perceptible: in other words, as long as any carbonic acid is given off. After this has quite ceased, and no change is observed, or any motion of the water in the tubes just alluded to has taken place, the operation may be considered at an end, care being taken, however, to keep the levels in the tubes C and D at precisely the same height. This having been done, the next step is to read off the height of the water at the scale on C, and simultaneously the thermometer.

Correction of the Volume Read off.—The table on the following page contains in the first column the figures 1 to 25, which correspond with the numbers on the scale fixed to C; the next 19 vertical columns contain the figures indicating the percentage of calcium carbonate sought at temperatures from 12° to 30° C. If, for instance, the experiment has been made at a temperature of 16°, and the reading of the scale at C corresponded to 9°, this indicates a quantity of calcium carbonate of 9·03 per cent. Since, however, every degree at C is divided into 10 parts, it is quite possible to read off tenths of a degree, and the corresponding quantity of calcium carbonate is also found by the aid of the table referred to, under the first 9 figures of the column, by simply altering from the right to the left hand the decimal point; for instance, we have found at 14° C. 7·8° at the scale C; we therefore have for 7 units 7·09 per cent., and for $\frac{8}{10}$ 0·81 (because 8=8·11), making together, for 7·8, 7·9 per cent. calcium carbonate.

Illustrative Examples.—

9·4° read off at C, at a temperature of 19°=9·289 per cent. of calcium carbonate.

14·9° read off at C, at a temperature of 13°=15·056 per cent. of calcium carbonate.

12·3° read off at C, at a temperature of 24°=11·799 per cent. of calcium carbonate.

11·7° read off at C, at a temperature of 16°=11·702 per cent. of calcium carbonate.

It is, however, for all practical purposes, quite sufficient to make round numbers of the figures following the decimal point, and instead of 9·289 to read 9·3; for 15·056 to read 15·06; for 11·799 to read 11·8; and for 11·702 to read 11·7.

The calcimeter is invaluable in cases where the frequent estimation of carbonic acid is required. With a little practice, 12 or 14 estimations may easily be made in an hour; and these, if upon the same finely powdered sample, will, with ordinary care, be found to agree almost absolutely. The saving of time by this process over the most expeditious of the ordinary gravimetric methods will be found to be very great. Starting, in each case, with the sample in powder, the difference in time is such as easily to repay the first cost of the instrument by a few hours' work. As the instrument is supplied with a

TABLE

For the Percentage Estimation of the Calcium Carbonate contained in Animal Charcoal, calculated from the volume of Carbonic Acid.

Observed Volume of Carbonic Acid	Degrees of Temperature (Centigrade)																		
	12°	13°	14°	15°	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	26°	27°	28°	29°	30°
1 .	0·80	0·80	0·79	0·79	0·79	0·78	0·78	0·77	0·77	0·77	0·76	0·76	0·76	0·75	0·75	0·74	0·74	0·73	0·73
2 .	1·88	1·87	1·86	1·86	1·85	1·84	1·83	1·82	1·81	1·80	1·79	1·79	1·78	1·77	1·76	1·75	1·74	1·73	1·72
3 .	2·95	2·94	2·92	2·91	2·90	2·89	2·87	2·86	2·85	2·83	2·82	2·80	2·79	2·77	2·76	2·74	2·73	2·72	2·71
4 .	4·01	4·00	3·98	3·96	3·94	3·93	3·91	3·89	3·87	3·85	3·83	3·81	3·79	3·77	3·75	3·73	3·71	3·70	3·68
5 .	5·07	5·05	5·03	5·00	4·98	4·96	4·93	4·91	4·89	4·86	4·84	4·81	4·79	4·76	4·74	4·71	4·69	4·67	4·65
6 .	6·11	6·09	6·06	6·03	6·01	5·98	5·95	5·92	5·89	5·86	5·83	5·81	5·78	5·75	5·71	5·68	5·65	5·63	5·61
7 .	7·14	7·12	7·09	7·06	7·02	6·99	6·96	6·92	6·89	6·86	6·82	6·79	6·75	6·72	6·68	6·65	6·61	6·58	6·56
8 .	8·17	8·14	8·11	8·07	8·03	8·00	7·96	7·92	7·88	7·84	7·80	7·76	7·72	7·68	7·64	7·60	7·56	7·53	7·49
9 .	9·19	9·16	9·12	9·07	9·03	8·99	8·95	8·90	8·86	8·82	8·77	8·73	8·68	8·64	8·59	8·55	8·50	8·46	8·42
10 .	10·20	10·16	10·12	10·07	10·02	9·98	9·93	9·88	9·83	9·79	9·73	9·68	9·63	9·58	9·53	9·48	9·42	9·39	9·34
11 .	11·20	11·15	11·10	11·05	11·00	10·95	10·89	10·84	10·79	10·74	10·68	10·63	10·57	10·52	10·46	10·41	10·35	10·30	10·25
12 .	12·20	12·15	12·09	12·03	11·98	11·92	11·87	11·81	11·75	11·69	11·64	11·58	11·52	11·46	11·40	11·33	11·27	11·22	11·16
13 .	13·20	13·14	13·08	13·02	12·96	12·90	12·84	12·78	12·72	12·65	12·59	12·53	12·46	12·40	12·33	12·26	12·20	12·14	12·07
14 .	14·20	14·14	14·07	14·01	13·94	13·88	13·81	13·75	13·68	13·61	13·54	13·48	13·41	13·34	13·26	13·19	13·12	13·05	12·99
15 .	15·20	15·18	15·06	14·99	14·92	14·85	14·78	14·71	14·64	14·57	14·50	14·42	14·35	14·27	14·20	14·12	14·04	13·97	13·90
16 .	16·20	16·13	16·05	15·98	15·91	15·83	15·76	15·68	15·61	15·53	15·45	15·37	15·29	15·21	15·13	15·05	14·97	14·89	14·81
17 .	17·20	17·12	17·04	16·97	16·89	16·81	16·73	16·66	16·57	16·49	16·41	16·32	16·24	16·15	16·07	15·98	15·89	15·81	15·72
18 .	18·20	18·12	18·03	17·95	17·87	17·79	17·70	17·62	17·53	17·45	17·36	17·27	17·18	17·09	17·00	16·91	16·82	16·73	16·63
19 .	19·20	19·11	19·03	18·94	18·85	18·76	18·67	18·59	18·50	18·40	18·31	18·22	18·13	18·03	17·94	17·84	17·74	17·64	17·55
20 .	20·20	20·11	20·02	19·93	19·83	19·74	19·65	19·55	19·46	19·36	19·27	19·17	19·07	18·97	18·87	18·77	18·66	18·56	18·46
21 .	21·20	21·10	21·01	20·91	20·81	20·72	20·62	20·52	20·42	20·32	20·22	20·12	20·01	19·91	19·80	19·70	19·59	19·48	19·37
22 .	22·20	22·10	22·00	21·90	21·80	21·70	21·59	21·49	21·39	21·28	21·17	21·07	20·96	20·85	20·74	20·63	20·51	20·40	20·28
23 .	23·20	23·09	22·99	22·88	22·78	22·67	22·56	22·46	22·35	22·24	22·13	22·02	21·90	21·79	21·67	21·55	21·44	21·31	21·20
24 .	24·20	24·09	23·98	23·87	23·76	23·65	23·54	23·43	23·31	23·20	23·08	22·97	22·85	22·73	22·61	22·48	22·36	22·23	22·11
25 .	25·20	25·08	24·97	24·86	24·74	24·63	24·51	24·39	24·28	24·16	24·04	23·91	23·79	23·67	23·54	23·41	23·28	23·15	23·02

normal weight and tables of calculated results, no time is lost in after-calculations. The volume of carbonic acid and the temperature indicated by the instrument are referred to the tables, where the percentage quantity of carbonic acid or calcium carbonate is at once found. One great advantage of such an expeditious method as this is that there is no temptation to be satisfied with first results, as a few minutes suffice to repeat the process.

Volumetric Estimation of Carbonic Acid by a Modification of Scheibler's Apparatus

(*A*) E. Nicholson recommends the apparatus figured on the following page. For the second graduated tube of Scheibler's apparatus, with its outlet pipe, reservoir bottle, and blowing-tube, E. Nicholson substitutes a reservoir which can be lowered as the pressure of gas forces down the column of water in the graduated tube. He dispenses with the diaphragm formed by the indiarubber bladder, relying on the impossibility of diffusion taking place beyond the double bulb during the short time which the operation requires. If the graduated tube be of 130 c.c., a quantity of gas equivalent to 0·5 gramme of calcium carbonate will not be beyond its capacity, at least in most European laboratories. The reservoir should be able to contain within its perfectly cylindrical part somewhat more than the quantity of water for which the tube is graduated.

To set the apparatus in working order, raise the reservoir (by means of the cord and counterpoise) until its lower end is 1½ inch, or 1 inch below the zero of the graduated tube, and then pour in distilled water until the column rises to that point. Note the lower level of the water in the reservoir, consequent on the smaller calibre of the graduated tube: this difference for capillarity should be maintained at all readings of the column of water. When the column is under pressure, as at the end of an operation, the difference can, if necessary, be accurately adjusted by means of a scale corresponding to that of the graduated tube, and marked on the frame, or by a sliding pointer; but this is really unnecessary, for the allowance can be made with sufficient accuracy by the eye. Considering that the height of the column is only affected by less than one-tenth of the amount of error in the adjustment of the reservoir-level, the possible error in an adjustment by the eye is trivial. An error of a whole centimetre of height in the adjustment would affect the reading to the extent of 0·06 c.c. only. Even with a reservoir of varying calibre, the greatest possible error arising from defective adjustment for capillarity is well within 0·1 c.c.

Mode of Operating.—Into the flask or bottle used for the reaction, a weighed quantity of powdered carbonate is introduced, together with a glass or gutta-percha tube containing either 5 c.c. or 10 c.c. of diluted hydrochloric acid. The flask being connected with the apparatus,

adjust the level of the water to zero, and then close the air-cock at the top of the bulb-tube. Holding the flask by the neck with the right hand, allow the acid to flow on to the carbonate while the left hand, on the cord of the counterpoise, lowers the reservoir as the gas forces the water down in the graduated tube. Agitate the flask as the action slackens, and when the column remains fixed, read off the height, the level of the reservoir being adjusted for capillarity. The operation being finished, disconnect the flask; raise the reservoir in order to drive carbonic dioxide out of the apparatus, and then open the air-cock; it may be left open until the next operation.

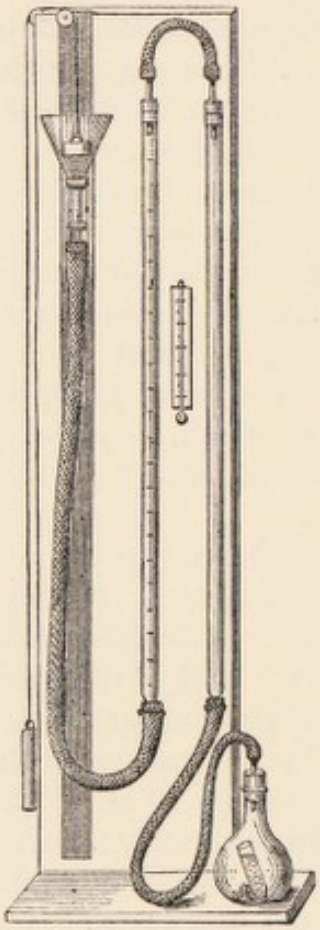


Fig. 26.

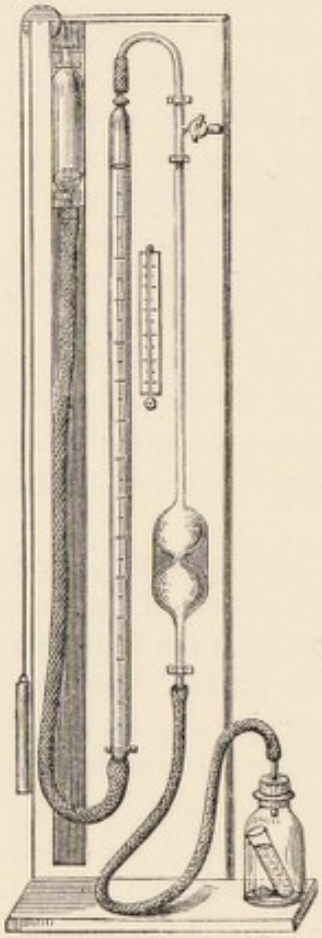


Fig. 27.

In the apparatus shown in fig. 26 there is no air-cock, and the level of the water-column, being depressed by the act of closing the flask, cannot be brought to zero; the reservoir must therefore be lowered to the proper level, the height of the column read off, and the number deducted from that found after the operation.

The sources of possible error in estimations by this apparatus are:—

1. From expansion of the gas disengaged in consequence of the heat produced during reaction.

2. From the absorption, or rather retention, of gas by the acid used for decomposition of the carbonate.

The first appears to be quite unimportant, except when the substance operated on contains much free base, as in the case of a partially carbonated lime; when operating on such a substance, the flask should be immersed in *air-warm* water during the reaction. The second error can be ascertained and allowed for; Dr. Scheibler sets it down at 0·8 c.c. for 10 c.c. of acid, sp. gr. 1·12. It is better for each operator to ascertain the error for the acid he uses: let him make two sets of experiments with the same quantities of calcium carbonate, decomposing this in one set by 5 c.c., in the other by 10 c.c. of acid. 1 c.c. for 5 c.c. of dilute acid (diluted with its bulk of

water) is a good allowance ; it is, if anything, slightly under the mark. The volume of gas obtained being corrected for absorption, the result may be calculated in two ways, as when the original apparatus is used. Either the experiment may be succeeded by a standard experiment on the same quantity of pure calcium carbonate (in this case there is no correction excepting for absorption, and a simple proportion gives the percentage), or the regular calculation may be applied.

(*B*) R. Warington considers that Scheibler's apparatus is one of great practical value, as very speedy results, of fair accuracy, can be obtained by its use. The mode of calculating the results described by Scheibler must, however, be abandoned so far as the use of a fixed correction for the retention of gas in the liquid and the employment of Table I. are concerned. By substituting a correction proportional to the volume of gas obtained, and reducing the volume of gas into terms of the carbonate sought by means of Scheibler's Tables III.–VI., the errors hitherto made will be avoided. It is not at all pretended that the proportional corrections there given will be found to hold good at all temperatures ; they are probably strictly true only for the temperature of the experiment. A far more complete series of observations is required. There are one or two points connected with the use of the apparatus which may be briefly mentioned. Any rise of temperature during the experiment entails a notable error, as the final reading is increased by the expansion of the whole volume of gas in the apparatus. A small rise in temperature is sure to take place if the operator stands before the instrument for two or three minutes while shaking the generating-bottle. This may be avoided by placing a narrow glazed screen between the instrument and the operator. The generating-bottle should also be wrapped in paper during the agitation. Bone charcoal, and many other substances in which carbonic acid has to be estimated, contain small quantities of sulphides ; to prevent sulphuretted hydrogen being evolved, a small quantity of mercuric chloride may be dissolved in the hydrochloric acid used.

Proximate Analysis of Coal

An elementary analysis of coal teaches little with regard to the nature or practical value of the combustible. A proximate analysis, on the contrary, enables us to learn something in regard to the real nature of the coal. The moisture and ash are not only diluents of the fuel, but are in themselves obstacles to its effectiveness ; the vapourisation of the moisture causes a serious loss of heat, while the ashes, by hindering complete combustion, and by the heat they contain when dropped through the grate, constitute another loss. By further estimating the total amount of volatile matter we learn both the percentage of coke in the fuel and the amount of carbon (fixed

combustible) and bitumen (volatile combustible matter). Although neither of these two products can be considered as simple chemical compounds, it is nevertheless of the utmost practical importance to know these two quantities, because of the great value of coke and gas in manufactures.

(*A*) The proximate analysis of coals has been worked out very fully by Professor G. Hinrichs. Before he instituted his researches no investigation as to its accuracy, nor the best method of conducting the work, was known. In Europe reliance was placed almost exclusively on elementary analysis, while in the Government Surveys of the United States proximate analyses seem to have been almost as exclusively practised. But while the former may readily be turned into approximate estimations of the heating effects of the fuel, the latter have never been used for such purposes, nor until Professor Hinrichs's researches was it at all apparent that they ever could be thus made useful. It is evident that the commercial applications of coal demand such an analysis, and it was therefore necessary for a rather extensive and thorough search into the method itself to be instituted in order to study its exact value.

(*B*) It is easily seen that the following data will modify the result of the amount of volatile matter driven off from a sample of coal contained in a covered platinum crucible:—Weight of coal and of crucible; degree and duration of heat; condition of coal. But notwithstanding all these considerations this estimation admits of an accuracy of $\frac{1}{10}$ of 1 per cent., equal to that of weighing a gramme exact to the milligramme.

The sample of coal used in these preliminary experiments was not selected, but taken at random. From this sample a very pure piece, free from any visible admixture of either gypsum or pyrites, was selected. Its specific gravity was found to be 1·328.

Estimation of the Volatile Matter.—A common Bunsen burner is used for producing a red heat, and also a gas-burner with six jets, surmounted by a French *soufflet cylindrique*, for obtaining a white heat, care being taken to keep the gas-cock in the same position by means of an arm of 10 inches in length. These two sources of heat are denoted respectively 'BB' and 'Blast.'

The time is measured by means of a small sand-glass, running exactly three and a half minutes; this duration is denoted by *t*. Thus BB, *t*, means that the crucible was exposed to the constant flame of the Bunsen burner during three and a half minutes.

Influence of Quantity of Coal.—1. Coal, pulverised, not dried; heat BB, *t*; cooled and weighed; then blast, *t*; then weighed again.[1]

[1] Weight = coal taken in grammes; crucible = weight of the same. Deviation per cent. from the mean given. These quantities are given in the same order in all subsequent tables, unless stated otherwise.

No. of Exper.	Weight.	Volatile matter, per ct.	Deviation.	Crucible.
d	5·360	48·24	− 1·14	19·2
n	1·910	49·58	+ 0·20	19·2
e	1·147	49·87	+ 0·49	11·6
o	1·031	49·85	+ 0·47	9·4
		Mean 49·38		

2. Coal in small fragments ; heat as in 1.

No. of Exper.	Weight.	Volatile matter, per ct.	Deviation.	Crucible.
h	3·743	48·30	− 0·94	19·2
g	1·130	50·18	+ 0·94	9·4
		Mean 49·24		

For the same heat, the amount volatilised is greater as the mass heated is smaller ; whether the coal is in small fragments or pulverised hardly makes any difference ; but since the bitumen passes off more regularly when the coal is pulverised, while, when in fragments, slight explosions sometimes occur, the coal should be pulverised for the estimation of the bitumen.

3. Coal, pulverised, between 1 and 2 grammes ; heat as above.

No. of Exper.	Weight.	Volatile matter, per ct.	Deviation.	Crucible.
n	1·910	49·58	− 0·19	19·2
e	1·147	49·87	+ 0·10	11·6
o	1·031	49·85	+ 0·08	9·4
		Mean 49·77		

giving as probable error of a single estimation only 0·108 per cent., or only 1 milligramme for 1 gramme of coal. This is not greater than that of the weighing itself, in which fractions of a milligramme were usually neglected.

4. Coal, pulverised (new portion), and between 1 and 2 grammes ; heat, BB, *t* ; immediately thereafter, blast, *t*, without cooling.

No. of Exper.	Weight.	Volatile matter, per ct.	Deviation.	Crucible.
a'	1·16	50·86	+ 0·14	9·4
n'	1·04	50·58	− 0·14	11·0
		Mean 50·72		

From 3 and 4 it is concluded that if the substance taken is from 1 to 2 grammes, the result will be constant for the same mode of heating.

Influence of Drying the Coal before Ignition.—5. Coal fragments ; heat, BB, *t* ; not cooled ; blast, *t*, with the probable error of one single estimation, 0·45.

No. of Exper.	Weight.	Volatile matter, per ct.	Deviation.
t	1·361	48·49	+ 0·76
u	1·060	47·26	− 0·47
v	1·030	47·43	− 0·30
		Mean 47·73	

Comparing this with 4 (same heating), it appears that about 3 per cent. less is volatilised by previous drying, and also that the accuracy of one estimation is four times less than when the coal is ignited without previous drying. In the arts, coal is not artificially dried before coking. For all these reasons, the amount of volatile matter is best estimated on undried coal.

6. In general, it was found, as means—

4 dried	coal gave	47·97	per cent.	volatile matter
10 undried	„	49·87	„	„ „

confirming the above.

Influence of Cooling after the Ignition over the Bunsen Burner, and before the Ignition over the Blast-flame.—7. Coal, pulverised, not dried ; heat, BB, *t* ; then blast, *t*, without cooling.

No. of Exper.	Weight.	Volatile matter, per ct.	Deviation.
x	1·314	49·01	−0·02
y	1·156	49·05	+0·02
		Mean 49·03	

which, compared with the corresponding case, 3, giving the mean 49·77 and maximum deviation 0·19, shows that by the intermediate cooling about $\frac{3}{4}$ per cent. more is volatilised. This probably is due to the fact that the crucible upon cooling is filled with atmospheric air, which, upon renewed ignition, must burn a corresponding amount of coal.

Influence of Repeated Heating, the Crucible being after each Ignition Cooled and Weighed.—8. Coal=*r*=1·628, in crucible 19·2, was dried, then ignited (BB, *t*), and lost 41·77 per cent. Being ignited again in the same way, it lost 2·76 per cent., or, in all, 44·53. Being successively ignited seven times, BB each time for six minutes, the total loss was 52·39, or, on the average for each of these six-minute BB ignitions, 1·12 (two of the estimations nearest this average were 1·06 per cent.).

Hereafter the same was exposed to the blast five times for three and a half minutes ; the volatile matter passed off amounted to 57·31, giving for each of these last ignitions the average loss of 0·98 per cent.

It now had been ignited fourteen times, each time having been cooled and weighed ; and we have fourteen ignitions, 57·31 volatile—first ignition, 41·77 volatile ; hence, average for each of the thirteen ignitions, 1·195, or 1·2 per cent.

This series of experiments shows that it is impossible to heat coal until no further loss is sustained ; for it is apparent that each heating, after complete cooling, produces, on the average, more than the additional volatilisation of 1. On 1 gramme of coal taken, 1 per cent. carbon burnt requires about 30 milligrammes, or 20 c.c. of oxygen.

We may therefore consider these excesses almost equal losses due to a real combustion.

Influence of Protracted Heating.—9. Coal, pulverised, not dried; heat, always first BB, t; and then immediately, without cooling, transferred to blast-lamp.

No.	Weight.	Blast.	Volatile matter.	Difference.	Difference per minute.
$a' + n'$	(mean)	3 min.	50·72	0·57	0·19
c'		6 ,,	51·29	1·04	0·35
b'		9 ,,	52·33	1·95	0·65
d'		12 ,,	54·28	2·93	0·16
k'		30 ,,	57·21		

By comparing each with the first mean, we obtain for each minute's blast after the first three, respectively—

0·24 0·39 0·27 0·20

showing less difference than the above.

The volatilisation, after the first three minutes blast, is therefore increasing $\frac{1}{4}$ to $\frac{2}{3}$ per cent. for six minutes, and then very slowly decreasing to about $\frac{1}{3}$ per cent. for half an hour. At this rate the loss is 12 per hour.

It is apparent that the loss is less than when cooled in the intervals, but it proves that a slight current of air must get at the coal in the covered crucible.

At any rate it is demonstrated that the rule which is sometimes given, to heat until no further loss is sustained, demands an impossibility.

Influence of the Degree of Heat.—10. Coal, pulverised, not dried; heat, BB, t; cooled and weighed; then blast, t; cooled and weighed again.

After BB.

No. of Exper.	Weight.	Volatile matter, per ct.	Deviation.
n	1·910	48·08	+ 0·42
e	1·147	47·69	+ 0·03
o	1·031	47·23	+ 0·43
	Mean . .	47·66	
	Prob. error .	0·284	

After Blast.

No. of Exper.	Volatile matter, per ct.	Deviation.
n	49·58	− 0·18
e	49·87	+ 0·11
o	49·85	+ 0·09
Mean . .	49·76	
Prob. error .	0·108	

showing that the higher temperature gives the most accurate results.

Result.—From these experiments it is concluded that—

The total volatile matter of coal is estimated with accuracy (1 milligramme on 1 gramme coal), by taking 1 to 2 grammes of undried, pulverised coal, heating it for three and a half minutes over a Bunsen burner (bright red heat), and then immediately, without cooling, for the same length of time over a blast gas-lamp (white heat).

Estimation of the Moisture.—(*A*) A flat-bottomed iron pan, of 20 centimetres in diameter, is filled evenly to the depth of 1½ centimetre with sand, and the latter is covered with a copper plate, on which the watch-glass containing the coal is placed. A thermometer (scale to 370° C.) is, by means of an indiarubber stopper, inserted in an iron arm of the tripod supporting the iron pan, and held with its bulb about half a centimetre above the copper plate. By means of a Bunsen burner it is found very easy to keep the thermometer perfectly constant at 115° C. This apparatus is a good substitute for Fresenius's iron plate.

The coal to be dried is finely pulverised, direct experiments having shown that the employment of fragments is not only very much slower, but also erroneous, on account of the peculiar property of bituminous coal treated of below.

These results show that the loss (called moisture) decreases regularly after the first hour of drying; that is to say, while the coal loses in weight during the first hour, it steadily gains in weight thereafter. It appears, furthermore, that the accuracy of an estimation, expressed in the smallness of the deviations from the mean, is greatest at the end of the first hour of drying, least after about three hours of drying, and thereafter increases again.

On account of these peculiar properties of bituminous coal, Professor Hinrichs advises that the loss in weight of the finely pulverised coal after one hour's drying at a temperature between 105° and 110° C., should be put down as moisture.

(*B*) For the analysis of coal and peat Sergius Kern gives a method well adapted for the laboratories of iron works, &c.

Estimation of Hygroscopic Water.—Three grammes of the substance in a finely divided state are dried in a porcelain crucible placed in a beaker with a small quantity of sand on the bottom of it. The beaker is covered with a watch-glass, and the whole is placed on a sand-bath and heated for about three hours to a temperature of 110°. The end of the operation is easily known by the dryness of the watch-glass. The substance when dried is weighed, and the percentage of loss is next calculated.

Estimation of Carbon and Hydrogen.—The best process was found to be Liebig's: the ignition of 1 gramme of coal or peat with lead chromate in a tube of hard glass 0·25 metre long. The resulting carbonic acid, water, and sulphuric acid are passed through a potash apparatus containing caustic potash (1 part of potassic hydrate dissolved

in 2 parts of water), and two U-tubes, the first containing ignited calcium chloride, the second a solution of lead nitrate. The increase in the weight of the potash apparatus and of the first U-tube will show the quantity of carbonic acid and water obtained. Knowing that carbonic acid contains 27·2 per cent. of carbon, and water 11·1 per cent. of hydrogen, the percentage of carbon and hydrogen may be easily calculated.

Calculation of the Calorific Power.—As 1 part of carbon in burning yields 8080 calorific units, and 1 part of hydrogen in burning 34,460 calorific units, the calorific power of the coal may be quickly found.

Example :—Coal from Donetz mountains, near the village of Grouchevka, South of Russia :—

	Per cent.
Carbon	58·0
Hydrogen	11·0
Sulphur	1·0
Ash	23·0
Hygroscopic water	6·0
	99·0

For calculating the amount of calorific units in this coal proceed as follows :

For carbon	0·58 × 8080 = 4686
For hydrogen	0·11 × 34460 = 3790
Total calorific units in the analysed specimen	8476

On the Slow Oxidation of Coal.—An increase in weight after the first hour's drying is found in all Iowa coals. It was also found to occur in a sample of coal (Steinkohle) from Beuthen, Silesia, which showed a loss of 3·62 per cent. at the close of one hour, and in four hours' further drying gained again 0·42 per cent. It was not noticed in brown coal from Bilin, Bohemia, nor in anthracite from Pennsylvania. It is therefore probable that it is a property peculiar to pit coal.

Pyrites might well be the cause of this phenomenon : the red ashes obtained in many cases may be ascribed to pyrites disseminated through the coal in invisible particles.

From an examination of a large series of analyses, it has been found that the more ferruginous ash does correspond to a slightly greater increase in weight ; but it is noticed also that this difference is very small as compared with the total amount of increase, being only $\frac{1}{5}$ to $\frac{1}{3}$ of the whole. Arranging these coals in the order of this hourly increase, it is found that the colours of the ashes do not at all form a regular series from white to red, as ought to be the case if this increase mainly depended upon the oxidation of the pyrites.

The greater increase of the pyritic coals is accounted for by the

oxidation of the pyrites they contain ; the comparatively great increase of coals giving a pure white ash seems to force the conclusion upon us that the bitumen of the coal itself oxidises, and that to this oxidation the main increase of all these bituminous coals must be ascribed. Bearing in mind the behaviour of bituminous coal from Silesia, anthracite from Pennsylvania, and brown coal from Bohemia, it seems not unlikely that this is another characteristic chemical difference between bituminous coal and other fossil coals.

Estimation of Ash.—(*A*) Incineration and an accurate estimation of ash are, in many substances, attended with not inconsiderable difficulties. These may arise from the sparingly combustible nature of the bodies, as in the case of anthracite or graphite ; from the presence of certain mineral substances which impede incineration, as silicic acid, phosphates, and fusible salts ; from a tendency to decrepitation observed in many vegetable matters, and in all coals ; from the partial volatility of various constituents of the ash, and from the chemical changes which the ash may undergo according to the degree and duration of the heat and the supply of air.

The first two of these difficulties affect principally the rapid execution of the process, while the remainder affect the composition of the ash and the accurate estimation of its weight. Peat and lignite require no special precautions ; they are readily inflammable, and rarely cake together, often smouldering away like tinder. In true coal all the above-mentioned difficulties may occur. All varieties of coal decrepitate more or less. The losses thus occasioned may be obviated by conducting the incineration at first in covered crucibles. This, however, is inconvenient where a great number of ash estimations have to be performed simultaneously. The incinerations are sometimes performed in porcelain crucibles, where unburnt coal is rarely projected over the edge. In general, flat platinum vessels are to be preferred ; in these the process is more rapid, but the chance of loss much greater. To prevent this source of error, it is advisable to reduce the coal to a very fine powder, and, above all, to heat very gradually. The latter precaution, especially in the case of caking coal, prevents the formation of coke, the incineration of which requires a much higher temperature, and a very considerable outlay of time. Every 'caking' coal loses this property entirely if very gently heated for a moderate time, and may then be almost completely incinerated at a temperature little above the melting-point of lead.

(*B*) Not every ash can be at once assumed quite free from carbon, and unburnt particles cannot be readily detected by stirring with a needle. Dr. F. Muck advises the use of alcohol for this purpose, when any unburnt portions are detected not merely by their colour, but by floating on the surface. Moistening with alcohol has the additional advantage that the ash, which lies very loose, adheres afterwards more closely to the sides of the crucible, and the complete incineration is

thus accelerated. Unburnt carbonaceous particles escape the eye most readily when the coal contains very little ash.

When sulphur and iron are present in large proportions, prolonged and repeated ignition is often necessary to reach a constant result. The question remains how the weight of the ash may be affected by the presence of a large proportion of lime. Lime may be present in the coal itself as silicate, as sulphate, as sulphide, and as carbonate.

The ash of coal (Westphalian at least) hardly ever effervesces with acids, and when this occurs to the slightest extent, it is due partially to sulphuretted hydrogen.

Ash containing much ferric oxide may be not at all, or but slightly red if much lime is simultaneously present, for calcium ferric silicate is colourless or yellowish, but not red. The following is the composition of a pale reddish coal-ash, which, if strongly ignited with the coal in question, melts to a vitreous slag. The ash scarcely effervesced with acids, and after being moistened with sulphuric acid and re-ignited it became red.

Silica	32·17
Alumina	17·87
Ferric oxide	17·42
Lime	17·83
Magnesia	6·97
Sulphuric acid (saturating 4·018 lime)	5·94
Matter not estimated	2·00

1·049 gramme of this ash moistened with alcohol, and then ignited for a considerable time in the muffle at a white heat, decreased to 1·0465 gramme. On treatment with ammonium carbonate, and gentle reheating, the ash weighed 1·056 gramme. The ash effervesced a very little more with acids; a trace of calcium carbonate had been decomposed during incineration. The practical results of Dr. Muck's experiments may be stated as follows:—

1. The chemical changes during the incineration of coal can only serve in rare and especial cases as an explanation of great differences in the estimation of ashes: for instance, when coal contains very much sulphur, and at the same time very little lime. In presence of much lime the combustion-products of the sulphur are more or less completely retained, while if little lime is present variable amounts of sulphur are driven off.

2. In case of a thoroughly homogeneous material—*i.e.* a finely powdered and well-mixed average sample accurately and carefully analysed—the estimations of ash may be expected to agree to within 0·1 to 0·2 per cent.

Larger differences, except in the peculiar cases just referred to, must be ascribed to defective work or great difference of the samples.

It is understood that the proportion of moisture must be taken

into consideration. In a thoroughly air-dry coal—not lignite—the highest limit of moisture is from 1 to 2 per cent.

The platinum crucible, according to the position of the flame, may be coated with soot. This coating may be easily burnt away, but care must be taken not to wipe a sooty place nor a place that has been sooty, without carefully checking the weight of the crucible after weighing the ash. In the places where soot has been formed by the dissociation of the hydrocarbons, the platinum becomes disaggregated and is coated with a black-grey deposit of finely pulverulent metal, which is easily rubbed off. The author has observed variations exceeding 8 milligrammes produced in this manner.

Determination of Specific Gravity.—Coarse fragments, freed by means of a sieve from all small particles, and averaging 0·1 c.c. in volume, are introduced into a 50-gramme flask provided with a thermometer stopper. The contents for this flask for temperatures varying from 50° to 80° F. are previously carefully estimated.

The given specific gravity corresponds to the coal perfectly soaked, so that all its pores are filled with water. That requires, on the average, twelve hours, permitting two estimates per day—one in the morning, another in the evening.

That this precaution is important may be seen from the following example:—2·76 grammes coal gave the sp. gr. 1·309 at 64° F., immediately after filling the flask with water; after about twelve hours' soaking, the sp. gr. had increased to 1·328 for the same temperature. According to this latter estimation, a cubic foot of this coal would weigh 82·76 lb.; according to the former, only 81·58, or 1·18 lb. less. This shows a considerable degree of porosity of the coal, and indicates the absurdity of giving the weight in pounds of a cubic foot of coal with four decimals, although no statement in regard to temperature or time of weighing is made.

Calculation of Results.—It may be sufficient here to state that, besides the percentage composition of the coal, it is proper to reduce the composition to the combustible=100, in order to obtain a proper comparative estimate of the character of the fuel itself (in regard to the proportion of bitumen and carbon), and of the amount and quality of the impurities (ashes and moisture). It has also been shown that, for considerable areas of the coal-field, the sum of the constituents on the scale of combustible=100 is the proper caloric equivalent, and that the percentage of the combustible in the fuel gives a proper estimate of its value.

Assay of Coal before the Blowpipe

The blowpipe method is well adapted to the assaying of coal. Not only does the portability of the apparatus make it very convenient for use away from home, wherever the balance can be set up; but its use at home is quite as satisfactory on the score of exactness as the

assay with the muffle or retort, or large platinum crucible and large balance. B. S. Lyman gives the following directions for carrying out this assay:—

Besides the ordinary pieces of the blowpipe apparatus, as made at Freiburg, all that needs to be made expressly for the coal assay is a small covered platinum crucible of the same size and shape as the clay crucibles of that apparatus; and there must be a little ring for the crucible to stand on, of German silver, about $\frac{3}{8}$ of an inch across and half that in height. Such a crucible cover and ring weigh about $2\frac{1}{2}$ grammes more than the ordinary metallic cup that rests on the pan of the balance; the crucible and ring without the cover weigh about 2 grammes more than the cup. If it be desired to estimate the amount of hygroscopic moisture in the coal, a small drying bath must be made too; but the hygroscopic water in ordinarily well-dried coals (not brown coals) is of little importance.

The size of the crucible allows the coking of 200 to 600 or more milligrammes of coal, according to the dryness of the coal and the extent of its swelling up when heated; and as the blowpipe balance weighs within $\frac{1}{10}$ of a milligramme, it is easy to weigh within much less than $\frac{1}{10}$ of 1 per cent. of the amount of coal assayed—much nearer, in fact, than the exactness of the coke assay in other respects. In this point, indeed, the blowpipe assay is quite as good as the assay with the larger balance, especially the muffle assay, where the coal must be brushed into a clay receptacle after weighing, and the coke or ash brushed off from it before weighing; while here the crucible is weighed each time without removal of its contents, and without danger, therefore, of losing anything or adding any dust. It may be objected that the smallness of the amount of coal that can be assayed with the blowpipe makes it a less trustworthy indicator of the general composition of the coal than a larger assay; but the size of the lumps or powder assayed may be made finer accordingly, so that when mixed up an equally just sample of the whole mass would be got, for the small assay as for the large.

Anyone who has a little experience both in the use of the blowpipe and in the ordinary muffle assay of coal will scarcely need any further teaching for the coal assay with the blowpipe. For others, it is worth while to say that the coal may be assayed either in a fine powder or in little lumps, and either with a slowly increasing or with a quickly increasing heat. A quick heat will give less coke by several per cents., but will often make a dry coal cake together that would not cake with a slow heat. The cover of the crucible should be left open a very little way for the easy escape of the gas, but covered enough to prevent any loss of solid material. The heat should increase to redness, and as soon as the escaping gas stops burning the heat should be stopped. As some coals part with their gas more quickly than others, of course no definite time can be fixed for heating all coals;

but the burning of the gas is a sufficiently good sign. Care should be taken not to let the coke take up moisture from the air before weighing, as it will quickly do if it has a chance. It follows that owing to the different effect of quick or slow heat, a certain uniformity of result, even with perfectly uniform samples of coal, can only be got, without error, by practice and by mechanical skill, by reproducing with nicety the same conditions in successive assays.

After the coke has been weighed it can be heated again with very free access of air, say with the crucible tilted to one side, with the cover off, until everything is thoroughly burnt to ashes; and these should be reheated until no change for the less is made in the weight. With free-burning, soft (semi-bituminous) coals this calcination is very slow, so that it is very fatiguing or even impossible to carry it out with the blowpipe; but in that case the crucible may be heated over a Bunsen gas-burner or an alcohol lamp, and left to glow for hour after hour. The coking is far more conveniently done in the same way than by blowing with the mouth.

As an illustration of the degree of accuracy which this method may be expected to give, the author adduces a pair of blowpipe assays, made five years ago, of some West Virginia asphaltum, that seemed itself to be much more uniform in composition than coal from different benches in one bed is apt to be:—

	Volatile matter.	Coke.	Ash.
No. 1 .	47·29 per cent.	52·71 per cent.	1·65 per cent.
No. 2 .	46·93 „	53·07 „	1·81 „
Mean .	47·11 „	52·89 „	1·73 „

Estimation of Sulphur in Coal and Coke

(*A*) Crossley has drawn attention to the fact that the process of estimating sulphur in coke, &c., by boiling in nitric acid gives results much below the truth. In the same sample he found the process of fusion with nitre, sodium chloride, and potassium carbonate gave 0·603 per cent., while boiling with nitric acid yielded only 0·477; in another sample fusion gave 1·23 per cent., and boiling with nitric acid 0·93 per cent. He has arrived at the conclusion that the cause of this loss is, not that some of the sulphur escapes oxidation, but that a portion is driven off by evaporation to dryness. Upon adding a little potassium nitrate to the nitric acid, for the purpose of fixing the sulphuric acid formed and thus preventing its volatilisation on evaporation to dryness, the results appear to be as accurate as those yielded by the fusion process.

(*B*) Dr. T. M. Drown uses bromine as an oxidising agent. He finds it especially valuable in the analysis of coal. By the treatment of coal as here described, results are obtained which agree very closely. The coal, as such, is not attacked, and the sulphur obtained therefore

represents that existing in the coal as pyrites, and also as soluble sulphates. The residue left by this treatment has been subjected again to the same process, and yields no more sulphur. On combustion, however, or by complete oxidation, either by oxidising acids or by fusion, additional sulphur may be obtained, which must represent that combined organically with the coal.

In comparing the bromine method with others it was found that the treatment with hydrochloric acid and potassium chlorate gave with coals containing but little sulphur in the form of pyrites the same results, while with coals containing much pyrites the results were decidedly lower than by the bromine method. The action of nitric acid and potassium chlorate depends upon the nature of the coal. Some coals are converted partly into a brown unmanageable solution, and others are oxidised completely to a clear solution. In the latter case, of course, the total sulphur could be obtained.

As was said above, the sulphur found by the bromine method represents both the sulphides and sulphates in the coal. The methods ordinarily given for the separate estimation of calcium sulphate are faulty. Sodium carbonate readily attacks pyrites, and dilute hydrochloric acid and even water, when heated for some time in contact with pyrites, with access of air, contain notable quantities of sulphuric acid. It would seem, therefore, necessary to dissolve out the calcium sulphate by means of water, with the careful exclusion of air.

(*C*) A. Eschka directs to powder as finely as possible 1 gramme of the sample, and mix intimately with 1 gramme of calcined magnesia and 0·5 gramme of anhydrous sodium carbonate. Heat over the lamp in an open platinum crucible, inclined so that only its lower half may be brought to a red heat. The ignition requires from forty-five to sixty minutes, and the mixture should be stirred every five minutes with a platinum wire. The process is complete when the ash becomes yellowish or brownish. Let it become quite cold, and mix intimately with the ash, by means of a glass rod, $\frac{1}{2}$ to 1 gramme of ammonium nitrate, and heat to redness for five or ten minutes, the crucible being covered with its lid. The residue is then placed in a precipitating glass and covered with water. The residue adhering to the crucible is detached by heating with the liquid, and the washings are added to the solution in the glass. The sulphuric acid is then estimated in the usual manner.

Valuation of Coal for the Production of Illuminating Gas

Take 100 grammes of the coal in small lumps, so that they may be readily introduced into a rather wide combustion-tube. This is drawn out at its open end (after the coal has been put in) so as to form a narrow tube, which is to be bent at right angles; this narrower open end is to be placed in a wider glass tube, fitted tight into a cork

fastened into the neck of a somewhat wide-mouthed bottle serving as tar vessel (hydraulic main of the gasworks). The cork alluded to is perforated with another opening, wherein is fixed a glass tube, bent at right angles, for conveying the gas, first through a calcium chloride tube, next through Liebig's potash bulbs containing a solution of caustic potash, having lead oxide dissolved in it. Next follows another tube, partly filled with dry caustic potash, and partly with calcium chloride; from this last tube a gas-delivery tube leads to a graduated glass jar standing over a pneumatic trough, and acting as gas-holder. Before the ignition of the tube containing the coal is proceeded with, all the portions of the apparatus are carefully weighed, and next joined by means of indiarubber tubing. After the combustion is finished, which should be carefully conducted so as to prevent the bursting or blowing out of the tube, the different pieces of the apparatus are disconnected and weighed again. The combustion-tube has to be weighed with the coal after it has been drawn out at its open end, and with the coke after the end of the combustion when it is again cold, and for that reason care is required in managing it. We thus get the quantity of tar, ammoniacal water, carbonic acid, and sulphuretted hydrogen (as lead sulphide). The gas is measured by immersing the jar in water, causing it to be at the same level inside and out. Empty the Liebig's bulbs into a beaker, and separate the lead sulphide by filtration, wash carefully, dry at 100° C., and weigh. From the lead sulphide the sulphuretted hydrogen present is calculated. This process, devised by the late Dr. T. Richardson of Newcastle-on-Tyne, was found by him to yield very trustworthy results, so as to be suitable for stating what quantity of gas a ton of coal thus analysed would yield.

Carbonic Acid

Estimation of Carbonic Acid in Natural Water. — Lory employs copper phosphate dissolved in a very slight excess of hydrochloric acid. The copper phosphate is obtained by precipitating a solution of copper chloride with ordinary sodium phosphate; the precipitate is collected on a filter, well washed, and, after having been removed from the filter, it is suspended in water and dissolved by the addition of a few drops of hydrochloric acid. When this reagent is added to any water containing alkaline or earthy metals in the state of carbonates or bicarbonates, the result is at first the formation of a bluish-coloured cloudiness, or turbidity. By the addition of a larger quantity of the reagent, this turbidity disappears, and the liquid becomes clear again. This point having been reached, the quantity of the reagent employed will be proportional to the total equivalent of the bases present, and consequently to the carbonic acid which was combined with these bases.

In order to titrate the reagent, dissolve 0·265 gramme (equal to

$\frac{1}{200}$ of an equivalent) of perfectly pure and dry sodium carbonate in water, and saturate this solution with carbonic acid in order to convert it into bicarbonate; excess of carbonic acid does not at all affect the reagent. 4·4 c.c. of this solution in 1 decilitre of pure water should produce, by the addition of the copper liquor, the reaction already alluded to, and these 4·4 c.c. correspond to 0·29 gramme of carbonic acid.

This reagent is unchangeable and easily prepared, and is effectual no matter what quantity of chlorides, sulphates, &c., be contained in the water; it may even be employed for the alkalimetrical estimation of very dilute liquids; but it should be remarked that the reaction is much more exact with bicarbonates than when the bases exist as neutral carbonates or free alkalies. By combining this quick and simple test with the test by the standard solution of soap, both in the natural water and also in the same water after boiling, the most important elements for the appreciation of its ordinary and hygienic qualities will be obtained.

Estimation of Carbonic Acid in Artificial Mineral Waters.—In these waters the gas is present under considerable pressure. H. Napier Draper has devised the following apparatus by means of which the entire quantity of gas is easily and simply estimated.

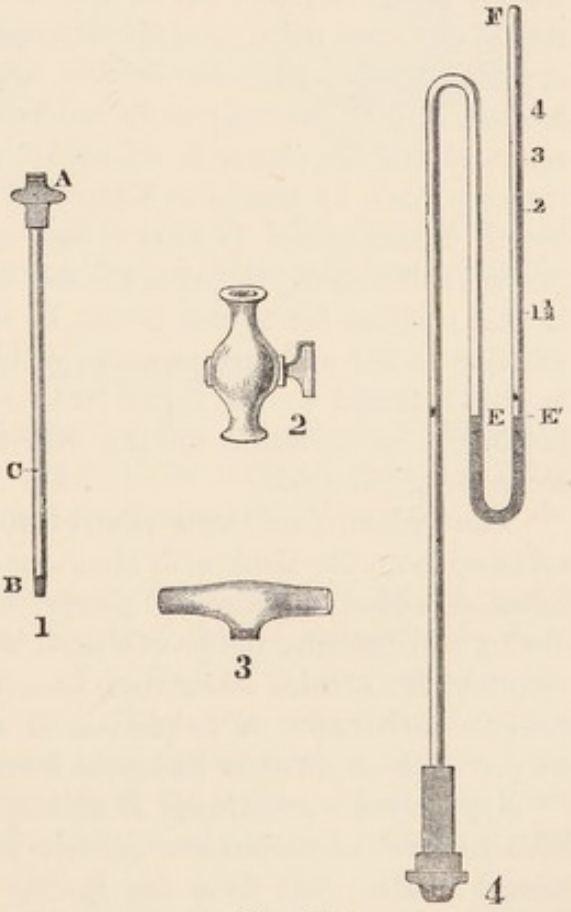


Fig. 28.

1 is a tube of strong brass furnished at A with a screw, and tipped at B with a sharp steel ferrule. This tube is open at both ends, and is pierced at C with two small holes.

2 is an accurately ground stopcock, which can be screwed on to A, No. 1.

3 is a handle like that of a gimlet, screwing on to the other end of the stopcock.

4 represents an air-pump syphon-gauge of stout glass tube, securely cemented into a short brass tube, which is also provided with a screw, the thread of which coincides with those of the stopcock and the tube No. 1. Mercury is poured into this tube and adjusted to the level E E'. The space E' F is then graduated, as shown in the figure, by first dividing it into two equal

portions and marking the point of division 2. The lower space is then subdivided in the same manner, and the separating line marked $1\frac{1}{2}$. The mark 4 is similarly obtained by dividing the upper space, and the 3 is placed at a point equidistant from 2 to 4.

There are two methods of using this apparatus. The first is more suitable in cases where great accuracy is required; the second is more practically applicable where an approximate knowledge of the gaseous contents of water is required, and where it is certain that these consist wholly of carbonic acid.

In the first case an ammoniacal solution of barium chloride is prepared by mixing a saturated solution of the salt with half its volume of strong solution of ammonia, and allowing the mixture to become clear by subsidence. The estimation is then proceeded with in the following manner:—A glass flask, capable of holding half as much more liquid than is contained in the bottle experimented upon, is fitted with a cork through which a glass tube passes nearly to the bottom of the flask. About 2 fluid ounces of strong solution of ammonia are now poured into the flask and mixed with 4 ounces of distilled water. The stopcock being adjusted to the tube at A, the handle is now screwed on to the free extremity of the former, and by its aid the steel point is made to penetrate the cork of the bottle to be experimented on until the orifices appear below its under surface. It is used, in fact, precisely as an ordinary cork-borer. The handle is now removed and the stopcock connected with the glass tube which passes into the flask, by means of a piece of vulcanised tubing about 6 inches long. The stopcock is next turned on just so much as will allow the gas to bubble slowly through the solution of ammonia. The whole is left in this position for twelve hours, by which time all the gas not held in solution at the ordinary pressure will have been absorbed. That which is still retained by the liquid may either be expelled by heating the bottle placed in water, or the entire liquid may be mixed with the contents of the flask.

The carbonic acid can now, of course, be estimated by mixing the solution from the flask with about an ounce of the ammoniacal barium solution above mentioned, gently heating, separating by filtration, drying and igniting the precipitated barium carbonate as usual. If the whole of the aërated water has been transferred to the flask, and if it contain carbonates or sulphates, or any earthy or metallic base, the weight of these must be deducted from that of the precipitate.

Approximate and Rapid Method of Estimation with this Apparatus. This method of estimation cannot be considered as giving absolutely correct results; but from the facility with which it can be performed, it will be found useful where great accuracy is not required. It must be premised, however, that the necessary correction for temperature must be made; when this is done the results coincide very closely with those obtained by the first-described method.

In this case the stopcock, instead of being connected with the flask, is screwed into the mercury tube, 4, and gradually turned until fully open. Now, as water dissolves at the ordinary pressure of 30 inches its own volume of carbonic acid, and as the quantity dissolved at other pressures is directly proportional to the pressure exerted, it is clear that if we know the amount of this pressure and the volume of the water in which the gas is dissolved, we can, knowing also the weight of an equal volume of carbonic acid, estimate by weight the quantity of the latter held in solution. Or, without knowing this latter number, we can express, as is most usual, the quantity of gas in cubic inches. Now it is also clear that as the volume of a gas is inversely as the pressure to which it is subjected, the mercury tube, graduated as in the figure, will show at a glance the number of atmospheres under which the carbonic acid is held dissolved.

Estimation of Carbonic Acid in Solid Carbonates.—Sir C. Cameron employs an apparatus shown in fig. 29. It consists of a light bottle, of the capacity of 75 cubic centimetres. The lower part is divided into two compartments, in one of which the carbonate is placed, in the other the acid. By inclining the bottle, the acid may be allowed to flow over on the carbonate as gradually as the operator pleases. One or two calcium-chloride tubes are inserted through the cork.

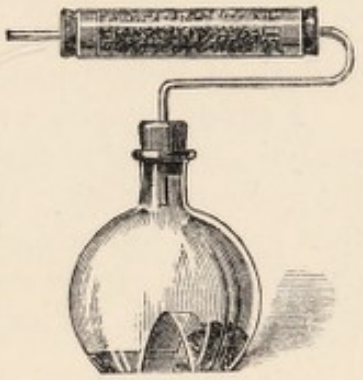


Fig. 29.

The use of anhydrous copper sulphate jointly with fused calcium chloride is preferable as a dryer in case hydrochloric acid is used in the analysis.

Estimation of Carbonic Acid

T. S. Gladding uses an apparatus for the estimation of carbonic acid by absorption. It has been used in the author's laboratory for several years, and has proved itself indispensable on account of its great convenience and accuracy.

It consists of the ordinary generating flask, followed by an empty U-tube to retain condensed water vapour: this is succeeded by four potash bulbs of the Geissler form. The first of these contains concentrated sulphuric acid to dry the gas. The next two contain potash solution, of sp. gr. 1·27, for absorbing the carbonic acid ; the last contains concentrated sulphuric acid to absorb the moisture taken up from the potash solution. Then comes a U-tube containing soda-lime, and serving as a guard.

The last three Geissler bulbs constitute the weighable portion of the apparatus. Perfectly dry air plus carbonic acid enters these, and perfectly dry air alone escapes. The increase in weight gives the amount of carbonic acid.

The advantages of this apparatus are :—

1. The superiority of concentrated sulphuric acid over calcium chloride as a drying agent on account of (*a*) its greater thoroughness ; (*b*) its non-absorption of carbonic acid, as is the case with calcium chloride, requiring its previous saturation by a current of the gas ; and (*c*) its greater cleanliness and simplicity of renewal, which takes but a moment, and is necessary only at long intervals.

2. The rapidity with which an analysis may be made. The bubbles of gas may pass at the rate of five per second with perfect safety, and an analysis including all weighings, and a final aspiration of 4 or 5 litres of air, be completed in less than two hours.

3. The large quantities of substance that may be used, and the consequent increase of accuracy obtained. Five grammes of sodium bicarbonate may be used as readily as 1 gramme in the old form, and duplicates easily agree within a few hundredths of 1 per cent. An analysis of Iceland spar, taking 5 grammes, gave 43·97 per cent.

A strong aspiration must be maintained from the beginning of the analysis, the flow of gas being regulated by a screw clamp placed before the generating flask. 100 c.c. of water are added to the carbonate, and then normal hydrochloric acid to slight excess. Not a trace of hydrochloric acid is carried over on boiling. All the corks are of soft rubber, and black rubber tubing is employed for connections.

BORON

Detection of Boron in Minerals

(*A*) After estimating the water of crystallisation, Professor Wöhler dissolves the mineral (tinkalcite) in hydrochloric acid, and after neutralising with ammonia, precipitates the calcium with ammonium oxalate, concentrates the filtrate, and estimates the boracic acid in the state of double boron and potassium.

In the case of minerals like tourmaline, which contain fluorine and boron, the question is not so simple. The volatile matters may be estimated by a process analogous to that employed in the case of silicon fluoride, the boron fluoride being changed into a mixture of calcium fluoride and boracic acid. Unfortunately we do not know a method of estimating boron directly in mineral substances, especially if associated with fluorine and silicon ; so that if we have boron fluoride, silicon fluoride, and alkaline fluorides, we can estimate the alkalies, but not the boron, silicon, and fluorine. In the absence of a quantitative method for estimating boron, we have an excessively delicate qualitative test.

(*B*) The best method of recognising the presence of boron, if no fluorine is present, is to mix the substance with a small quantity of calcium fluoride and potassium bisulphate, having previously ascertained

that the two reagents do not contain boron; two experiments must therefore be made, one on the reagents, and the other on the substance mixed with the reagents. The mixture is slightly moistened, and held on the extremity of a perfectly clean platinum wire. Direct the reducing flame of the blowpipe on to the paste; at the moment when the mixture appears to boil the flame assumes a vivid green colour, characteristic of boron. When but little boron is present, this must not be tried in full daylight, and it should be viewed against a dead-black background; the colour of the flame will then be easily detected.

(*C*) Dr. M. W. Iles finds that borax moistened with glycerin gives before the blowpipe a blue flame which soon changes into a deep green. In subsequent experiments he found it was best first to calcine the mineral, powder, and moisten with sulphuric acid, heat to expel the acid, then to moisten with glycerin and allow it to take fire. Thinking that the carbon exerted some action upon the borate, finely divided charcoal and a borax bead were tried, but they gave negative results.

Glycerin and a sodium carbonate bead gave simply a yellow flame. Various metallic bases in a sodium carbonate bead and glycerin also gave negative results in regard to flame. A 'salt of phosphorus' bead and glycerin gave the light green phosphoric acid flame, but of less intensity than that noticed when a potassium chlorate match is burned. A large number of bases and acids were also experimented upon in connection with glycerin, using different beads; also substances were treated on charcoal with glycerin, with various results, some of which were without doubt sufficiently characteristic for qualitative reactions.

Estimation of Boracic Acid

(*A*) In order to estimate directly the boracic acid contained in datolite, a calcium borosilicate, Professor Wöhler proceeds as follows:— Place the mineral in a small tubulated retort, decompose it with hydrochloric acid, and distil the mixture to dryness; pour on to the residue the distillate (which contains boracic acid), and allow it to digest to separate the silica. In the liquid, precipitate the calcium by means of potassium oxalate, taking care not to add it in too great excess. Then, after filtration and concentration, precipitate the boracic acid in the form of double boron and potassium fluoride. For this purpose add a little potash to the material in a platinum capsule, then pour over the mixture a slight excess of hydrofluoric acid, and evaporate the solution to dryness. To remove the other salts it suffices to treat the mass with a moderately concentrated solution of potassium acetate; then allow it to digest, and throw on to a filter the residual double boron and potassium fluoride, and wash it with the same solution of acetate. Then wash with dilute alcohol to remove the potassium acetate. The double fluoride is dried at 100° C., and weighed.

(*B*) If it be required to estimate boracic acid contained in a solution in which it is present alone, or in combination with alkaline oxides, A. Ditte proposes to add a little ammonia to the liquid in order to neutralise any free acid, and then an excess of a saturated solution of pure calcium chloride. All the boracic acid is then found as calcium borate, in the form of a gelatinous precipitate, soluble in heat in calcium chloride in excess. The matter introduced into a platinum capsule may then be evaporated to dryness without the least trace of boracic acid being volatilised. When dry, the crucible is filled with a mixture of equal equivalents of pure crystalline sodium and potassium chlorides and heated moderately at first, and then to fusion. The calcium borate, much less fusible, collects at the bottom of the crucible in a spongy mass more or less agglomerated, and dissolves partially in the melting saline mass. If at the bottom of the crucible a temperature is maintained higher than in the upper part, the dissolved calcium borate crystallises on the surface of the liquid, and forms a ring, which rises along the side of the crucible, just above the surface. Soon all the borate is conveyed into this ring, and nothing remains at the bottom of the crucible. The crystals are insoluble both in hot and cold water. A cold concentrated solution of alkaline chlorides does not affect them ; if hot it dissolves a very small quantity. The matter, when cold, is separated from the crucible, and treated with cold water, when the chlorides dissolve. The crystals are washed on the filter, dried, detached from the filter, and weighed. Care must be taken not to fuse the amorphous calcium borate which occupies the bottom of the crucible in an early stage of the operation. The temperature of the bottom of the crucible should be kept as high as possible short of such fusion. The crucible cannot be sufficiently heated with a Bunsen burner. On approaching the point at which the calcium borate is fused, the volatilisation of the alkaline chlorides becomes visible. There should be 1 part of pure dried calcium chloride for 3 parts of the mixture of alkaline chlorides.

Boracic acid is insoluble in anhydrous ether at the ordinary temperature, but it is slightly soluble in ether saturated with water (0·188 gramme in 100). On the other hand, it is not at all volatile in dry vacuo at the ordinary temperature, neither is it carried over by ether vapour.

A. Partheil and J. A. Rose[1] apply this principle in the following manner :—The apparatus used for the exhaustion by percolation consists of a tared matras into which 20 to 30 cubic centimetres of ether are poured : this vessel communicates with a vertical condenser by means of a straight tube and a serpentine. In this latter, place the solution in which is to be estimated the boracic acid (for example, a borate with dilute hydrochloric acid), and arrange the tubes in such a manner that the ether falling back from the condenser goes to the

[1] *Chemical News*, Feb. 20, 1903.

bottom of the serpentine tube, ascends this latter throughout its whole length while traversing the column of boriferous liquid, and finally discharges into the distilling flask without carrying with it any of the aqueous solution. The ether is kept boiling briskly for eighteen hours; the whole of the boracic acid having passed into the flask by this time, nothing remains but to detach the latter, allow the ether to evaporate off in a sulphuric acid desiccator, and weigh; the difference in weight gives the boracic acid. It is important that the solution under examination should not contain sulphuric, nitric, phosphoric, or arsenious acids, nor notable quantities of ferric or zinc chloride.

Analysis of Borates and Fluoborates

In solutions which contain only boracic acid and alkalies, Marignac estimates the former as follows:—The solution is neutralised with hydrochloric acid, and magnesium chloride, or preferably the double magnesium and ammonium chloride, is added in such quantity that to 1 part of boracic acid at least 2 parts of magnesia are present. The liquid is now made ammoniacal, and finally is evaporated to dryness in a weighed platinum vessel. Should the addition of ammonia cause a precipitate which does not readily disappear on warming, sal-ammoniac must be added until the liquid becomes clear. During the evaporation it is well to add a few drops of ammonia from time to time. When the mass is dry it is heated to redness, then treated with boiling water; the residue is collected on a filter, and washed with hot water until the washings are not in the slightest degree affected by silver nitrate.

The first residue contains, together with excess of magnesia, the larger part of the boracic acid. A small amount of the latter always goes into solution. The filtrate and washings are treated with ammonia and again evaporated, ignited, and washed as before. The second filtrate and washings are once more treated in the same manner, when great accuracy is required.

The three residues are ignited together in an open crucible as strongly as possible, and sufficiently long to decompose the traces of magnesium chloride which they may contain. When they are weighed, it only remains to estimate the magnesia in them to find by difference the quantity of boracic acid. This can be done either by dissolving in an acid and precipitating magnesium ammonio-phosphate, or more rapidly by dissolving in a known volume of standard sulphuric acid at a boiling heat and estimating the excess of acid by means of a standard alkaline solution.

Should an insoluble, heavy, grey residue remain on treating with acid, it must be collected and its weight deducted from that of the magnesium borate; it will be platinum.

From insoluble compounds the boracic acid is obtained in solution by fusing with three times their weight of sodium carbonate, and exhausting the mass with water. In case of silicates the alkaline solution is digested with ammonium chloride to precipitate silica.

When operating with a fluoborate, the solution of the sodium carbonate fusion is digested with sal-ammoniac to decompose a good proportion, but not all, of the sodium carbonate, and is then precipitated with a neutral or ammoniacal solution of calcium chloride. The precipitate of calcium fluoride and carbonate is washed—a matter easily accomplished—dried, gently ignited, treated with acetic acid, evaporated to dryness, and the pure calcium fluoride collected, washed, and weighed. The filtrate, after removing calcium by addition of carbonate and a few drops of ammonium oxalate, may be treated as before described for the estimation of boracic acid.

SILICON

Decomposition of Silicates in the Wet Way

By Means of a Fluoride and Acid.—C. E. Avery finds that silica and silicates, such as felspar and glass, may be completely dissolved in the cold by a mixture of some normal fluoride with almost any of the stronger acids, whether concentrated or dilute.

When mixed with the sodium, barium, aluminium, and lead fluorides, or the double fluorides of these metals, the silicates in question can be readily decomposed by nitric, hydrochloric, or sulphuric acid, either concentrated or diluted with 4 volumes of water.

If strong sulphuric acid is used, a part of the silicon passes off as gas: if the dilute acid is used, portions of many silicates remain undissolved as insoluble sulphates.

The same decomposition of the silicates is effected, though less easily, by the action of oxalic, acetic, tartaric, and like acids, on the mixed fluoride and silicate. Carbonic acid, even as dilute as it is in the air, does the same, but less rapidly.

Strong nitric acid gives a perfect solution and acts rapidly, dissolving a moderately fine powder of felspar or quartz in a few hours, even in the cold. The loss of silica is very slight if the experiment is properly conducted; hence, all the constituents of a siliceous mineral can be estimated in the solution produced.

In analysing silicates in this way, it is best to use the fluoride of some metal which is not to be estimated in the analysis; since if we use a fluoride whose metal is present in the mineral, we must know the weight of fluoride taken. Of the various fluorides those of barium and lead seem to be the most promising.

An objection to the use of ammonium fluoride is that, as usually made, it contains ammonium sulphate, so that insoluble sulphates might be formed and solution retarded.

If sodium fluoride, as made from cryolite, were not so hard to purify, it would be well fitted for the analysis of silicates free from sodium.

Decomposition of Silicates in the Dry Way

For Professor J. Lawrence Smith's process for the decomposition of alkaline silicates, see *ante*, page 23.

By Hydrofluoric Acid at a Red Heat.—F. Kuhlmann treats silicates at a dull red heat with a current of hydrofluoric acid. The apparatus for this process consists of a platinum retort, of which the body may be of lead; the acid is produced in it by means of sulphuric acid and white cryolite, or pure calcium fluoride. The neck of the retort fits tightly into a tube of platinum, which contains, in boats of the same metal, the matter to be analysed; this tube, by means of a short adapter, also of platinum, communicates with a condensing or absorbing apparatus; this apparatus may be of vulcanised indiarubber. One hour's heating suffices for the treatment of 10 grammes of mineral, but not more than 2 grammes should be employed.

By Fusion with Baryta.—A. Terreil attacks silicates with perfectly pure barium hydrate, fused and pulverised, using 7 to 8 parts to 1 of the silicate. The operation is performed in a silver crucible at 350°, the temperature being raised a little when the fused mass has again solidified, but not so as to reach dull redness. The mass, after cooling, is boiled in pure water in the crucible, and the filtrate is treated with a current of well-washed carbonic acid, raised to a boil, and filtered. The alkalies will be found in the filtrate.

By Fusion with a Fluoride.—Dr. F. W. Clarke [1] recommends that 1 part of the very finely powdered mineral should be mixed with 3 parts of sodium fluoride, and that this mixture, after having been placed in a platinum crucible, should be covered with 12 parts of powdered potassium bisulphate, and the whole raised to a red heat. Not only are silicates readily decomposed in this manner, but such minerals as chrome-iron ore, red hæmatite, tin ores, rutile, corundum, &c., are very readily brought to fusion and disintegrated by this flux, even with no more heat than that obtained from a good Bunsen gas-burner.

Opening up Silicates by Means of Pure Lead Carbonate

P. Jannasch [2] has described a method for decomposing silicates by means of lead carbonate.

The requisite chemically pure lead carbonate is suitably obtained by precipitating a hot solution of lead acetate with the calculated quantity of ammonium carbonate.

[1] *Chemical News*, vol. xvi. p. 232. [2] *Ibid.* Aug. 2, 1895.

The granular precipitate obtained is first washed in a tall beaker by repeated decantation, then distributed on several rapid filters (made by Desaga, of Heidelberg), not folded filters, perfectly washed with boiling water, finally by suction, carefully removed from the paper without injuring it, and then completely dried in a capacious porcelain capsule at the heat of the water-bath and with stirring.

For opening up silicates use a large thick-sided platinum crucible, of 52 to 53 millimetres in height, 45 millimetres in width at the top, and weighing, together with its cover, 72 grammes. We thus obtain better melts, and most completely avoid the volatilisation of traces of alkali.

For effecting the fusion we put into the crucible from ten to twelve times the quantity of dry lead carbonate, add the very finely pulverised and air-dried specimen (which has been weighed in a small tube), and mix thoroughly with a glass rod, and heat the whole—under cover, at first gradually, approaching the crucible with a flame of an inch in height for about fifteen to twenty minutes, whereby the greater part of the carbonic acid escapes ; it is then more strongly heated to fusion at redness, but only about one-third of the height of the crucible must be actually red-hot. It is remarked that if the silicate contains organic matter, this must be first destroyed by gentle ignition before admixture with lead carbonate. It is also stated that the platinum crucible is less attacked than by a fusion with sodium carbonate or an alkaline hydrosulphate.

Care must be taken to use a thoroughly non-luminous flame, so as completely to obviate any action of reducing gases upon the contents of the crucible. After fusion for ten to fifteen minutes the crucible, as glowing hot as possible, is plunged into cold distilled water, displacing the cover of the crucible by the tongs as little as possible. To prevent the projection of any small particles of the melt, with the aid of tapping the bottom of the crucible and gentle pressure of the sides, the cake is caused to fall into a large flat Berlin capsule, corresponding quantities of pure concentrated nitric acid and hot water are added, and the whole is evaporated down on the water-bath, continually comminuting all the fragments of the melt as they are gradually disintegrated and softened, until there remain at last only light-coloured flocks of silica floating in the liquid. In the meantime, the residue of the melt, which forms only a slight coating in the crucible, is placed, along with water and some strong nitric acid, on a boiling-water bath, and, after a short time, the solution obtained, including some silica, can be mixed with the chief quantity. The saline mass, after being sharply dried on the water-bath, is again moistened with at least 20 to 25 cubic centimetres of concentrated nitric acid, and again evaporated down until as dry as dust. This residue, when cold, is moistened with 10 cubic centimetres of concentrated nitric acid, allowed to stand at rest for ten minutes, and then mixed

with from 750 to 1000 cubic centimetres of water, heated for fifteen minutes on the water-bath, and filtered from the silica, which is finally most carefully washed with boiling water, to which at first a little nitric acid is added.

The filtrate from the silica is mixed in the cold with a large excess of concentrated hydrochloric acid, in order to separate the bulk of the lead as a chloride, which, after subsidence, is then filtered by suction and washed with cold hydrochloric acid (1 volume concentrated acid and 1 volume water). This filtrate is again evaporated to dryness in a capacious capsule, especially for the complete expulsion of any free nitric acid. The residue is mixed with 30 cubic centimetres of dilute hydrochloric acid (1 : 4), and as much water, heated on the water-bath for fifteen minutes and allowed to cool, when any residual traces of lead chloride are collected upon a very permeable filter, and quickly washed with cold water. The resulting filtrate now contains unimportant quantities of lead, which are finally quantitatively precipitated with hydrogen sulphide. To this end the gas is first introduced in the cold; it is then heated for some time until the lead sulphide has settled, and the liquid is finally allowed to cool in a current of sulphuretted hydrogen.

The precipitate, which is generally slight, is filtered off and washed with warm water, to which fresh sulphuretted hydrogen water is constantly added. Above all, care must be taken that the precipitation of the lead is really complete, as otherwise the further course of the analysis will be disturbed in the most troublesome manner, and inaccurate results will be obtained.

Then from the filtrate free from lead all hydrogen sulphide must be removed, by concentrating the solution before the iron is oxidised, by means of nitric acid or hydrogen peroxide, on undertaking the general procedure for separating iron, alumina, manganese, lime, magnesia, potash, and soda.

By Fusion with Bismuth Subnitrate.—W. Hempel in conjunction with Dr. Koch has made a number of experiments with this agent, and found it very difficult to prepare a chemically pure lead oxide. The red lead and the litharge of commerce were found always to contain silica along with other impurities. The preparation of chemically pure lead oxide from metallic lead by dissolving it in nitric acid and igniting the nitrate thus formed, involves great mechanical difficulties, since the lead nitrate melts before decomposing, and froths strongly, so that small quantities only can be obtained in each operation. All these difficulties are overcome by substituting bismuth oxide for lead oxide, simply igniting the silicate in question with bismuth subnitrate.

This compound is easily obtained in a state of the utmost chemical purity, and it has the further advantage that it does not melt at its temperature of decomposition. The opening up can be performed

in the smallest platinum crucibles, as the hyponitric acid liberated fumes slowly away and does not carry with it any of the substance. The resulting melt is dissolved in hydrochloric acid, while in the lead process nitric acid is required, which must be afterwards expelled.

Repeated experiments have shown that it is advisable to work with a large excess of bismuth oxide, so as to have a very basic melt, which is easily decomposed by means of hydrochloric acid. The operation succeeds easily if ½ gramme of a silicate is heated gently with 10 grammes of bismuth subnitrate till red fumes no longer escape, and is finally kept in fusion for about ten minutes. The melt is poured as far as possible while still liquid into a platinum capsule floating upon cold water, and the mass thus obtained and the crucible are treated with concentrated hydrochloric acid. The resulting solution is evaporated to dryness for the elimination of silica; the residue is taken up with hydrochloric acid; the silica filtered off and washed with water acidulated with hydrochloric acid.

On diluting the filtrate with water the greater part of the bismuth is precipitated as oxychloride. It is filtered off, washed, and from this second filtrate the remainder of the bismuth is precipitated by means of sulphuretted hydrogen. The further treatment of the filtrate is effected in the ordinary manner.

In order to throw a light upon a possible error due to the volatilisation of the alkalies at the melting temperature of bismuth oxide, a felspar was decomposed by this method, and by the hydrofluoric process. The results were:—

With bismuth—

Potash	7·60, 7·70
Soda	4·71, 4·72

With hydrofluoric acid—

Potash	7·86, 7·77
Soda	4·70, 4·84

The operation can be safely conducted in a platinum crucible if care be taken that it is not in a reducing atmosphere. If reducing gases are present, metallic bismuth is formed, which destroys the crucible. Silicates which contain organic matter must first be ignited with access of air. A number of meltings have been performed in the same crucible, which suffered no injury.

As bismuth is a costly metal, it is prudent to work up all the precipitates into subnitrate. This may be conveniently done by melting the residues and the filters along with soda in a Hessian crucible, dissolving in nitric acid the metallic bismuth thus obtained, and precipitating the solution with water as a basic nitrate.

The decomposition of silicates should be effected under a draught-hood, as the bismuth oxidises slightly at the melting-point, and the vapours seem to be very poisonous.

Separation of Silica in the Analysis of Limestones, Iron Ores, &c.—(*A*) The mineral is decomposed by hydrochloric acid, evaporated to dryness, and then treated with hydrochloric acid and water. Silica in the insoluble condition, and the bases as soluble chlorides, are thus obtained, and these are separated by filtration.

Many silicates, however, do not yield to this treatment, prominent among them being clay. This aluminium silicate is hardly ever absent as a more or less intimate admixture in such samples of limestones, iron, and manganese ores, and other minerals, as are used for manufacturing processes. Consequently, if silica be present in the form of clay, or any other non-decomposable silicate, the insoluble residue referred to above is not pure silica, but contains alumina or other bodies.

(*B*) Dr. Percy, in the analyses of British iron ores which were made in his laboratory, and are given in his *Metallurgy of Iron*, examined separately the soluble and the insoluble part of the samples. On referring to these tables, it will be found that the insoluble residue is, with one exception, never pure silica, but contains alumina, and generally other bases. If the quantity of insoluble substance be small, say below 2 per cent., and iron and certain rarer bodies are known to be absent, we may safely, unless absolute accuracy is required, treat it with hydrofluoric and sulphuric acids, ignite, and assume the difference to be silica, the residue being alumina. If the appearance of the insoluble matter be that of pure quartz, we may take it to be all silica.

(*C*) For more accurate analysis, however, and when the insoluble residue is considerable in quantity, either the whole of the sample under treatment, or the insoluble part, must be fused with sodium carbonate, or some other basic flux, in order to obtain a more basic compound, which is readily decomposed by hydrochloric acid. This way of proceeding has two drawbacks, which, whenever possible, are eschewed by the analyst, viz. considerable expenditure of time, and the introduction of a large quantity of foreign matter into the substance under examination.

(*D*) H. Rocholl proposes to utilise as flux the bases present in the mineral itself. He prepares by mere ignition, a basic silicate decomposable by hydrochloric acid.

As regards *limestones*, specimens have been successfully treated containing up to 21·2 per cent. silica and 6·5 alumina, care being taken to prove the purity of the silica obtained. In this case the same portion of the finely powdered sample which has served for the estimation of water and carbonic acid by ignition in a platinum crucible is utilised. It is transferred into a dry basin, and carefully treated with

a little water; the lime left in the crucible is then washed into the basin with water and hydrochloric acid, and more acid is added until solution has taken place. The evaporation to dryness is then quickly effected, as only small quantities of liquid have to be employed. The silica obtained is perfectly pure.

(*E*) For the analysis of *ores* a somewhat more circuitous procedure is necessary, as the sample after ignition has to be re-weighed and re-powdered. Weigh out into a tared platinum crucible a quantity of the finely powdered sample, something more than what is required for actual analysis: then ignite, at first gently, afterwards for about twenty minutes, to nearly a white heat, either in a good muffle or within a clay jacket over a strong blowpipe flame. An incipient fusion should take place. Weigh and carefully detach as much as possible from the crucible: this will be effected easily if the substance before ignition had been pressed into one corner of the crucible, and not spread over the bottom. The mass will be found exceedingly hard, and is best treated by being at first roughly powdered in a steel mortar and then finished in an agate or Wedgwood mortar.

In weighing out a portion for analysis, an allowance may be made in proportion to the loss sustained in the ignition, so that subsequently calculations may be made on the weight usually taken for analysis. The powder is then digested in a porcelain dish with strong hydrochloric acid. If the treatment has been successful, a clear jelly or solution will readily form, and the analysis can be proceeded with in the ordinary way.

(*F*) The ignited silica may still contain certain impurities in small quantities. Titanic acid has to be looked for in certain iron ores, and barium sulphate in manganiferous ores; indeed, H. Rocholl says he has met with a red hæmatite which contained 19 per cent. of the latter body. It is advisable, in the presence of baryta, to precipitate it completely as sulphate before filtering the silica. The ignited residue, on treatment with hydrofluoric and sulphuric acids, will leave the whole of it, the difference being silica. The residue may be examined for titanic acid by the known methods.

The applicability of this method is limited by the percentage of silica. It was successful with ores containing up to 25 per cent. silica, but not with an ore containing 31 per cent. The latter was a magnetic ore, containing 41 per cent. of iron; the gangue consisted of quartz, greenstone, and garnet. In order to try if the want of success was merely owing to the excessive amount of silica, and not to the nature of the compounds in which it occurred, to a fresh portion 50 per cent. of ferric oxide was added, so bringing the silica down to about 21 per cent. After ignition, a mass was obtained which was readily decomposed, even in rough lumps.

Calcined Cleveland ore, a very heterogeneous mixture of numerous compounds, which does not even yield the whole of its iron to hydro-

chloric acid, is readily decomposed after semi-fusion of the finely powdered sample.

The platinum crucible, after use, is best cleaned by fusing some sodium carbonate in it. Although hydrochloric acid slowly dissolves whatever adheres to the sides, its use is better avoided on account of the possible presence of manganese.

The idea of letting the base contained in the mineral act as a flux for its impurities seems so readily to suggest itself, that other chemists may have been employing it, particularly for limestones, where its advantages are greatest.

Estimation of Ferrous Oxide in Silicates.—(*A*) W. Earl proceeds as follows:—

About 2 grammes of the finely powdered mineral are placed in a deep platinum crucible, and 40 c.c. of hydrofluoric acid (containing about 20 per cent.) are added. The whole is heated to near the boiling-point, and occasionally stirred with a platinum wire until the disintegration of the silicate is complete, which usually takes place in about ten minutes. Ten c.c. of sulphuric acid diluted with an equal volume of water are now added, and the heat is continued for a few minutes. The crucible and its contents are then quickly cooled, diluted with water which has been freed from oxygen by previous boiling, and the ferrous salt present is estimated by titration with potassium permanganate or bichromate.

It may be remarked that hydrofluoric acid which has been prepared in a leaden vessel invariably contains sulphurous acid. In order to render such acid fit for use, potassium permanganate must be added until the colour just ceases to be discharged.

In the analysis of a large number of trap-rocks, it was found that in every case a far larger percentage of ferrous oxide was obtained by dissolving the mineral in hydrofluoric acid than by fluxing it with sodium and potassium carbonate.

Thus, in the analysis of a trap-rock which contained 1·2 per cent. of manganous oxide, 5·73 per cent. of ferrous oxide was obtained by solution in hydrofluoric acid, whereas the method of fluxing only yielded 1·3 per cent.

(*B*) W. Knop gives the following method for separating the alkalies in silicates from ferric oxide, alumina, lime, and magnesia.

If in dissolving a siliceous mineral we employ a mixture of $\frac{1}{3}$ fuming hydrochloric acid and $\frac{2}{3}$ hydrofluoric acid, everything dissolves during evaporation to a clear liquid, but on further concentration hydrochloric acid escapes, and the alkaline silicofluorides reappear along with the iron, aluminium, calcium, and magnesium chlorides.

If a silicate contains a quantity of silica equal to its proportion of alkaline metals, or if, supposing the silica to be insufficient or totally wanting, we dissolve the substance in 10 to 20 c.c. of water and a few c.c. of hydrochloric acid, and add a corresponding quantity of silica, we

can convert its alkaline metals completely into silicofluorides, by adding the requisite quantity of fuming hydrofluoric acid and evaporating.

The alkaline silicofluorides are entirely insoluble in a mixture of ether and absolute alcohol strongly acidified with hydrochloric acid. Hence the alkaline silicofluorides may be precipitated from a hydrochloric solution in the form of a crystalline deposit by the addition of ether and absolute alcohol. But if the hydrochloric solution contains also iron, aluminium, calcium, and magnesium chlorides, the alkaline silicofluorides are deposited, not in a pure state, but in combination with small quantities of the above-mentioned metals, the bulk of which, however, remain in solution as chlorides.

The process is carried out as follows :—The weighed substance is mixed in a platinum crucible with a few c.c. of water, and in case of need with a corresponding quantity of silica. A sufficiency of hydrofluoric acid is then added and all the liquid is evaporated off. The dry residue is covered with 2 to 3 c.c. of fuming hydrochloric acid, when it is readily detached from the crucible. It is washed into a beaker by means of an alcohol washing-bottle, using 25 or at most 50 c.c. of absolute alcohol for washing out the crucible ; the acid liquid is allowed to act for some time upon the precipitate. 100 c.c. of ether are then added, and the whole is allowed to stand for twelve hours.

The ethereal liquid is poured off from the precipitate, and the alkaline silicofluorides are brought upon a filter by means of an alcohol washing-bottle. The use of a feather is admissible only at the beginning ; a glass rod is objectionable because it makes the precipitate adhere again to the inside of the glass. The precipitate may be transferred easily if the beaker is held in a sloping position over the filter, and a few c.c. of alcohol are ejected behind the precipitate so as to wash it into the filter.

The filter is then washed slightly with alcohol, so as to remove the ether ; it is then dried, the precipitate removed, the paper is burnt completely in a platinum capsule ; the precipitate is added to the ash, mixed with concentrated sulphuric acid, allowed to stand for some time until the silicofluoric acid has chiefly escaped, and then ignited so long and at so low a temperature that the alkalies may remain behind as acid sulphates and be unable to react upon the silica liberated.

The residue in the capsule is drenched with 10 to 20 c.c. of ammonia and evaporated to dryness, or at least to a paste-like condition. The mass takes again an acid condition by the loss of ammonia, and strong ammonia is therefore added drop by drop until the reaction is again alkaline. The mixture is then allowed to stand for an hour to allow of the complete separation of the ferric oxide and the alumina. Upon the pasty mass is then poured about 20 c.c. of a solution of ammonium monocarbonate (prepared by mixing 180 c.c. of ammonia, sp. gr. 0·92, with 230 grammes of ammonium sesquicarbonate and

water enough to make up 1 litre), and allowed to stand for twelve hours in the covered platinum capsule.

The quantities of ferric oxide, alumina, lime, and magnesia thus separated are so slight that the entire precipitate may be collected upon a very small filter. It is washed with the smallest possible quantity of the above-mentioned ammonium carbonate.

The filtrate is now exposed first for some time to a very gentle heat, a quantity of ammonium bitartrate corresponding to the ammonium sulphate present in the solution is added, the liquid is evaporated to dryness, and the residue is heated for some time in the air-bath to a temperature above 100°. The object of adding ammonium bitartrate is to prevent spirting during the ignition of the ammonium sulphate. The residue is ignited till perfectly white, and weighed. It is then redissolved in hot water, mixed with 2 to 3 drops of the solution of ammonium monocarbonate, and set aside to see if any further deposit of iron oxide and alumina takes place.

If this is the case the liquid is again evaporated to dryness. These supplemental deposits generally attach themselves so firmly to the platinum that a clear solution is obtained on drenching the residue with 10 to 20 c.c. of boiling water. This solution is decanted into a second platinum capsule in which the solution is evaporated to dryness and the capsule is again strongly ignited and weighed. It is recommended to add a few drops of sulphuric acid during the second evaporation.

Separation of Crystalline Silicic Acid, especially Quartz, when mixed with Silicates.—E. Laufer takes advantage of the property of phosphorous salt to dissolve metallic oxides at a melting heat, and to isolate silicic acid from silicates without attacking quartz. To the finely powdered material weighed in a platinum capsule, phosphorous salt is added in a larger quantity than is required for the solution of the silicates supposed to be present, the crucible not being more than half full. It is gradually and cautiously heated in the air-bath, then melted, the heat being finally urged with the blast till the mixture is in tranquil fusion. The cold mass is easily separated from the crucible, and is then boiled for a length of time with dilute hydrochloric acid, washed by decantation, and filtered, the silicic acid being then extracted from the residue with boiling soda.

Separation of Silicic Acid from Tungstic Acid

H. L. Wells and F. J. Metzger [1] have examined the action of hydrofluoric acid on tungstic acid in the presence of silicic acid; as Herting's statement throws doubt upon the method that is generally used, they dissolved some of Kahlbaum's tungstic acid in ammonia, precipitated with nitric acid, washed with water by decantation, digested repeatedly

[1] *Chemical News*, July 5, 1901.

with sulphuric acid of sp. gr. 1·378 to separate any molybdic acid that might possibly be present, washed the residue, and ignited it. The tungstic acid thus prepared was used for the experiments that follow.

A weighed quantity of tungstic acid in a platinum crucible was mixed with about an equal quantity of pure silica. The mixture was covered with dilute sulphuric acid, a liberal amount of pure hydrofluoric acid added, the liquid carefully evaporated, and the residue ignited over a Bunsen burner. Then another portion of silica was added, and the operation repeated.

The greatest error found in these experiments was 0·0001 gramme, and they show that the process is perfectly exact under these conditions.

Other experiments showed that long ignition of the mixed tungstic and silicic acids over the Bunsen burner before expelling the silicic acid had absolutely no effect upon the results. It was thought that in the absence of sulphuric acid a loss might occur by the treatment of tungstic acid with hydrofluoric acid, and experiments were made to test this point, no sulphuric acid being used.

In these experiments, the greatest error, 0·0002 gramme, is well within reasonable limits; hence, it is evident that the absence of sulphuric acid has no effect. It is to be noticed that in these cases also, the tungstic acid was ignited by the Bunsen flame only.

Attention should be called to the fact that tungstic acid must not be ignited by means of the blast-lamp, since at the temperature thus produced, it volatilises to a considerable extent. The books of reference do not give proper warning in regard to this matter. The following table gives the results of a series of experiments made by heating some of the substance (which showed no loss of weight over the Bunsen burner) over the blast-lamp in a platinum crucible:—

	Weight of tungsten trioxide. Gramme.	Loss. Gramme.
Taken	0·3007	—
Ignited for two minutes . . .	0·2978	0·0029
„ „ „ again . .	0·2962	0·0016
„ „ „ „ . .	0·2946	0·0016
„ „ „ „ . .	0·2932	0·0014
„ „ „ „ . .	0·2924	0·0008
„ „ „ „ . .	0·2916	0·0008
„ „ „ „ . .	0·2906	0·0010
„ five „ „ . .	0·2872	0·0034
Total loss . . .		0·0135

All the ignitions except the last were made with a lamp provided with a water-blast, which gave a flame of only moderate power. The last ignition was made with a lamp connected with a foot bellows, which gave a considerably higher temperature. It is noticeable that the losses show a tendency to diminish after the first ignition, but this is probably due to a change in the physical condition of the oxide rather

than to the removal of some more volatile substance. It is hardly possible that our carefully purified tungstic acid, which showed no loss when heated with a good Bunsen burner, could contain an amount of molybdic acid or other volatile substance sufficient to give the results that have been obtained. The loss shown in the table above amounts to nearly 5 per cent., while in another experiment 0·1955 gramme of tungstic acid lost over 7 per cent. after heating with the blast-lamp for twenty minutes. It should be stated that the platinum crucible in which these ignitions were made showed no loss in weight after it had been cleaned.

The authors have thus shown that Herting's criticism of the usual method for separating silicic and tungstic acids is without foundation, and it appears probable that his difficulties were due to igniting tungstic acid at a too elevated temperature.

CHAPTER XIII

ELECTROLYTIC ANALYSIS, GAS ANALYSIS

ELECTROLYTIC ANALYSIS[1]

For measuring the strength of an electric current, the spring galvanometer of Kohlrausch is especially adapted. In the laboratory of the Technical High School at Aix-la-Chapelle, instruments are used with a scale graduated from 0 to 2 ampères, enabling the subdivisions of the ampère to be read off.

Hitherto most chemists who have been engaged in electrolytic work have expressed the strength of currents in chemical terms, *i.e.* in c.c. of detonating gas; and for measurement, they have made almost exclusive use of the voltameter.

It is a known fact that the detonating-gas voltameter is quite useless for scientific measurements, because among other things it requires for itself a considerable tension which, under some circumstances, may be much greater than that required for the experiment. Comparable results with detonating-gas voltameters are possible only when the platinum plates are both the same size and are placed at equal distances from each other, and when the concentration of the acid is the same.

Further, the statements hitherto to be found in the literature of the subject relate exclusively to the measurement of the current before the introduction of the decomposition-cell, and not to a simultaneous introduction into the circuit of the voltameter (or galvanometer) and the decomposition-cell. If, in my experimental work described below, I have retained this manner of measuring the strength of the current, it has been done on account of its simple execution, and especially as a knowledge of the strength of the current obtained as above is fully sufficient for the purposes of quantitative analysis. As it will appear below, for the performance of a quantitative determination or separation, a *quite definite* strength of current is not required; it always fluctuates within certain limits, so that in the majority of methods of

[1] The contents of this section, on Electrolytic Analysis, are taken from the German edition of Dr. Alexander Classen's *Quantitative Chemical Analyses by Electrolysis*, by kind permission of the author.

determination several c.c. of detonating gas more or less per minute is not of importance. It is only thus possible for electrolytic analyses to be effected without further difficulties.

The indications of strength of currents given below are, of course, trustworthy, only on the assumption that the repetition of the experiments takes place under conditions as similar as possible (equal size and shape of the electrodes, equal respective distances, approximate concentration, &c.).

If we wish to be independent of the shape of the electrodes, in addition to knowing the strength of the current, a knowledge is required of its *density* (*i.e.* the proportion of the strength of current to the polar surface on which the electrolysis takes place). If we call the density of the current D, the strength of the current I, and the polar surface of the electrode on which the metal is to be precipitated O, then $D = \frac{I}{O}$. In this case the surface O must be approximately determined. If we always use one and the same form of electrode, *e.g.* a platinum capsule as a negative electrode, it is convenient to know its surface, on filling it with liquid up to different heights.

For the platinum capsule here figured and described below, there exists the following approximate proportion between surface (expressed in square centimetres) and contents (given in c.c.).

Surface. square cm.	Contents. c.c.	Surface. square cm.	Contents. c.c.
63	50	113	150
92	100	124	175

In the laboratory of the Munich High School, the proportion of the strength of current to the surface of the electrodes has been determined for a number of metals. The normal density of current to be used in each case is indicated as $N.D_{100}$, referred to 100 square centimetres of the polar surface upon which the metal is to be precipitated.

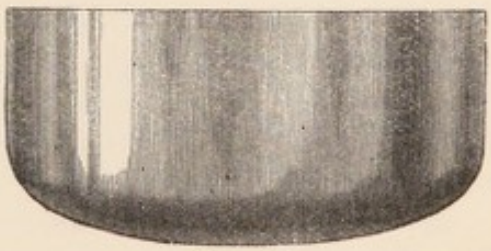


FIG. 30.

For a surface of the size O, the corresponding strength of current can be derived from the formula, $I = (N.D_{100})\frac{O}{100}$.

If, *e.g.*, for the separation of iron from a solution of the ammonium double oxalate $N.D_{100} = 0{\cdot}5$ ampère, then, if O = 180 square centimetres, the strength of the current in ampères $= 0{\cdot}5 \times \frac{180}{100} = 0{\cdot}9$.

All the statements of the Munich laboratory refer, of course, to a simultaneous introduction of the ammeter and the decomposition-cell into the circuit.

The Performance of the Analysis

The performance of a quantitative analysis by electrolysis demands, above all things, the utmost cleanliness. As little as it is possible in galvano-plastic to produce any metallic coating upon an object if the latter before immersion in the bath has not been most carefully cleaned, just as little can we carry out successfully a quantitative electrolysis if the metallic surface serving as cathode has not been previously rendered faultlessly clean and free from grease. The same precaution extends also to the metallic contacts of the elements, to the supports used in the introduction of the current, as otherwise an interruption or enfeebling of the current is unavoidable.

From the nature of the case, it appears advantageous to make the surface of the cathode as large as possible, so that the metal deposited may adhere the better. If any metal separates from a solvent in a dense form—as is the case in the electrolysis of double oxalates—the increased possibility of oxidation of the metal by an enlargement of the cathode is unimportant.

In the deposition of peroxides (*i.e.* lead or manganese peroxide), which altogether adhere badly, the size of the electrodes upon which the deposition is to take place plays a great part.

To use platinum crucibles for electrolytic deposition is therefore admissible only where it is required to separate a few milligrammes, since, independently of the small surface of the cathode, the distance of the two electrodes from each other is not sufficient to allow of the separation of the metal in a dense form.

On this account I use as negative electrode a platinum capsule (fig. 30) wrought out thin, about 35 to 37 grammes in weight, of 9 cm. in diameter, 4·2 cm. deep, and containing about 200 c.c. The capsule is shown in the figure, half its true size. Capsules which in the course of time have become rough internally, scratched, or bent, cannot be used for electrolysis.

Several metals are not deposited as well in hammered capsules as in such as are smooth and polished on the lathe. If, *e.g.*, we use hammered capsules for the reduction of zinc from the double oxalate, there remains, after dissolving the zinc in acid, always a grey shade of platinum black, which cannot be readily removed even by melting potassium hydrosulphate, and interferes with future determinations in the capsule. On the latter account it is recommended to use for electrolysis capsules which are polished faultlessly smooth, and which are, above all things, thoroughly clean, and to reserve them exclusively for the purpose in question.

As anode or positive electrode, I use moderately thick sheet platinum of about 4·5 cm. in diameter, which is fixed conductively to a rather stout platinum wire. It is desirable, in order, during the

electrolysis to facilitate intermixture of the solution, to perforate the sheet platinum by means of a cork-borer. If this is omitted, it is found that by the union of a number of small gas-bubbles a larger bubble is formed beneath the anode, and bursts at the edge of the capsule, projecting out a certain quantity of the solution, which may possibly occasion slight losses.

More recently I have used a positive electrode of the shape of the platinum capsule shown in fig. 31, 50 mm. in diameter and 20 mm. in depth. In order to secure a better circulation of the liquid and a more expeditious reduction, the electrode is perforated in five places. This form of electrode is especially suited for the determination of those



Fig. 31.

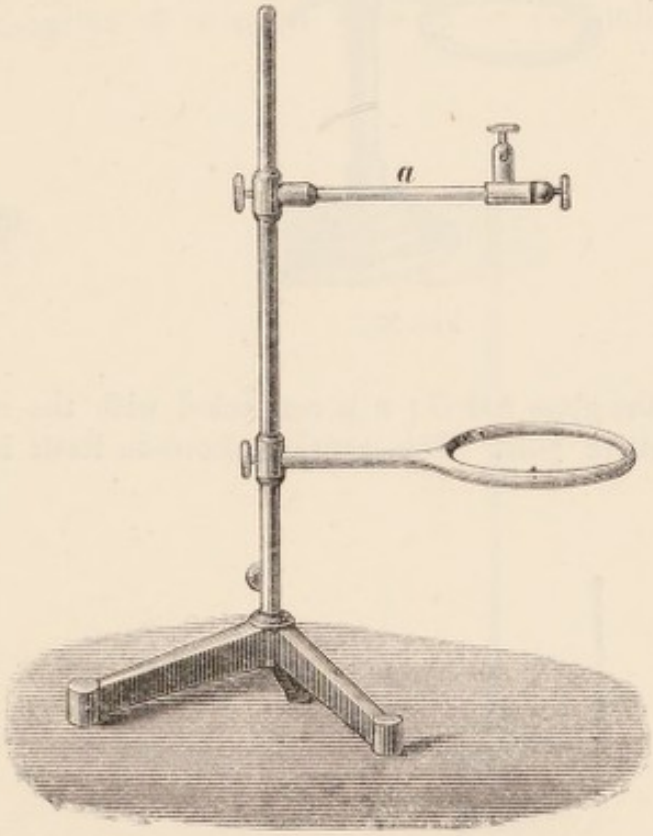


Fig. 32.

metals which, under certain conditions, are disposed to deposit in a spongy form, as, for instance, cadmium and bismuth.

For the reception of the anode and cathode there were formerly used, as suggested elsewhere, two special supports. I have combined these into a single stand (fig. 32) which is provided with a metal ring for receiving the platinum capsule, and to which there are riveted three short contact rods of platinum, and an insulated arm, *a*, of glass intended to secure the positive electrode.

The use of this stand has, however, the disadvantage that the brass support to which the ring and the glass arm are secured is strongly attacked by the fumes in the laboratory, which may occasion

interruption of contact during electrolysis. For some time the stand (fig. 33) has proved very serviceable. The ring and arm are fixed movably

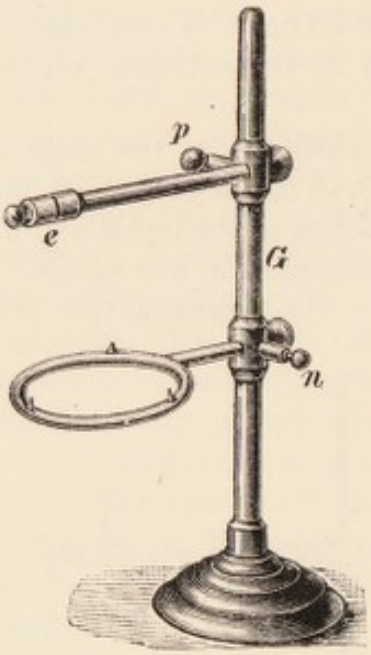


Fig. 33.

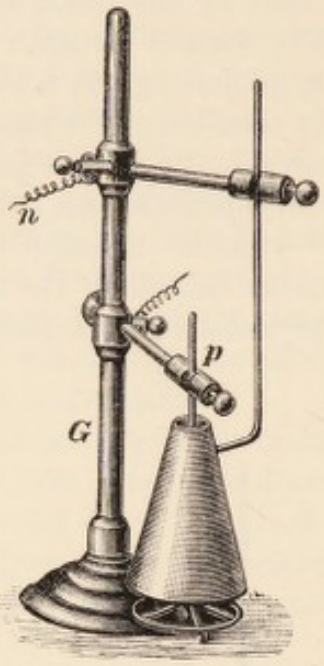


Fig. 34.

to the glass rod G; n is connected with the negative, and p with the positive pole. The positive electrode itself is secured at e. If it is

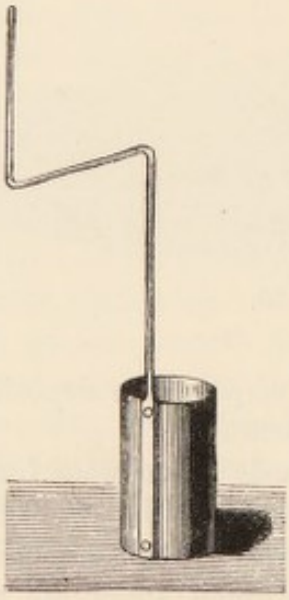


Fig. 35.

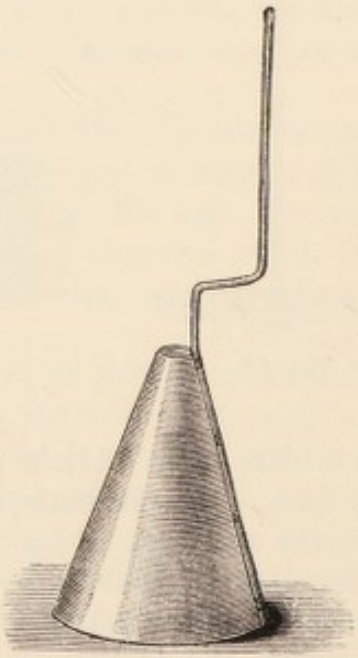


Fig. 36.

desired to use, instead of a platinum capsule, a platinum cone for the separation of a metal, we fix on the glass rod two arms, as is shown in fig. 34.

This arrangement is suitable if it is required to separate metals from acid solutions: the support, with the electrodes, is quickly lifted out of the liquid, immediately immersed in a glass filled with water, and the water is then removed from the negative electrode by washing with alcohol.

If a platinum capsule is used, we may place it upon a metal triangle, and this again upon a beaker; and after the decomposition is completed, the acid may be removed from the capsule by means of a stream of water.

The electrodes proposed by the managers of the mines and furnaces at Mansfeld, and almost exclusively used there for the determination of copper, are shown in figs. 35 to 40. According as larger or smaller quantities of a metal have to be determined,

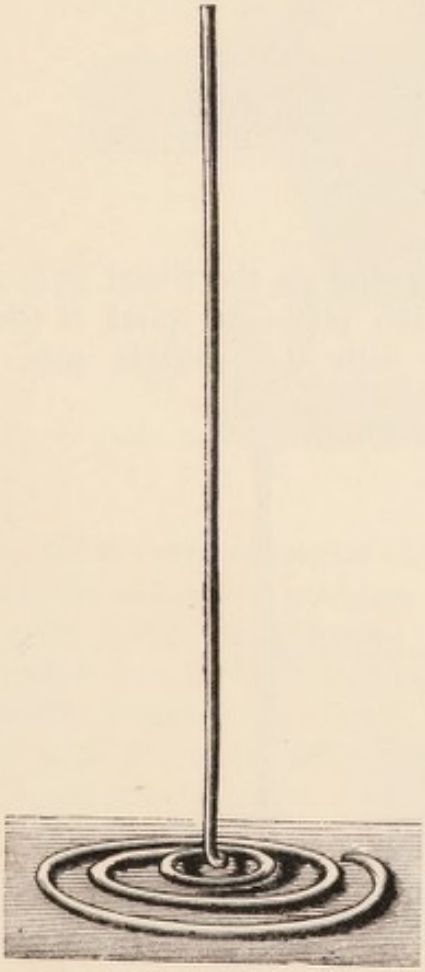


Fig. 37.

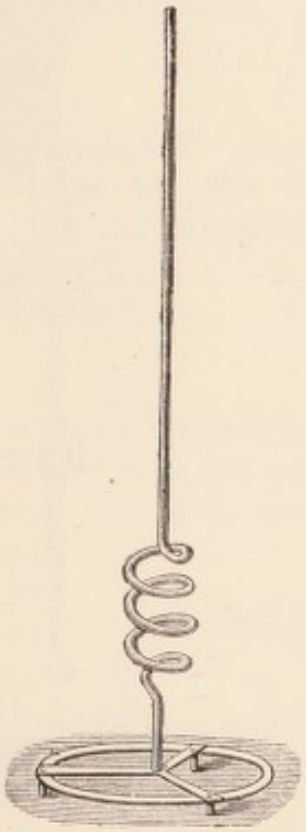


Fig. 38.

there is used either the cylinder of sheet platinum or the conical platinum jacket shown in figs. 35, 36, both one-third their natural size.

As a positive electrode, there is used either a thick platinum wire, coiled spirally as in fig. 37, or the electrode shown in fig. 38.

The arrangement of the several parts, when two stands are used

instead of the support described, can readily be understood from figs. 39 and 40.

Herpin uses, in the execution of electrolyses, the apparatus shown

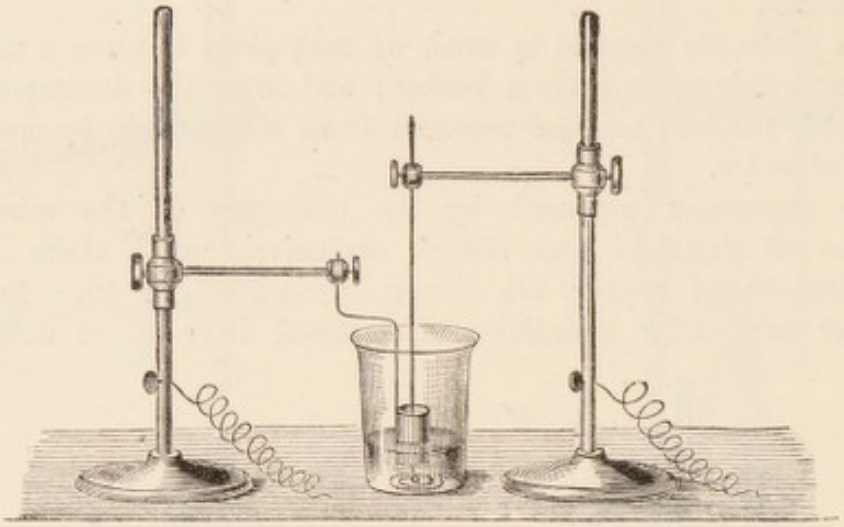


FIG. 39.

in fig. 41. The platinum capsule P, resting on the tripod F, is connected with the negative pole, and the platinum spiral, S (shown separately in fig. 42), is connected with the positive pole. In

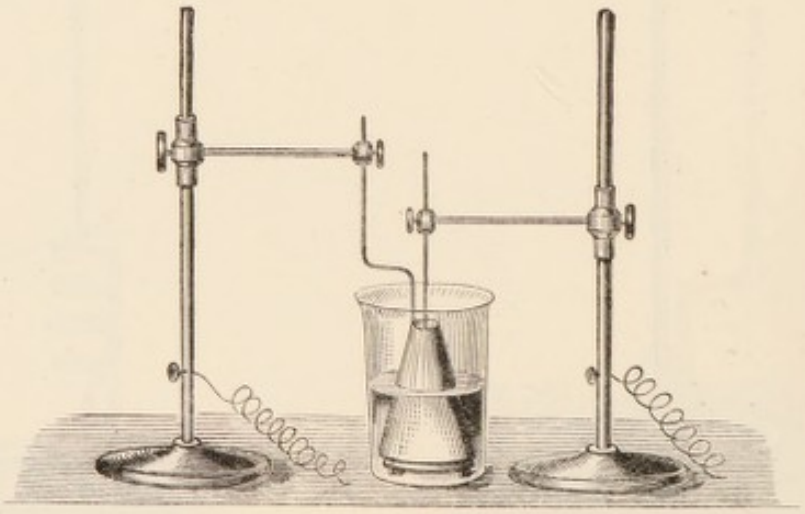


FIG. 40.

order to prevent loss by spirting, the capsule is covered with the glass funnel T.

Riche uses, as a cathode, a platinum cone of the form of a crucible open at both ends and provided with a handle. In order to facilitate a uniform concentration of liquid, longitudinal openings are cut in the cone. It is then immersed in a platinum crucible so that the distance

from the sides is from 2 to 4 mm. The entire arrangement is shown in figs. 43, 44.

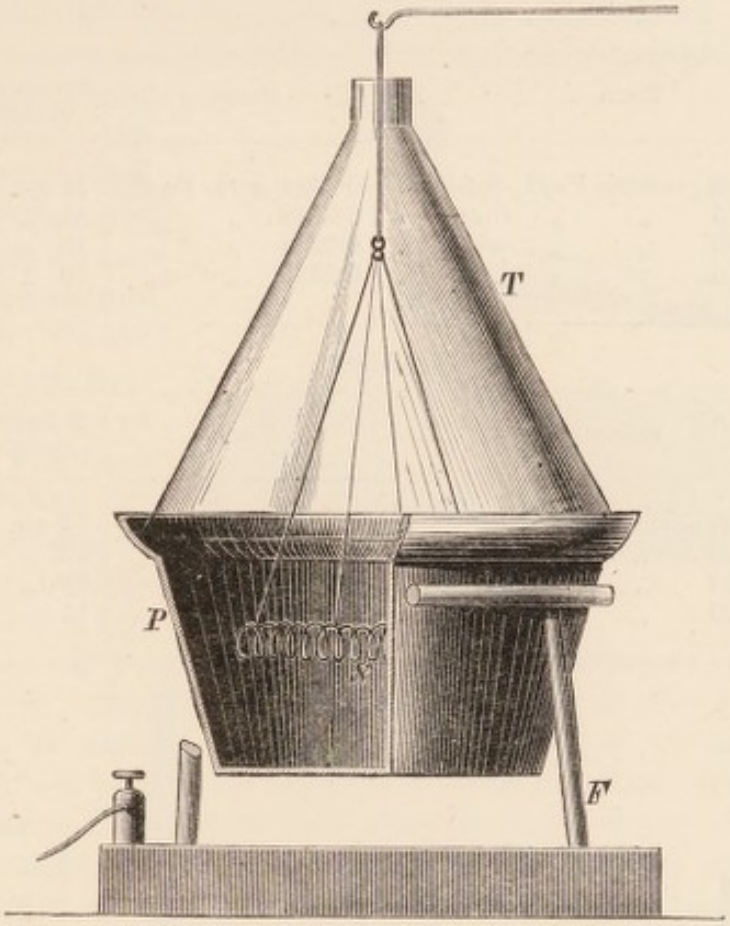


Fig. 41.

As for the performance of electrolysis, sulphates are best adapted for conversion into double oxalates, chlorides are less suitable, and nitrates are quite unfit. If chlorides have been used, and if a smell of chlorine is detected during electrolysis, we must gradually dissolve ammonium oxalate in the liquid until the odour disappears. For forming the double salts, there is used sometimes potassium oxalate, sometimes ammonium oxalate, and sometimes a mixture of both salts.

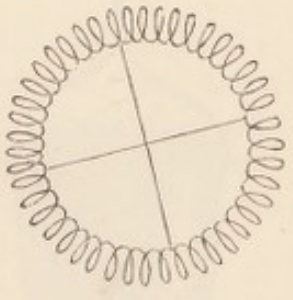


Fig. 42.

As hot liquids conduct the current better, the liquid is often heated before being submitted to electrolysis. In some cases, however, the execution of the process requires a liquid of the ordinary temperature.

For the performance of some determinations and separations it is advisable to heat the liquid to be acted upon continually to a temperature not exceeding 50°. The following experiments show the influence of heat on the duration of the electrolysis. Approximately equal quantities of iron and of nickel were precipitated under closely similar

conditions (strength of current, concentration, &c.), in one case from a solution at about 50°, and in another from a solution at about 15°.

IRON

	Taken	Found	Strength of Current	Time required
				h. m.
I.	0·2385 gramme Fe_2O_3 (cold) .	0·2384 grm. Fe_2O_3	11 c.c. .	4 20
	0·2345 ,, ,, (hot) .	0·2342 ,, ,,	11 ,, .	2 10
II.	0·2246 ,, ,, (cold) .	0·2244 ,, ,,	10 ,, .	4 10
	0·2369 ,, ,, (hot) .	0·2369 ,, ,,	10 ,, .	2 15

NICKEL

	Taken	Found	Strength of Current	Time required
				h. m.
I.	0·2660 gramme Ni (cold) .	0·2660 gramme Ni	13 c.c. .	7 25
	0·2660 ,, ,, (hot) .	0·2659 ,, ,,	13 ,, .	2 20
II.	0·2660 ,, ,, (cold) .	0·2661 ,, ,,	13 ,, .	7 30
	0·2660 ,, ,, (hot) .	0·2660 ,, ,,	13 ,, .	2 20



FIG. 43.

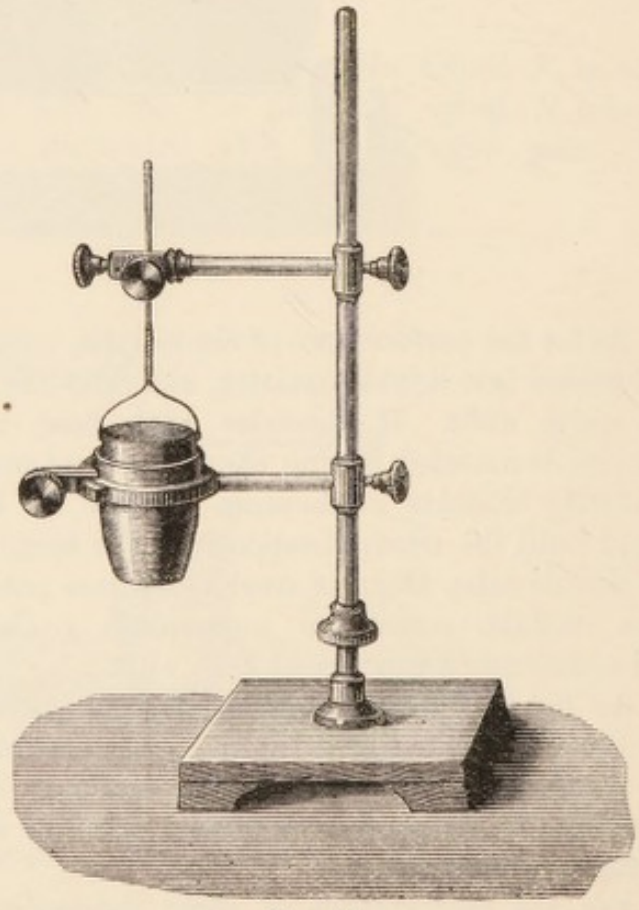


FIG. 44.

From the above experiments, it appears that when using hot solutions the strength of the current may be considerably reduced when an acceleration of the process is not essential.

The instructions here given refer to solutions at the ordinary temperature, unless the contrary is stated.

For heating the liquid to about 50° (the temperature must not, under any circumstances, be raised to that of ebullition, as otherwise the reduced metal would exfoliate from the platinum capsule, and consequently could not be determined) we use burners of the accompanying form. Or the tube of a Bunsen burner may be unscrewed and the luminous gas-flame burning out of the zigzag-shaped cutting is to be reduced to the height of a few mm. and used for heating the liquid. The distance of the capsule from the burner must be about 15 cm. In order to effect a uniform separation of the metal to be reduced, at all points of the capsule, the platinum surface should be uniformly heated. This may best be effected by means of a layer of thin asbestos paper, so cut out that the platinum contacts of the stand supporting the capsule may remain free. The use of asbestos paper also prevents the liquid from reaching ebullition.

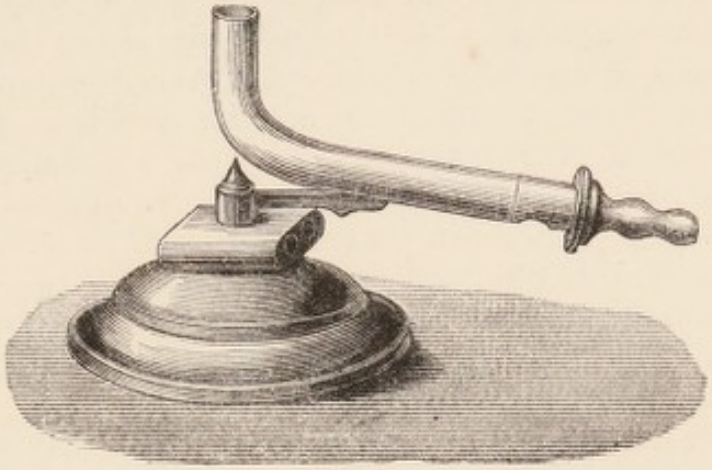


Fig. 45.

On a prolonged action of the current, the evaporation of a small quantity of the liquid cannot be avoided. In consequence, a part of the reduced metal is exposed to the action of watery vapour and air. To avoid the oxidation of the metal thus exposed, we pour from time to time a little water upon the glass covering the capsule, so that the metal is always covered by the liquid.

When the precipitation is completed, the liquid in the capsule is poured, without loss, into a beaker; the capsule is rinsed three times successively with about 5 c.c. of cold water, and then three times with pure absolute alcohol. The capsule is dried for five minutes in the air-bath at 70° to 90°, allowed to cool completely in the desiccator, and its weight is then determined.

Referring to Dr. Classen's work on Electrolytic Analysis, the following notes have been written by Dr. T. O'Connor Sloane:—In Classen's work upon the subject, the voltage of the circuit is duly considered, and an elaborate rheostat for regulating the voltage within somewhat crude limits ($\frac{1}{2}$ volt) is described. This is in one of the introductory chapters. The rheostat is for use with a 600-watt dynamo. But the author also mentions batteries, and describes his method of

conducting determinations with these sources of electromotive force. The current strength is then the standard, and it is determined by the volume of oxyhydrogen gas which the current can liberate in a definite time. In other words, the ampèrage of the current alone receives direct attention. By using the same-sized electrodes, the author states, the conditions are kept sensibly the same. Here we have an indirect recognition of the influence of electromotive force. But the attempted maintenance of the most uniform conditions is a poor reliance. The conditions will inevitably vary, and the temperature of the room and gradual change of the nature of the solution operated on will cause variations in resistance that will affect the difference of potential. To show how little regard is paid to voltage, we are directed in iron determinations to use two and sometimes three Bunsen cells. Any change in the number of cells in series would cause great variations in the voltage, in the case cited about 50 per cent. If the cells were kept in parallel, and any resistance, such as that of a voltameter, were in series with the decomposing apparatus, a great variation in voltage would even then ensue by changes in the number of cells.

The object of these notes is to plead for a greater recognition of the influence of difference of electric potential in analytical work. The facts of the case are these:—For the decomposition of every solution a definite and absolutely fixed voltage is required. The strength of current affects only the condition of the deposit. Thus a current of any number of ampères might be passed through acidulated water without decomposing it until the voltage passed a fixed point, when decomposition would at once begin. A single gravity cell, large or small (sulphate of copper, zinc-copper couple), cannot decompose water because its voltage is too low. The minutest bichromate cell will at once begin to decompose it, because its voltage is high enough.

Again, the ampèrage of the current should not be broadly stated without reference to absolutely fixed conditions of electrodes. The proper way would be to state it as referred to unit area of cathode and anode. Probably the cathode reference would be all that is needed. As ordinarily put, the cathode is supposed to be a platinum dish of more or less definite size, filled with a variable depth of liquid, and the electrolytic gas set free in one or more minutes is given. All this tells nothing.

It would seem obvious that a definite and absolutely fixed difference of potential being required for the decomposition of each compound, the voltage could be made the basis for analytical work. It would be possible to effect successive separation of metals from the same solution by modifying the voltage, starting, of course, with the lowest. How far the precipitation of mixed metals, so-called alloys, would interfere with such attempts is not definitely recorded. It amounts to nothing to state, as is done, that a weaker current than is required for iron or some other metals, will precipitate copper. The strength of the

current has nothing to do with it. It is the difference of potential that affects the result. The varying of such difference corresponding in a general way with the strength of the current, as the operations were conducted, has doubtless occasioned the confusion.

In stating the results of, or giving directions for, conducting electrolytic separations, two factors should always be stated. One is the difference of potential, the other the ampèrage per unit area of cathode. Then something definite would be known. It seems probable that by working on these lines, some exceedingly interesting results in the way of double decompositions, as well as of separations, might be obtained.

Should any such result be obtained as the determining of a series of potential differences available for separations of metals from single solutions, it would be highly interesting. The heat of combination of a vast number of compounds has been obtained and is readily reduced to volts, but such reduction is theoretical and does not accurately hold for all cases. The principal trouble would lie in the regulation of the voltage. But, at the least, there seems ground for research in the direction here suggested.

GAS ANALYSIS [1]

Analysis of a Mixture of Oxygen, Carbonic Acid, and Nitrogen

(*A*) Introduce a portion of the mixture into a graduated tube over mercury, and note accurately the volume.

To estimate the carbonic acid, pass into the tube, by means of a curved pipette, a small quantity of a concentrated solution of potash, and agitate several times until there is no further variation in the level of the liquid; the carbonic acid will be absorbed by the potash. To obtain the volume accurately, transfer the gas to a vessel of water so as to allow the alkali to fall out; then retransfer the gas to another tube and estimate its volume, saturated with moisture.

To estimate the oxygen, first introduce into the tube a concentrated solution of potash, then a little pyrogallic acid. Upon agitation, the oxygen is absorbed, and the nitrogen remains. The bulk of the latter gas may be obtained by taking the same precautions as in the former instance.

After having removed the carbonic acid, phosphorus may also be employed to absorb the oxygen. The experiment may be performed in two ways:—

a. In the Cold.—In the tube containing the gas (over mercury) pass up a long stick of moist phosphorus, the sides of the tube being

[1] These methods are principally founded on instructions given by Drs. Grandeau and Troost.

at the same time moistened. The oxygen combines with the phosphorus, giving phosphorous acid, which dissolves in the water. At the end of an hour the absorption is completed. It may be known by the absence of white fumes on the stick of phosphorus. Remove the latter, dry the gas, and measure its volume ; it will be nitrogen.

b. With Heat.—The analysis is effected much more rapidly in the following manner :—In a curved tube containing the mixture of oxygen and nitrogen standing over water, introduce by means of an iron wire a small piece of phosphorus, so that it rests in the upper curved portion of the tube ; then remove the iron wire and heat the phosphorus, at first carefully, to volatilise the water which remains in the bend of the tube, and then rapidly, so as to inflame the vapour of phosphorus. A greenish flame will be seen to advance, gradually absorbing the oxygen of the air. When it has descended to the level of the liquid it disappears, and the experiment is terminated. Allow it to cool, and estimate the volume of the residual nitrogen.

(*B*) The analysis of a mixture of carbonic acid, oxygen, and nitrogen may be effected with a little more accuracy in the following manner :—The dry mixture being contained in a graduated tube standing over mercury, introduce a piece of caustic potash fixed to the extremity of a platinum wire, and slightly moistened. When the carbonic acid is absorbed, withdraw the piece of potash, and a simple observation gives the residual volume of the mixed oxygen and nitrogen perfectly dry.

The residue is introduced into a mercurial eudiometer. Add to the mixture double its volume of hydrogen, and pass the electric spark. Water will be produced by the combination of the hydrogen and oxygen in the proportion of 2 volumes of the former to 1 volume of the latter. One-third of the diminution in volume, therefore, represents the volume of oxygen. The volume of nitrogen is obtained by difference ; it will be the excess of the original volume of the mixture over the sum of the volumes of oxygen and carbonic acid.

The estimation of oxygen by the eudiometer is not exact unless this gas is present in tolerable quantity in the mixture. If there is only a very small proportion, it is necessary, in order to ensure complete combustion, to take the precaution to introduce into the mixture a sufficiently large quantity of oxyhydrogen gas, obtained by decomposing acidulated water with 3 or 4 Bunsen elements. The gas should be passed through concentrated sulphuric acid in order to dry it.

(*C*) For the estimation of oxygen in the gases escaping from the lead chambers Vogt uses an apparatus by which a known volume of the gas is collected after passing through a solution of potassium chromate and caustic lye contained in Liebig's bulb-tubes. He then adds to the gas a solution of ammonium-ferrous sulphate and ammonia enough to throw down all the ferrous oxide, by which the oxygen of the gaseous mixture is entirely absorbed. Water is then allowed to

re-enter the apparatus, when the quantity absorbed indicates the volume of oxygen which has disappeared. Or the precipitate of oxide may be redissolved in sulphuric acid and titrated with permanganate. The apparatus consists of an aspirator flask filled with water recently boiled. This aspirator is connected with the gas to be examined, and the water is allowed to escape. The apparatus is filled with the gas, which has been previously freed by a passage through the bulb-tubes from all gases except oxygen and nitrogen. There is a tube with a tap fixed to the flask for the introduction of the reagents.

Mixture of Oxygen, Hydrogen, and Nitrogen

(*A*) After having measured the volume of the mixture, absorb the oxygen by potash and pyrogallic acid, or by phosphorus, as already described at page 627.

Pass the remainder into a curved tube over mercury, and introduce into it a piece of compact copper oxide,[1] and heat it for about twenty minutes; all the hydrogen is then absorbed; the residue will be nitrogen; it may be transferred to a graduated tube, and its volume measured.

After the absorption of the oxygen the hydrogen may be estimated by introducing it into the eudiometer with half its volume of oxygen. Two-thirds of the diminution of volume occasioned by the passage of the spark represents the volume of hydrogen. The nitrogen is given by difference.

(*B*) The analysis may also be effected entirely by the eudiometer. Introduce the original mixture into the eudiometer, with twice its volume of hydrogen, and pass the spark. The volume of hydrogen which enters into combination will be two-thirds the diminution of volume, the oxygen being represented by the other third. This first experiment will therefore give the amount of oxygen. In order to ascertain the amount of hydrogen in the mixture, add to the residue of the first explosion half its volume of oxygen, and pass the spark a second time. Two-thirds of the diminution of volume will be hydrogen. The excess of the sum of the volumes of hydrogen burnt in these two experiments over the volume of this gas introduced into the eudiometer represents the volume of hydrogen found in the original mixture. The nitrogen will still be given by difference.

Mixture of Hydrogen, Marsh Gas, and Nitrogen

Introduce the mixture into a mercurial eudiometer, with twice its volume of oxygen, and pass the spark. The free hydrogen and that in the marsh gas combine with the oxygen to form aqueous vapour,

[1] This oxide is prepared by fusing 2 parts of copper oxide with 1 part of lead oxide. The fused mass is run on to a plate of copper, then broken into pieces and preserved in bottles.

which condenses. The carbon becomes carbonic acid. The residue is therefore a mixture of nitrogen, oxygen, and carbonic acid.

Pass these gases into a graduated tube, and after having observed the volume, absorb the carbonic acid with potash. The diminution of volume gives the volume of carbonic acid, which will be equal to the volume of the carburetted hydrogen originally present.

If a little pyrogallic acid is then introduced into the potash, the rest of the oxygen is absorbed, and the volume of nitrogen is obtained as a residue.

The amount of the hydrogen which existed in the free state in the original mixture is obtained by taking the excess of the volume of the original mixture over the sum of the volumes of nitrogen and marsh gas.

Mixture of Sulphuretted Hydrogen, Carbonic Acid, and Nitrogen

(*A*) The mixture is measured into a graduated tube standing over mercury. Introduce a solution of copper sulphate and agitate. The diminution of volume represents the amount of sulphuretted hydrogen present.

(*B*) Bunsen recommends in preference for the absorption of the sulphuretted hydrogen a ball of manganese binoxide impregnated with phosphoric acid. To obtain a ball of manganese binoxide which does not tend by reason of its porosity to absorb other gases besides sulphuretted hydrogen, Bunsen prepares by levigation a fine powder which is formed into a thick paste by a little water. This paste is then pressed into a mould round a platinum wire, the extremity of which is twisted into a spiral. The mould is then dried at a gentle heat, when the ball of binoxide is readily detached; for greater precaution, the sides of the mould may be smeared with a little oil. The ball is then moistened several times with a syrupy solution of phosphoric acid.

The remaining gas, transferred to an appropriate tube, is then submitted to the action of caustic potash, which absorbs the carbonic acid. The residue is nitrogen.

Mixture of Hydrochloric Acid, Sulphuretted Hydrogen, Carbonic Acid, and Nitrogen

When the exact volume of the mixture has been measured in a tube over the mercury, the hydrochloric acid is absorbed by a fragment of hydrated sodium sulphate fixed to the extremity of a platinum wire. To obtain these fragments melt ordinary sodium sulphate in its water of crystallisation, and dip the end of the platinum wire in several times. There adheres to the wire a small lump of the sulphate, which augments in volume with each fresh immersion.

Then remove the sodium sulphate and measure the volume again. The diminution observed will represent the volume of hydrochloric acid gas.

The sulphuretted hydrogen is absorbed by a ball of manganese binoxide soaked in phosphoric acid, and the carbonic acid is afterwards absorbed by potash. The residue gives the nitrogen.

Mixture of Sulphurous Acid, Carbonic Acid, Oxygen, and Nitrogen

(Gas issuing from Craters of Solfataras)

The volume of the mixture being measured dry in a graduated tube over mercury, the sulphurous acid is absorbed by a ball of manganese binoxide impregnated with phosphoric acid. After having removed this ball and noted the diminution of volume, a fragment of potash is introduced to absorb the carbonic acid. The second diminution of volume will give the carbonic acid.

The oxygen can then be absorbed by potash and pyrogallic acid, or it may be estimated eudiometrically, as described at page 629. The nitrogen will remain as residue.

Sulphuretted Hydrogen, Carbonic Acid, Hydrogen, and Nitrogen

(Fumeroles of Volcanoes)

Commence by absorbing the sulphuretted hydrogen by introducing into the mixture a ball of manganese binoxide impregnated with phosphoric acid. The absorption of the carbonic acid is then effected by means of a fragment of moist caustic potash.

The hydrogen is then estimated as at page 629, either by the eudiometer, or by passing the mixture of hydrogen and nitrogen into a curved tube and introducing compact copper oxide into the upper part of the bend. By heating the part of the tube containing this oxide for a quarter of an hour, the complete absorption of the hydrogen is effected. The nitrogen will form the residue.

Carbonic Acid, Carbonic Oxide, Hydrogen, and Nitrogen

(Gas from Blast Furnaces where Wood is used)

(*A*) After having accurately measured the volume of the mixture over mercury, absorb the carbonic acid with a fragment of caustic potash.

Then estimate the carbonic oxide by introducing into the graduated tube a solution of copper subchloride in hydrochloric acid, agitate, and the absorption will be complete.

(*B*) Instead of introducing the liquid itself, it will be better, as Bunsen advises, to introduce a ball of papier-mâché impregnated with this acid solution of copper subchloride.

This experiment should be made over another separate mercurial trough, for the copper subchloride attacks and fouls the mercury.

In withdrawing the ball impregnated with chloride, before reading off the volume, it is necessary to remove the hydrochloric acid vapours given off by the chloride.

The estimation of the hydrogen can then be effected as already described, either by the eudiometer or by absorption with copper oxide. The nitrogen remains as a residue.

Carbonic Acid, Carbonic Oxide, Hydrogen, Marsh Gas, and Nitrogen

(Gas from the Mud of a Pond)

First estimate the carbonic acid by means of potash, then with a ball of papier-mâché introduce into the mixture a concentrated solution of copper subchloride in hydrochloric acid. After the absorption has terminated, withdraw the ball of chloride and replace it by a ball of potash to remove the vapours of hydrochloric acid given off by the acid chloride. If the mixture which contains carbonic oxide also contains oxygen, the latter gas is estimated first by pyrogallic acid and potash. The estimation of the hydrogen and marsh gas is then effected eudiometrically, as already shown at page 629.

Sulphuretted Hydrogen, Carbonic Acid, Carbonic Oxide, Olefiant Gas, Marsh Gas, Hydrogen, and Nitrogen

(Coal Gas)

The mixture is first accurately measured in a graduated tube standing over mercury. The sulphuretted hydrogen is then estimated by means of a ball of manganese binoxide impregnated with phosphoric acid.

After removing the manganese binoxide and measuring the remaining volume, introduce a ball of caustic potash, which absorbs carbonic acid.

The carbonic oxide is estimated by means of acid copper subchloride.

To estimate the olefiant gas introduce into the residue a fragment of coke soaked in a concentrated solution of anhydrous sulphuric acid in monohydrated sulphuric acid. The absorption of the olefiant gas takes place very rapidly; the coke is then withdrawn and the acid vapours absorbed by potash.

The estimation of the hydrogen and marsh gas is then performed as described at page 629. The nitrogen remains as a residue.

The olefiant gas, as well as the marsh gas and the hydrogen, may also be estimated by the eudiometer. To effect this pass the mixture of these three gases and the nitrogen into the eudiometer with three times its volume of oxygen, and pass the spark. The free hydrogen, as well as that of the carburets, combines with oxygen to form water, while the carbon becomes carbonic acid. Then pass the residue of the combustion into a graduated tube, and estimate the carbonic acid with potash, and the excess of oxygen with potash and pyrogallic acid. The residue left after this double absorption gives the nitrogen.

The volumes of olefiant gas, marsh gas, and hydrogen may then be obtained by a simple calculation. The reactions which take place show:—1. That the combustion of olefiant gas requires thrice its volume of oxygen, that of marsh gas double its volume, and that of hydrogen half only. 2. That the olefiant gas produces double its volume of carbonic acid, and the marsh gas its own volume exactly.

Therefore, calling x, y, z the volumes of the olefiant gas, the marsh gas, and the free hydrogen, of which the sum is known and represented by c, we have—

$$\begin{aligned} 3x + 2y + \frac{z}{2} &= a \\ 2x + y &= b \\ x + y + z &= c \end{aligned}$$

a and b are the volumes of oxygen employed, and of the carbonic acid produced—volumes which have been determined by experiment.

To find the values of x, y, and z, subtracting the first equation from the sum of the two others, we find—

$$\frac{z}{2} = c + b - a\,;\ \text{whence}\ z = 2(b + c - a).$$

Then subtracting the last from the second, we find—

$$x - 2(b + c - a) = b - c\,;\ \text{whence}\ x = 3b + c - 2a.$$

The second equation then gives—

$$y = 4a - 5b - 2c.$$

Rapid Analysis of Mixtures of Gases.—In gas works and also in many iron and steel works, it often becomes necessary to make a number of analyses of mixtures of gases daily, which, of course, is only possible with simple apparatus.

(*A*) The earliest and simplest form of apparatus was a tube for the estimation of carbonic acid, very much like an inverted burette, used by C. Stammer.

(*B*) This tube was further modified by F. M. Raoult, who used two stopcocks, one above and the other below; and to the upper stopcock

was attached a funnel, which serves to introduce the chemicals in solution for treating the gas. After treating the gas, Raoult washed out the chemicals used with water introduced through the funnel, and the gas was measured by bringing the tube to a nearly horizontal position and allowing water to run in through the funnel.

(*C*) Wilkinson modified this tube of Raoult by placing it in a wider tube having a stopcock below, and omitting the stopcock upon the lower end of the measuring-tube. By this means he could adjust the pressure upon the gas by adding water to or drawing it from the exterior tube.

But the difficulty with these methods is the necessity of washing out the chemicals used to absorb the various gases. For example, after treating a gas mixture with potassium pyrogallate, it is necessary to wash out all the pyrogallate before adding bromine to absorb the illuminants; otherwise the bromine is absorbed by the alkali before it can act upon the gas.

(*D*) To obviate this difficulty and one or two others, Arthur H. Elliott uses the apparatus shown in fig. 46, next page. The tube A is of about 125 c.c. capacity, while B, although of the same length, holds only 100 c.c. from the mark D, or zero, to the mark on the capillary tube at C, and is carefully graduated into 0·1 c.c. The attachments to these tubes below are seen from the drawing, except that the stopcock I is three-way, with a delivery through its stem. The bottles K and L hold about one pint each. The tubes A and B are connected above with one another and with the funnel M, by capillary tubing about 1 millimetre in internal diameter. There is a stopcock at G and another at F, while the funnel M, holding about 60 c.c., is ground to fit over the end of F above. At E is a piece of rubber tubing uniting the ends of the capillary tubes, which are ground off square to make them fit as close as possible.

In beginning the analysis of a mixture of gases, the stem exit of the three-way cock I is closed by turning it so that L and A are connected through the rubber tubing; the stopcocks F and G are opened, and water is allowed to fill the apparatus from the bottles K and L, which have been previously supplied. When the water rises in the funnel M, and all air-bubbles have been forced out of the tubes, the stopcocks F and G are closed, the funnel M removed, and the tube delivering the gas to be tested attached in its place. By now lowering the bottle L slowly, and simultaneously opening the stopcock F, the tube A is nearly filled with gas, and the stopcock F is closed. The tube delivering the gas is now removed, the funnel M replaced, the bottle L raised, the bottle K lowered, and by opening the stopcock G the gas is transferred to the graduated tube B. By placing the bottle L on a stand at about the level of the water in A, the level in B and in the bottle K can be adjusted to the zero point, and the stopcock G is closed. The excess of gas in A is expelled by opening the stopcock F

and raising the bottle L. The gas remaining in the capillary tube between C and the vertical part is disregarded, or in very careful work it may be measured and an allowance made in not filling the tube B quite to the zero mark, but usually it is too small to be worth notice.

Having measured the gas to be tested, it is now transferred by means of the bottles K and L into the tube A, and the liquid chemicals added by placing them in the funnel M and allowing them to flow down the sides of the tubes slowly, care being taken *never* to let the liquids run below the level of the top of the vertical tube in the funnel. It is best to have a mark on the outside of the funnel at least $\frac{3}{4}$ of an inch above the top of the level of the vertical tube, and never to draw the liquid down below this point.

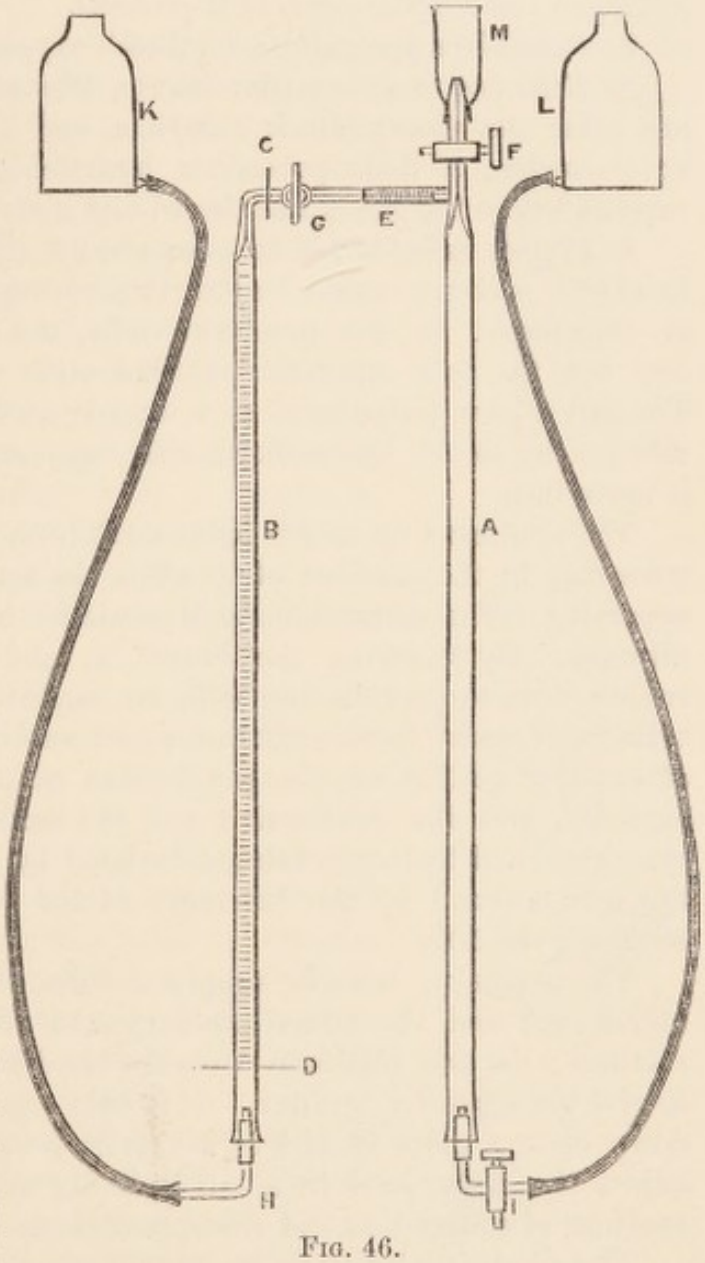


Fig. 46.

Having treated the gas with the reagent, it is transferred by means of the bottles to the tube B, to be measured. If the reagent gets into the horizontal capillary tube, the passage of a little water from the bottle K will remove it, before transferring the gas. When the gas residue is in B, and the liquid in A has been adjusted at the mark C on the horizontal tube, the stopcock G is closed the bottle K is lowered till the level of the water in it and that in the tube B are the same, and the reading is then made. The tube A is now filled with the reagent just used, and water. By turning the stem of the three-way cock I, so that it communicates with A, and also opening the stopcock F, the contents of the tube can be run out, and water run through the funnel M to clean the tube for a new absorption. When the tube is clean, by

turning the stopcock I, so that A and L communicate, the water is forced into A, and the whole is ready to receive the gas for fresh treatment. By this means the gas is removed from the action of the water used to wash out the chemicals, and the chemicals are completely removed from any interference with each other when treating a mixture of gases. In using this apparatus the solutions are added in the following order :—

1. *Potassic hydrate*, to absorb carbonic acid (also sulphuretted hydrogen and sulphurous acid if present).

2. *Potassium pyrogallate*, to absorb oxygen.

3. *Bromine*, to absorb illuminants, like olefiant gas and acetylene ; and after the absorption is complete, and the bromine vapours cause an expansion, a little potassium hydrate is added, to absorb these vapours before the gas is transferred and measured.

4. *Copper subchloride* in concentrated hydrochloric acid solution, to absorb carbonic oxide. After this absorption is complete the gas is transferred to the measuring-tube, the contents of the tube A run out, the tube washed, and filled with water from the bottle L. The gas is now transferred to A, and treated with potassium hydrate solution to absorb hydrochloric acid vapours before the final reading is made in B.

The treatment up to this point takes from twenty to thirty minutes, according to the amount of practice the operator has had with the apparatus. The gas residue still contains marsh gas, hydrogen, and nitrogen. By removing the funnel M, and attaching in its place a rubber tube communicating with an explosion eudiometer in a deep cylinder of water (both eudiometer and rubber tube being drawn full of water) a portion of the gas residue can be mixed with oxygen, exploded, and the contraction and the carbonic acid estimated, the marsh gas and hydrogen being calculated by the usual formula. The nitrogen is found by the difference of the addition of the other constituents and 100.

The explosion tube is simply a tube like A without the lower attachment and the lateral capillary tube above, the funnel M being retained ; the two platinum wires are fused into the glass near the top to give the spark for ignition. It is only necessary to clamp this tube down upon a piece of cork in a vessel of water during explosion, and adjust the water-level in a tall cylinder of water when making the readings of contraction and absorption of carbonic dioxide.

The whole analysis can be readily completed in forty-five minutes, and with due care gives results that are practically correct.

The great advantage of this apparatus over the single tube method is that the gas is not submitted to the action of the water used to wash out the chemicals, which is found to reduce the volume of the illuminants by 2 per cent.

Of course this method will not compare with the methods of

Bunsen and others, where very delicate readings and nice precautions are taken, but it gives very good results for rapid work, and answers every purpose in everyday practice in a gas or metallurgical works.

The water used in the apparatus should be of the same temperature as the room in which the analysis is made, and by careful handling little or no chemicals get into the bottle L.

When working in a warm place the tube B should be surrounded with a water-jacket to prevent change of volume in the gas while under treatment.

(*E*) Thomas M. Morgan has designed an apparatus which is simple in construction, and requires but a small supply of mercury. The eudiometer tube A B (fig. 47) is drawn out at B until it has a diameter of 5 or 6 millimetres; C D, a shorter piece of the same tubing, is sealed on at one side in the manner shown in the figure, and both tubes have corresponding millimetre scales etched upon them. The capacity of the divisions on A B must be known, and can be estimated by Bunsen's method. The same tube has platinum wires at A, and to B a piece of strong caoutchouc tubing is firmly secured and provided with a clamp, E. The apparatus is filled with mercury through F or C; in the former case C must be closed with the cork, in the latter B F is compressed by the clamp E.

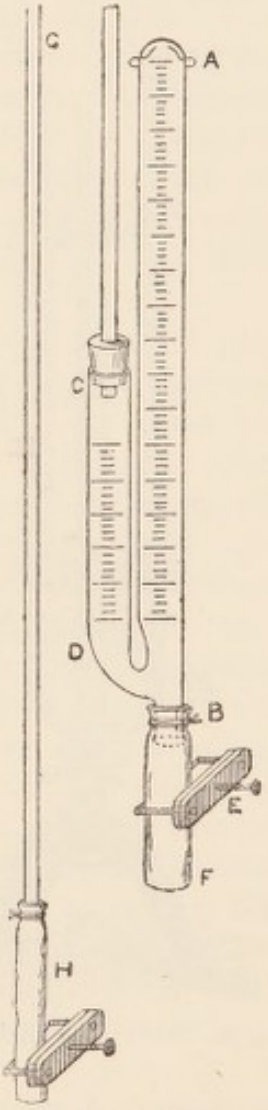


Fig. 47.

If C D be kept closed with a cork, the gas may be introduced by a small funnel at F, when the apparatus is held obliquely over the mercury trough, with C D undermost; or a delivery-tube may pass down C, while E is opened sufficiently to allow the displaced mercury to escape; or should the gas be in a sealed tube, the latter is attached to F, E is opened for the expulsion of enclosed air, and the point is then broken off; if the gas is under pressure its admission may be regulated by stopping the end C with the thumb.

Before measuring, the mercury in the short limb is brought to a proper level by allowing a sufficient quantity to flow out at B; and that a known temperature may be quickly arrived at, the apparatus is placed vertically in a cylinder of water, the short limb being fitted with a long tube as shown in the figure; the volume, temperature, and pressure are then read off.

Any absorbent to which the gas may have to be submitted is placed in the short limb and caused to pass into the long one by allowing mercury to run out below until a sufficient quantity has entered; the

short limb is then filled up with mercury, closed, and by agitation the absorbable constituent is removed, or the apparatus may be allowed to stand the requisite time.

The absorbent is removed by means of a stout glass tube, G H, 1 millimetre internal diameter, and considerably longer than the eudiometer; one end has a strong caoutchouc tube and clamp attached to it; the other, after being rubbed with a little grease, is inserted at F and tied sufficiently tight to prevent escape of mercury, and yet to allow of freedom of motion up and down. By gradually opening the clamp E, the air is carried out of this tube, and it is left filled with mercury. The clamp H is then closed, that at E is opened to its fullest extent, and the tube is thrust up until within 2 millimetres of the absorbent; then, as a slow stream of mercury is allowed to descend, it is alternately raised into the liquid and pulled down below it. Portions of absorbent and mercury thus follow each other down the tube, but it is evident that if a proper proportion of the latter be not drawn in, the current will cease. After one or two trials it is not difficult to leave a meniscus free from liquid; should any of the gas enter, it may be expelled again by quickly compressing the tube at the bottom. In order to obtain the residual gas saturated with aqueous vapour of normal tension, a little pure water may be introduced and removed in the manner described.

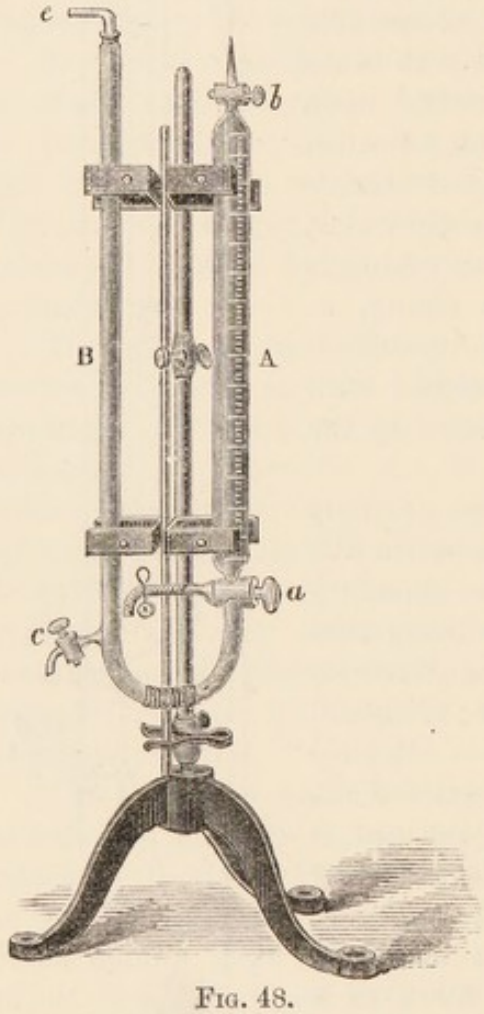


Fig. 48.

An estimation of nitrates and nitrites by Frankland's method may be made in this apparatus, and it can also be used in an organic analysis by Schulze's method.[1]

The apparatus may be strengthened and made more convenient for manipulation by attaching it to a light wooden frame.

(*F*) Clemens Winkler proposes the following apparatus. It consists of a two-limbed tube (fig. 48), one limb of which, A, can be closed air-tight by two slightly greased glass taps, *a* and *b*. This shut-off portion of the tube contains about 100 c.c., and it is once for all

[1] *Watts' Dictionary of Chemistry*, 1st suppl. p. 143.

carefully measured, and the amount inscribed upon the glass. This tube, which we may call the measuring-tube, is graduated from tap to tap into cubic centimetres and decimal parts thereof, the divisions being carried out on the narrower parts of the tube close to the taps. The measuring-tube serves for the reception of the gas in question, and is filled with it by opening both taps, and drawing the gas through by means of an aspirator, until it is certain that all atmospheric air is expelled. The tap communicating with the aspirator is then first closed, and afterwards the one through which the gas enters. If the filling of the tube is not effected by means of an aspirator, but by connection with an apparatus in which the gas is generated, or with a gasometer, or under the pressure of a column of liquid, the outlet-tap of the measuring-tube is likewise closed first, and the entrance-tap last. The extra pressure is then got rid of by momentarily opening one of the taps, and the gas is thus brought in equilibrium with the external air. We have also to be satisfied that the gas to be examined is saturated with watery vapour; this is effected by allowing it, before entering the measuring-tube, to pass through wet cotton-wool, which serves also to remove mechanical impurities, such as soot, flue-dust, &c.

When the tube A has been filled, with the above-mentioned precautions, the next step is the estimation of the several gaseous constituents by an absorptio-metric process. The limb B serves for the reception of the absorbing liquid; it is selected wider or narrower as the case requires, and it is connected with the limb A by means of a piece of caoutchouc tubing. On pouring the absorbing liquid into the tube B, there is formed under the tap *a*, affixed to the measuring-tube, a collection of air, which must first be removed. For this purpose the tap is provided with two perforations: the one is the ordinary transverse aperture, and serves to place both limbs of the tube in connection; the other goes in the direction of the tap-handle, which terminates in a pointed tube, which again can be closed by means of a piece of caoutchouc tube and a pinchcock. In this manner it is practicable to let out the included air through the longitudinal aperture of the tap *a*, and, when this has taken place, to prevent the liquid from escaping by means of the pinchcock. This construction of the tap also enables the measuring-tube to be placed in direct communication with the external air. The different positions which may be given to the tap *a* are seen in fig. 49.

Position *a* connects both limbs of the tube, position *b* connects B with the external air, and position *c* places the latter in connection with the measuring-tube A. After filling the measuring-tube with the gaseous mixture, the tap *a* is in the position *b*, and a cautious opening of the pinchcock releases the enclosed air through the liquid in B. The gas and the liquid are now only separated by the tap *a*; by turning this round 90°, it takes the position *a*, fig. 49. A communication

between both limbs is thus effected, and absorption begins, aided by the pressure of the column of liquid. To expedite it, however, the support bearing the tubes is so arranged that they can be alternately placed either horizontally or vertically. Before being placed in a horizontal position, the tap *a* is placed in the position *b*, fig. 49, and the tube *c*, bent at right angles, is connected with the limb B, in order to prevent the escape of the liquid when the tube is inclined. In the horizontal position of the tubes the absorption is very active, as may be perceived if the tube be replaced in the vertical position, and the tap *a* reopened; immediately a fresh quantity of liquid forces its way into the measuring-tube. This alternating inclination of the tubes, the tap *a* being closed each time, is continued until no further entrance of the liquid into the measuring-tube can be perceived—a result which is mostly effected in a few minutes. It is now necessary to bring the liquid in the two connected tubes to the same level, which is effected by the exit-tap *c*, fig. 49. The volume of liquid which has entered into A represents the number of c.c. of absorbed gas, and when it is multiplied by 100, and divided by the total capacity of the measuring-tube, the percentage of the absorbed constituent is found.

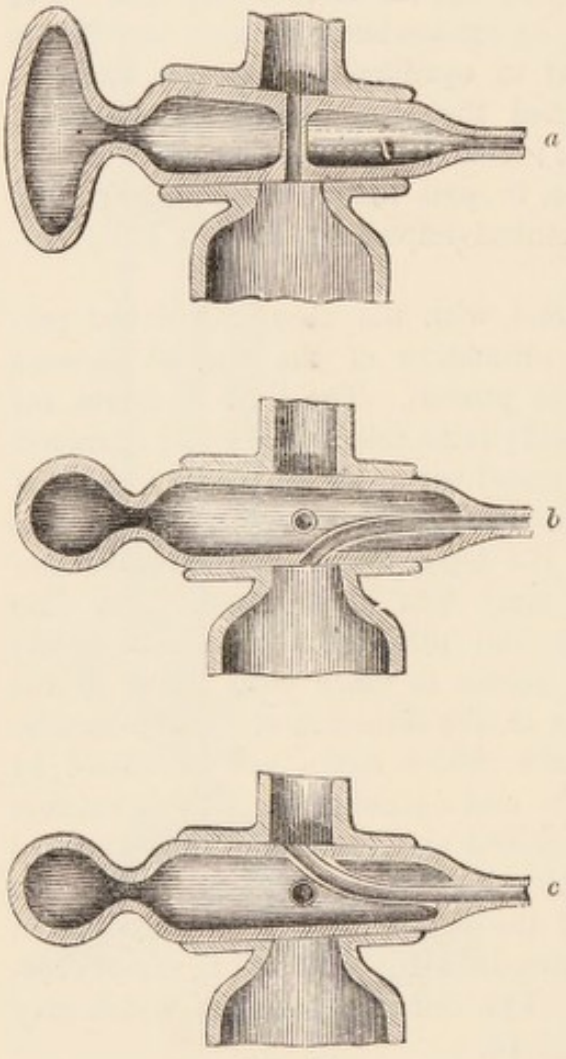


FIG. 49.

From the above it appears that only one gaseous constituent, or the sum of several, can be estimated at once. If a complete analysis is required, as many apparatus can be used at once as there are gaseous constituents to be estimated. The measuring-tubes are connected together with caoutchouc tubes and filled at once. The analyst has thus the advantage of operating upon a set of portions filled under the same conditions of temperature and atmospheric pressure, and equally saturated with watery vapour, so that the customary corrections for temperature may be dispensed with. The estimations take so little time that an alteration of the volume of

the gas from a change of temperature is not to be feared. Care must be taken that the various absorption liquids have all the same temperature. To regulate the temperature of the gaseous mixture, it is allowed to pass through a bottle of mercury, which is kept along with the absorbents. If it is required to estimate relatively small amounts of a gaseous constituent, a somewhat modified construction of the measuring-tube is needful. The lower part nearest to the tap *a* is made narrower, so as to admit of a more accurate graduation, say to 0·5 of a c.c. In this case the graduation need not be continued for the whole length of the tube.

1. **Aqueous Vapour.**—All gases are saturated with aqueous vapour prior to measurement. The estimation of the water present is not necessary in every case. If it is required to find the amount of aqueous vapour in a gaseous mixture, concentrated sulphuric acid is used as the absorbent liquid. By inclining the tubes a few times, the gas is dried completely. Before reading off, the sulphuric acid is allowed to stand for a few minutes.

If the gas under examination contains originally a certain amount of water, without being saturated, two estimations are required.

One apparatus is filled direct with the gaseous mixture, without allowing it to pass through the tube filled with wet cotton-wool; while another is filled with gas which has been thus saturated. The difference which appears between the two subsequent measurements with sulphuric acid corresponds to the volume of aqueous vapour which the gas took up in passing through the damp cotton-wool.

108·7 c.c. air, treated direct with sulphuric acid, required 0·9 c.c. =0·82 volume-percentage of water.

106·8 c.c. air, saturated with aqueous vapour, required 2·3 c.c. sulphuric acid=2·11 volume-percentages of water.

The water taken up for saturation amounted, therefore, to 2·11 −0·82=1·29 volume-percentages.

The estimation of oxygen in the air saturated with aqueous vapour yielded 20·44 per cent.; consequently, the original unsaturated gas—

$$100-2{\cdot}11 : 100-0{\cdot}82 = 20{\cdot}44 : x$$
$$x = 20{\cdot}7 \text{ per cent. (measure) oxygen.}$$

Hence it follows that the air in question contained—

Oxygen	20·70
Nitrogen	78·48
Aqueous vapour	0·82

2. **Carbonic Acid.**—The estimation of carbonic acid is not only very rapid, but yields results which, in point of accuracy, leave nothing to be desired. A moderately concentrated solution of the potassium hydrate is used as absorbent.

3. **Nitrogen.**—The direct estimation of nitrogen has not hitherto

been found possible. It is estimated from the difference, and, as a matter of course, the residue, representing nitrogen, is burdened with every error in the whole analysis.

4. **Sulphurous Acid.**—The method employed for carbonic acid can be used in many cases where it is needful to ascertain the amount of sulphurous acid present in a gaseous mixture. The absence of carbonic acid and of other gases soluble in alkaline solutions must, of course, be ascertained with certainty; otherwise the result would be found too high. For certain furnace gases produced without the use of fuel, *e.g.* by roasting pyrites in kilns, the potash process is directly applicable, since the error occasioned by the trace of carbonic acid present in the air supporting the combustion is too trifling to be appreciated.

If, in a gaseous mixture under examination, the other gases absorbable by potash-lye are present in addition to sulphurous acid, a solution of iodine in potassium iodide is used as absorbent, of the strength of the decinormal solution used in volumetric analysis. It must be remembered that this liquid is also not quite without action upon carbonic acid, which it dissolves mechanically to some extent, as water does. This difficulty is got over by using a solution through which a current of carbonic acid has been passed for some hours. When the iodine solution penetrates into the measuring-tube, it is immediately decolourised, and it is only after repeated inclinations that an excess of iodine becomes perceptible within the tube. This excess must be present if the estimation is to be correct. If the liquid remains colourless, it is a sign that the solution of iodine employed is not sufficiently concentrated, and that in consequence a part of the sulphurous acid is not oxidised, but mechanically dissolved.

The volumetric estimation of oxygen in gaseous mixtures is effected by means of a solution of pyrogallic acid in potash-lye. The liquid is prepared specially for each estimation by dissolving 1 to 2 grammes of pyrogallic acid in a little water, and adding about 100 c.c. of a tolerably concentrated potash-lye. The absorption is rapid at first, but becomes slow towards the end. Hence it is prudent, after the action is apparently over, to leave the liquid still for some minutes in contact with the gas, turning the tubes occasionally. Before reading off it is necessary to wait till the brown froth has subsided. An estimation requires about ten minutes.

If, in a mixture containing oxygen, gases are present which are absorbable by alkaline liquids, such gases are naturally absorbed by the potassium pyrogallate. This is the case if carbonic acid is present. Under such circumstances, the carbonic acid present is estimated separately in one apparatus by absorption with potash-lye, and in a second the joint amount of oxygen and carbonic acid is absorbed by potassium pyrogallate, and the net volume of oxygen is then found

by subtraction. If, in addition to oxygen, nitrogen, and carbonic acid, sulphurous acid be also present, we estimate :—

By potassium pyrogallate, $O + CO_2 + SO_2$
By potash-lye, $CO_2 + SO_2$
By iodine solution, SO_2
The residue is nitrogen.

5. **Nitric Oxide and Nitrous Acid.**—The volumetric estimation of the lower nitrogen oxides is a matter of great importance. A saturated solution of green vitriol seems to have a sufficient absorptive power for the volumetric estimation of nitric oxide, though the numbers obtained are not, so far, as constant as might be desired. The absorption of nitrous acid can be effected by means of concentrated sulphuric acid. While, however, we may assume with tolerable certainty that nitrous acid may be absorbed by means of sulphuric acid in gaseous mixtures containing nitric oxide, it is questionable whether, conversely, nitric oxide can be estimated by green vitriol in presence of nitrous acid. It appears that green vitriol absorbs nitrous acid also in not inconsiderable amount, whether by simple solution or by some chemical change being not yet decided. If this is confirmed, then in all cases where the two gases are jointly present, it will be requisite to estimate the nitrous acid direct in one apparatus by sulphuric acid, while the nitrous acid must be withdrawn from the gaseous mixture as a preliminary to the estimation of the nitric oxide by green vitriol in a second apparatus. This would be effected by passing the mixed gases through a washing-bottle filled with sulphuric acid, previous to their admission into the measuring-tube.

6. **Chlorine.**—The estimation of chlorine can be effected in most cases by means of a moderately concentrated solution of the potassium hydrate. The process is rapid, and can be recommended when no other gas capable of absorption by alkalies is present along with the chlorine. An admixture of such gases, especially of carbonic acid, is found when chlorine gas is evolved from a calciferous manganese. In such cases the chlorine must be absorbed by a liquid which has no action upon carbonic acid. A solution of iron protochloride, mixed with hydrochloric acid, answers the purpose satisfactorily; it must, however, be previously saturated with carbonic acid, by passing that gas slowly through it for some hours.

7. **Hydrochloric Acid.**—Potash-lye is employed with satisfactory results. If carbonic acid is simultaneously present, hydrochloric acid gas might possibly be absorbed by water previously saturated with carbonic acid.

8. **Ammonia.**—The absorption of ammonia is most readily effected by means of dilute sulphuric acid.

9. **Sulphuretted Hydrogen.**—A solution of potassium hydrate absorbs this gas rapidly and completely. If carbonic acid is simultaneously present, the case is not free from difficulties. Pass the

gaseous mixture through a washing-bottle filled with a concentrated solution of iodine previously saturated with carbonic acid; in this the sulphuretted hydrogen is oxidised and the sulphur deposited. The remaining gases, including the carbonic acid, pass on into the measuring-tube. The carbonic acid is then estimated in one apparatus, in the portion of gas thus freed from sulphuretted hydrogen, by means of potash-lye. A second apparatus is filled with the gas in its original condition, and carbonic acid *plus* sulphuretted hydrogen. It may here be remarked that sulphuretted hydrogen is advantageously collected over petroleum, by which it is not at all absorbed.

10. **Carbonic Oxide.**—The discovery of a simple and accurate method of estimating carbonic oxide in a gaseous mixture is of the utmost importance for the right management of combustion under a variety of circumstances. The absorbent used is a solution of copper subchloride in hydrochloric acid. The subchloride for this purpose is obtained by precipitating cupric chloride with stannous chloride. The white crystalline precipitate is first repeatedly washed with cold water by decantation, then twice washed with strong alcohol, and finally once with ether. It is then dried at 80° to 90° C. in a current of carbonic acid. The white salt is preserved in air-tight bottles. It is easily and plentifully dissolved in hydrochloric acid, and if a spiral of copper wire is kept in the liquid, reaching from the bottom to the neck of the bottle, the latter being carefully stoppered, it may be preserved for a long time free from change. The solution should not be too concentrated.

A solution suitable for the purpose is obtained by saturating hydrochloric acid at sp. gr. 1·11 with copper subchloride. The liquid absorbs the gas very greedily.

The estimation of carbonic oxide in gaseous mixtures whose other constituents act neither chemically nor mechanically upon the copper subchloride offers no difficulties. Less easy is the estimation when other absorbable gases are present. The error which might arise from the presence of carbonic acid may be evaded by saturating the solution of copper subchloride previously with carbonic acid. Oxygen has a very disturbing influence, and must be removed before the estimation of the carbonic acid. This is effected by allowing the gaseous mixture, before its entrance into the measuring-tube, to pass through a Liebig's potash apparatus filled with the solution of pyrogallic acid in potash-lye. In this manner oxygen, carbonic acid, &c., are absorbed, and only carbonic oxide, hydrogen, and nitrogen passed on into the measuring-tube. The amount of carbonic oxide is then estimated in the gas so treated, while the oxygen, carbonic acid, &c., are estimated in separate portions of the original gas.

Estimation of Nitrous Oxide

A. Wagner has examined whether nitrous oxide could be estimated by means of its oxidising action upon an ignited mixture of chromium sesquioxide and sodium carbonate in the absence of air, and was completely successful. The nitrous oxide decomposed can be estimated either by the volume of the nitrogen liberated or by the quantity of sodium chromate formed, since 1 volume nitrous oxide yields 1 volume nitrogen, and 1 part chromium oxide requires 0·3136 oxygen for conversion into chromic acid. The author found by special experiments that by heat alone, in the absence of the mixture of sodium carbonate and chromium sesquioxide, only 28·2 per cent. of the nitrous oxide is decomposed. A mixture of equal volumes nitrous and nitric oxide is entirely decomposed under the same conditions, giving up all its oxygen, while any excess of nitric oxide escapes unchanged.

Estimation of Free Oxygen in Water

C. C. Hutchinson gives the following account of a modification of Schützenberger's process. The reducing agent is sodium hydrosulphite prepared as follows:—A concentrated solution of caustic soda, sp. gr. 1·4, is taken; sulphurous anhydride is passed through it till the liquid is thoroughly saturated and smells strongly of the gas. The yellow liquid (which is kept cool during the process of saturation by immersion in cold water) is sodium bisulphite; it increases slightly in bulk, and is reduced to the sp. gr. of about 1·34. 100 grammes (75 c.c.) of this solution are then briskly agitated in a flask with 6 grammes of powdered zinc, air being excluded; a rise of temperature occurs, the bisulphite being converted partly into the hydrosulphite, together with the formation of sodium sulphite and zinc sulphite. After agitation for about five minutes, the liquid is allowed to cool; 400 c.c. of water recently boiled are added; 35 c.c. of milk of lime, containing 200 grammes of calcium oxide per litre, are also added, and the mixture allowed to stand until clear, when it is decanted into well-stoppered bottles and kept in the dark. The lime solution not only precipitates the zinc salt, but also renders the solution less absorbent of free oxygen, although it acts very rapidly upon dissolved oxygen. Before use this is further diluted with three times its bulk of distilled water recently boiled.

The liquid recommended by which the change of colour detects the completion of the process is either sodium sulphindigotate, or Coupier's aniline blue; 10 grammes of the extract of indigo are recommended to be dissolved in 1 litre of water, the product being kept in well-stoppered bottles, also in the dark.

An ammoniacal solution of pure copper sulphate is also recommended to be made, containing 4·46 grammes (or more correctly, 4·471 grammes) of the crystallised salt per litre. This is to be used for the standardisation of the above two solutions.

Since the reducing agent is so sensitive to the presence of oxygen, it is necessary to make the estimations in an atmosphere of pure hydrogen. To ensure the purity of the hydrogen, it is passed through a solution of silver nitrate, in addition to the sulphuric acid and the tube containing pieces of caustic potash.

We begin by finding the volume relation between the indigo and hydrosulphite. The burettes of the apparatus are filled, one with indigo carmine solution, the other with hydrosulphite ; a rapid current of hydrogen is passed through the apparatus, a small quantity of warm distilled water added, coloured by the addition of a small quantity of indigo. We now add cautiously the hydrosulphite ; the blue solution turns first green and finally to a clear yellow tint. If the whole of the air has been expelled from the apparatus, the yellow tint will remain unchanged ; the slightest trace of oxygen causes the surface of the liquid to become blue. A known volume of indigo (25 c.c.) is now added, and the hydrosulphite solution again run in until the yellow tint appears, indicative of the reduction of the whole of the indigo. The colour change is exceedingly sharp, one drop being sufficient to change the colour from green to yellow. If the solution be acid, the blue colour changes first to red, and finally the yellow tint appears.

We next require to find the reducing power of the hydrosulphite in terms of oxygen, finding from this the amount of oxygen any volume of the indigo will yield. This being a stable solution, the hydrosulphite (being liable to change) can be readily standardised at any future time. This reducing power can be found by finding the quantity necessary to reduce the ammonia copper solution, *i.e.* the amount which brings the blue solution to a colourless state, by the reduction of the cupric to cuprous oxide ; 10 c.c. of this solution yield 1 c.c. of oxygen (0° C. 760 millimetres pressure) to the reducer. 25 c.c. are operated on in a smaller apparatus similar to the one used for the water estimations. It was found, however, that the colour change in this plan is so indefinite and difficult, even to the practised eye, to detect, that the exact point cannot be determined with any degree of certainty.

The method for the estimation of oxygen contained in a water is as follows. Owing to the change which the hydrosulphite undergoes, it is necessary that a comparison between it and the indigo should be made each day. After this has been done and the apparatus freed from air by means of the hydrogen, 200 c.c. of warm water (temperature about 50° C.) are then added ; 50 c.c. of indigo are now run in. This is usually effected in portions of about 15 c.c. at a time, decolourising each portion by means of the hydrosulphite, thus utilising this

step for the comparison of the two reagents ; effecting thereby a saving of time and material. The liquid in the apparatus being now brought to the yellow neutral tint, a measured volume of the water under experiment is added—75 c.c. is a convenient quantity—taking care that no air is admitted at the same time. The bleached indigo will now become re-oxidised, turning from yellow to blue, in proportion to the amount of oxygen present in the water. The hydrosulphite is now cautiously added until we again arrive at the yellow tint, free from green ; a single drop of the reagent is sufficient to effect the colour change at the proper point. From the quantity used we find the amount of oxygen present in the 75 c.c. of water. The operation can be repeated over again on another volume of the water until the apparatus becomes inconveniently full. The temperature of the apparatus must be kept at about 50° C. by the addition of warm water at intervals ; the amount of hydrosulphite required becomes gradually less as the apparatus cools, giving the results too low.

CHAPTER XIV

MISCELLANEOUS PROCESSES AND GENERAL METHODS OF MANIPULATION

Standard Soda Solution

GERRESHEIM has published an article on ammoniacal mercury compounds, wherein he calls attention to the pronounced basic properties of the so-called Millon's base, which is obtained by the action of ammonia upon mercuric oxide. He states that a soda solution to which hydrochloric and sulphuric acid, &c., have been added can be freed from these by shaking with Millon's base. Mercury is not found in the solution. This method has been employed in order to obtain a chemically pure standard soda solution from the ordinary so-called pure caustic soda, and we have found all that the author claims verified. The soda contained large quantities of chlorine, sulphuric acid, and also silicic acid, and carbonic acid. For 2 litres soda solution about 30 grammes of Millon's base are employed. The chlorine disappears first, then carbonic acid, silicic acid, and sulphuric acid. The process is complete after about one week's standing, the mixture being shaken about once or twice each day.

Allow the Millon's base to settle in the solution, and draw off with a syphon as required. Shaking from time to time removes any carbonic acid which in the course of time may be absorbed by the soda. Millon's base absorbs carbonic acid from the air rapidly, and is also not easily filtered and washed. It is therefore not completely washed free from the last traces of ammonia, as it is preferable to remove these by the addition of a small quantity of mercuric oxide when the Millon's base is brought into the soda solution.

Casamajor's Burette.—P. Casamajor has been led to adopt an entirely different form of burette, which is represented in figs. 50 and 51. It consists of a cylindrical tube closed at the bottom, and inserted in a stand or foot made of japanned tin. The cylindrical portion of this tin stand is only partially soldered on to the flat part, to allow the portion left free to act as a spring in holding the glass cylinder tightly.

The upper portion of the glass tube has the shape shown in fig. 50, to prevent the liquid from running out when the tube is inclined.

Immediately under the curved portion of the burette is a beak, from which the liquid drops when the instrument is inclined and properly turned. By making a transverse section through this beak we obtain figs. 52 and 53, which show the shape of the beak, and its position in relation to the stem for two positions of the tube.

To allow the liquid to drop from the burette, it is inclined as in fig. 52, in which position the curved portion at the upper end prevents the liquid from pouring out. Keeping the tube inclined as in this figure, we may either prevent the outflow of its contents or allow it to run with more or less rapidity. To effect this it is merely necessary to turn the instrument round its own axis, so that the beak may be either raised or lowered, as shown in figs. 52 and 53. When the beak is allowed to take the position shown in fig. 52, the liquid in the tube does not run out, while in the position shown in fig. 53 the drops run out quite rapidly. At some intermediate point it will be found that the liquid runs out slowly in drops, which may be accelerated or retarded by turning the tube round its axis, but without changing the inclination of this axis.

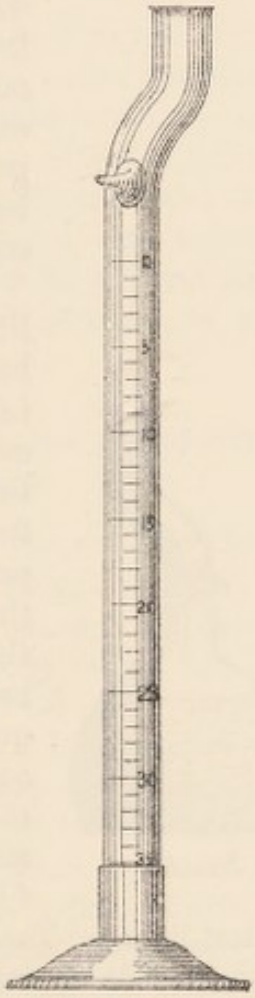


FIG. 50.



FIG. 51.

The motion imparted to the burette by holding it in the hand and simply turning it round its axis is an easy one for the operator, who is not obliged to watch the liquid in the instrument with any degree of attention. As the liquid runs out of the burette it becomes necessary to incline its axis more and more, to keep a supply of liquid near the beak; but there is no difficulty connected with this, as the liquid runs out with equal ease when the instrument is full to the 0 mark as when it is nearly empty. When the changes which occur in the liquid under examination indicate that the operation is nearly ended, the liquid may very easily be made to fall in single drops by



FIG. 52.



FIG. 53.

turning the beak down gradually, and raising it again with a sudden motion. This is soon learnt by a little practice, and does not require a close watch on the contents of the burette.

The most convenient position for the operator is to hold the tube almost horizontally and to let the foot roll on a block of proper height, while the necessary motions are given to the instrument by holding it with one hand near its open end. This presents the additional advantage that the portion which becomes heated by the hand is not in contact with the liquid contents of the tube.

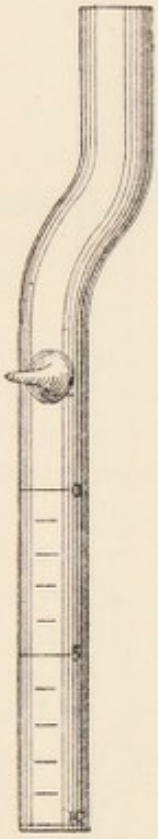


Fig. 54.



Fig. 55.

Whenever it becomes necessary to lift the instrument, the beak should be previously raised by turning the tube, as otherwise a drop of liquid may escape and run down the side of the tube. After the operation is ended, the burette should be left in a vertical position for some minutes, to allow the liquid to run down before reading the indication of the scale. As the beak holds by capillarity a certain quantity of test-liquor, it will be found convenient to keep it full whenever the indications of the scale are observed. This beak usually becomes filled of itself at the time of filling the instrument with test-liquor. The open end of the burette may be provided with a lip on the side opposite to the beak, as shown in fig. 51. This is to allow the test-liquor to run out faster.

Many chemists are unwilling to trust to volumetric analysis, for fear of the changes of volume which are due to changes of temperature. They are, however, willing to use the solutions of this method of analysis, and they have adopted a gravimetric system, which consists of weighing instead of measuring their test-liquors. For this manner of using test-solutions the gravimetric burette represented in fig. 55 may be used. The manner of using this burette is precisely the same as for the volumetric instrument, and it does not require any further explanation.

The weight of test-solution used in an analysis is best determined by double weighing. The flask or gravimetric burette, containing a greater quantity of test-solution than will be required by the analysis, is placed on the scales and counterbalanced with shot or any other material. After the operation is ended, the flask should be replaced on the same pan of the scale and be made to counterbalance the original

quantity of shot by adding weights, which represent the weight of test-solution that has been used. A common balance carrying 200 grammes and turning to 1 centigramme is sufficient for this method of testing.

Ammonia-free Water

D. B. Bisbee has described a very easy way of obtaining ammonia-free water. It is to acidulate the water, before distilling, with sulphuric acid. The acid holds all ammonia in the retort, the first portions even of the distillate being ammonia-free. But this acidulation naturally causes the nitric acid and nitrous acids in the water to distil over. For some purposes, however, nitrates are not objectionable. When it is desired to obtain chemically pure water for any use, take distilled water, which is nitrate-free, acidulate with sulphuric acid, and distil, at once getting *pure* water.

Simple Method of Estimating the Temporary Hardness of Water

V. Wartha, in order to ascertain the alkalinity of spring waters on the spot, with samples not exceeding 10 c.c., and with a single reagent, makes use of a tube of 30 to 40 centimetres long, closed at the bottom, and with a mark showing the capacity of 10 c.c. From this mark upwards the tube is graduated into 0·1 c.c. To estimate the temporary hardness the tube is filled to the lowest mark with the water in question, and a little piece of filter-paper, which has been previously steeped in extract of logwood and dried, is thrown in, thus giving the water a violet colour. Centinormal hydrochloric acid is then added from a dropping bottle till the colour of the liquid inclines to orange. The tube is then closed with the thumb and well shaken. The greater part of the carbonic acid escapes, and the liquid becomes red again. Acid is again added, and the shaking repeated until the next drop of the acid turns the liquid to a pure lemon-yellow, a point which with a little practice is easily reached. The amount of acid used is read off on the tube itself. The author proposes to express the alkalinity of a water by the number of centimetres of centinormal acid needed to neutralise 10 c.c. He thinks that this method will be found useful both for sanitary and geological purposes.

New Test for Reducing Agents

Edwin Smith has published a method of illustrating the de-oxidising property of sulphurous acid, by exposing a slip of bibulous paper, dipped in a mixed solution of iron sesquisulphate and potassium ferricyanide, to the vapour rising from a bit of sulphur burning in air. The iron persalt being reduced to a protosalt by giving up an equivalent of oxygen to the sulphurous acid, a blue reaction takes

place with the potassium ferricyanide present in the solution. A solution of sulphurous acid, or of a sulphite or thiosulphate, gives the same result; while only a very slight greenish tinge is imparted to the mixture by a sulphate, except in the case of iron protosulphate. With this exception, a useful test seems to be afforded between sulphites and sulphates. The same test will discriminate a nitrite from a nitrate.

To the mixed solution of iron sesquisulphate and potassium ferricyanide add a few drops of nitric acid; then add a little of the solution to be tested. If the latter contains a nitrite, a greenish-blue precipitate will begin to fall, and quickly increase; if a nitrate, only a slight greenish tinge will be imparted to the test. Nitric oxide or nitric trioxide passed into the mixed solution throws down the same characteristic precipitate which is produced by the decomposition of a nitrite in the previous case. Carbonic oxide will act in the same way, and if a slip of paper dipped in the test-mixture be held over the clear part of a bright coal fire, it turns blue with the carbonic oxide or sulphurous acid there given off. Again, if a bit of phosphorus is dropped into a little of the test-mixture in a porcelain dish, the phosphorus immediately becomes coloured a greenish blue, and on stirring about, gradually imparts the same tinge to the solution. Phosphorous acid may be discriminated from phosphoric acid, just as sulphurous acid is distinguished from sulphuric acid by the blue reaction. Phosphites are also distinguished from phosphates. A solution of phosphorous acid shows the reaction readily on being shaken up with the test-mixture. Lastly, if copper turnings are boiled in the mixed solution for a few minutes, a greenish-blue tint is imparted to it, which becomes gradually deeper with the oxidation of the copper and the consequent reduction of the iron persalt to the state of a protosalt.

Improved Methods of Oxidation

Professor Storer points out the superior oxidising power of a mixture of ordinary nitric acid and potassium chlorate over that of the mixtures of potassium chlorate and hydrochloric or sulphuric acid commonly used in analysis.

Blowpipe Analysis. Employment of Silver Chloride

Among the phenomena which characterise different bodies before the blowpipe, and serve for their distinction, the colour of the flame is of no small importance, especially when the eye observations are supplemented by the use of a spectroscope. This power of colouring the blowpipe flame is not, however, exhibited by all bodies with sufficient intensity to enable them to be distinguished by it with certainty, and some substances, such as hydrochloric acid, are consequently usually employed with barium, strontium, and calcium compounds,

partly to form and partly to set free volatile compounds. By this means, however, although the intensity of the colouration is heightened, its duration is not increased, as the acid evaporates, for the most part, before it has acted sufficiently, so that the colouration lasts only for a few moments.

Dr. H. Gericke overcomes this difficulty by the employment, instead of the volatile hydrochloric acid, of a chloride which will retain the chlorine at a high temperature, so that it may only be set free by degrees in small quantities, while the body forming its base may be without action upon the colouring power of the body under investigation. For this purpose silver chloride appears to be the best, especially as it may readily be prepared in a state of purity. The best plan is to stir it with water into a thick paste, and keep it in a bottle.

In regard to the action of silver chloride upon the colouration of the blowpipe flame, the author has investigated several compounds of potassium, sodium, lithium, calcium, barium, strontium, copper, molybdenum, arsenic, antimony, and lead, and mixtures of these substances. Silver chloride has no action upon borates and phosphates.

Platinum wire does not answer well as a support, as it is soon alloyed by the metallic silver which separates, and is thus rendered useless. Silver wire is too readily fusible, and also is difficult to obtain free from copper, which may give rise to errors when in contact with the silver chloride. Iron wire is best fitted for experiments with silver chloride, as, from its cheapness, a new piece may be employed for each experiment, while the silver may be readily recovered in the form of chloride from the broken pieces.

The results obtained by the employment of silver chloride in comparison with those obtained without this reagent are as follows:—

With potassium compounds, such as saltpetre, potash, &c., the flame is decidedly of a darker colour with silver chloride; and even with potassium ferrocyanide, which, when treated by itself with the blowpipe, colours the flame blue, the addition of silver chloride produces a distinct potassium colouration.

The action of silver chloride upon sodium salts is not so marked, although with some, such as sodium nitrate, common soda, and labradorite, the flame acquires a more intense yellow colour by the addition of silver chloride. This reagent produces no observable difference with other sodium compounds, such as sodium sulphate and analcime. This also applies to the lithium compounds, some of which give a finer purple-red colour on the addition of silver chloride, while upon others it has no such effect.

With calcium compounds silver chloride acts favourably upon the colouring power. Thus, the addition of silver chloride to calcareous spar or gypsum (in the reduction-flame) gives the flame a more distinct yellowish-red colour; but stilbite gives no calcium colouration either with or without silver chloride. With fluorspar the colouration

cannot well be observed, as it decrepitates too violently under the blowpipe.

The action of silver chloride upon barium and strontium compounds is decidedly advantageous, as both the intensity of the colouration and its duration leave nothing to be desired. Sicilian cœlestine, which when heated by itself in the forceps scarcely colours the flame, immediately produces a permanent red colouration when heated with silver chloride.

Although it appears from the preceding statements that the employment of silver chloride presents no advantage with some substances, it may be used with good results in the treatment of mixtures of alkalies and earths. Thus, with petalite alone, the lithium colouration is first produced; a slight sodium colouration is afterwards obtained; while, with silver chloride, the sodium colouration appears very distinctly after that of lithium. With lithion-mica alone a very distinct lithium colouration is presented, but in the presence of silver chloride a colour is first produced, which may lead to the conclusion that potassium is present but the lithium colouration is weakened. Rhyacolite, heated by itself in the blowpipe flame, only gives a distinct sodium colouration; but with silver chloride a slight potassium colouration is first produced, and the colouration of sodium then appears very distinctly; the calcium contained in it cannot, however, be detected by the colouration of the flame, although evident in the spectroscope.

Silver chloride may be employed with still greater advantage with the following metals, but in these cases it is particularly necessary that the operator should become familiar with the colour as well as the spectrum produced by each individual substance.

With copper compounds, such as red copper ore, malachite, copper pyrites, copper sulphate, &c., when contained in other minerals so as to be unrecognisable by the eye, the employment of silver chloride may be of great service, as the smallest quantities of copper, when treated with silver chloride under the blowpipe, give a continuous and beautiful blue colour to the flame. With silver chloride, the presence of copper may be distinctly ascertained by the blowpipe, even in a solution which is no longer coloured blue by the addition of ammonia.

The employment of silver chloride will be equally advantageous with molybdenum, as in this case also the flame gains greatly in intensity. Arsenic, lead, and antimony are already sufficiently characterised, the former by its odour, the two latter by their fumes; but even with these metals silver chloride may be employed with advantage to render their reactions still more distinct. It is only necessary to observe that the greenish-blue flame of antimony appears greener and more like that of molybdenum under the influence of silver chloride.

Silver chloride may also be employed with compounds containing several of the above-mentioned metals. If bournonite be heated in the

oxidising flame of the blowpipe, a fine blue flame is first produced, which indicates lead with certainty; if silver chloride be now applied, copper is also readily shown. The antimony contained in bournonite cannot be ascertained by the colouration of the flame; but this may be easily detected upon charcoal or in a glass tube open at both ends. Native lead molybdate without silver chloride only gives a blue colour to the blowpipe flame; with silver chloride this blue colouration of lead comes out more distinctly, but at the same time the tip of the flame, particularly when the reduction-flame is employed, appears of a beautiful yellowish-green colour from molybdenum. With mixtures of arsenic and copper, or antimony and copper, the flame first appears a greyish-blue or greenish-blue colour, from the oxidation of the arsenic or antimony; the copper may be then very easily detected by silver chloride. This applies also to mixtures of arsenic and molybdenum, or antimony and molybdenum; with silver chloride the yellowish-green flame of molybdenum appears distinctly. It will be more difficult to analyse mixtures of arsenic and lead, or antimony and lead, in this manner, and if a compound contains both arsenic and antimony, these two bodies are not to be distinguished with silver chloride under the blowpipe.

Silver chloride is particularly to be recommended in testing metallic alloys for copper. Thus, to test silver for copper, silver chloride may be applied to the ends of silver wires, and on the application of heat the smallest quantity of copper will furnish a distinct reaction. This is as sensitive as any of the known copper reactions, and may be performed quickly and easily. In testing metallic alloys for traces of copper, it may be advisable to submit those which contain antimony, zinc, lead, and other volatile metals, to roasting, so as to drive off these metals before the addition of the silver chloride.

A New Method of Quantitative Chemical Analysis

In comparing together the results of a large number of chemical analyses it is seen that the numbers obtained vary between 99·17 and 100·67, giving a difference of about 1·5 per cent., or, supposing a quantity of 1·5 gramme of substance has been taken and the weighings carried to 0·0001 gramme, a difference of 225 units. The analyses here alluded to are by no means those which would be called bad or indifferent, but are such as have been made and published by eminent chemists. It ought further to be remembered that very many analyses yield results varying from 97 to 102 per cent. instead of 100, while the really bad ones never see the light at all. Under ordinary circumstances slight differences do not usually affect the result of an analysis, but if it is desired to employ the sum of the substances found to control the results, an incorrect total fails to serve this purpose, as there is no means of knowing upon which of the substances the error really falls.

Moreover, in many instances, only small quantities of material are available. A more accurate and improved method of analysis would admit of the employment of smaller quantities, as well as effect a great saving of time and labour.

It would appear that neither the methods and processes in use nor the impurities of reagents are greatly at fault, because it is found that when the same substance is analysed under exactly the same conditions the results often differ. It would therefore appear that accuracy depends chiefly upon the manipulations, among the most dangerous of which may be mentioned decantation, the removal of substances from a filter, the ignition of the filter-paper, and the calculation of the ash; the employment of a great number of vessels may either add something to solutions or withdraw something therefrom.

Dr. H. Carmichael has proposed a very ingenious apparatus for overcoming these difficulties. His apparatus is represented in the accompanying figures.

Fig. 56 (represented one-fourth of its natural size) consists of a doubly bent glass tube, with a funnel-shaped expansion at one of its ends, the wider part being perforated with a large number of small holes; the other bend of the glass tube is fitted in the T-shaped tube BCD, closed air-tight at B by means of a vulcanised indiarubber ring; the tube is fastened in the glass plate E F, and fitted air-tight by means of a similar contrivance to the one just mentioned; E F is covered with a cap made of vulcanised caoutchouc, while between B and C a tube is fitted laterally, bent at D, at right angles (this part is not represented in full in the figure) and fitted with a small-bore vulcanised indiarubber tube closed by a spring clamp. The cap and the ring, B, should be touched with some grease. The edges of a beaker can be readily rubbed on a piece of fine-grained and thoroughly smooth and level sandstone, to take off the vitreous glaze, so that a plate of ground glass may fit quite tight thereon; this having been done, the cover E F (a ground-glass plate) may be fitted so tightly that it is possible to keep in the interior of the beaker-glass as good a vacuum as in the receiver of an air-pump.

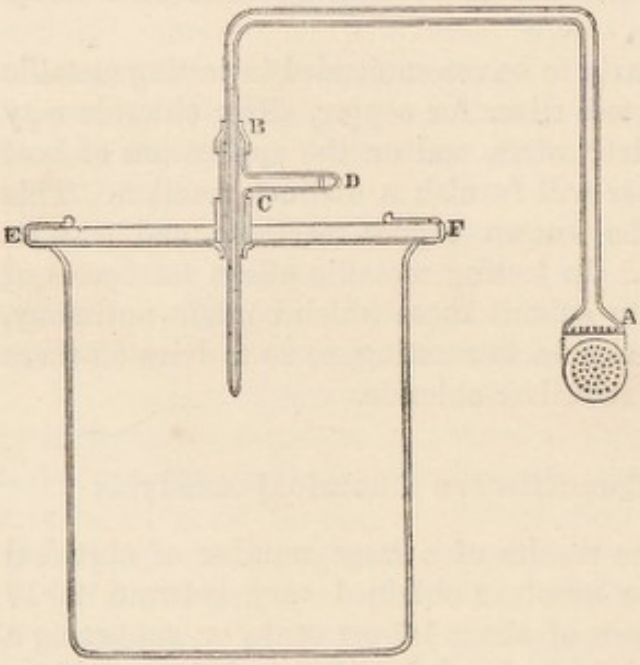


Fig. 56.

The filtering-bulb, A (fig. 56), being the most essential portion of this apparatus, its construction requires the greatest possible attention, and should be managed as follows :—Take a glass tube having an inner bore of 2 millimetres, blow at one end a thick bulb (see A, fig. 57), flatten the bulb at the bottom, keep this bulb so hot that the glass is only slightly soft, and while in that condition make holes in it by means of a white-hot steel wire ; these holes should be close together, and not larger than 0·7 millimetre. The width of the edge, *a b* (fig. 57), differs according to the kind of filter-paper which it is intended to use. For ordinary filter-paper the width should be 3 millimetres, for Swedish paper a width of 2 millimetres is sufficient; the perforated glass knob thus obtained is also ground slightly on sandstone. The tube to which the bulb is blown should be so bent as to make the leg B somewhat longer than the leg A ; the height of the bulb must not be great ; that is to say, it should be sufficiently flat to carry along with the air at the end of the filtration all the liquid into the beaker. The most suitable diameter of the bulb for general use is 2·5 centimetres ; the number of holes ought to be 50, but a smaller number will do when the holes are connected together by means of small channels cut in the glass with hydrofluoric acid. The apparatus is connected with an air-pump by a strong india-rubber tube.

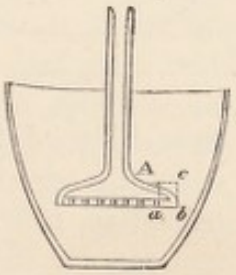


Fig. 57.

In order to use the apparatus the air is pumped out, water being poured simultaneously on A. The rapidity of the current thus called into play effectually removes all impurities, and the water serves also to clean the beaker. This having been done, a circularly cut piece of filter-paper, of the same diameter as A, is pressed against A. It remains fixed there, even when the apparatus is blown into ; a vacuum is again made while the filtering-disc is placed in the solution of the substance to be analysed, care being taken not to let the disc touch the bottom of the vessel in which that solution is contained ; as soon as the solution is filtered off from the sediment, some pure water is added, the vacuum being still maintained, after which the apparatus, with the precipitate adhering to it, is removed from the vessel in which the solution was contained, while any sediment therein remaining is transferred by careful manipulation into a previously tared crucible.

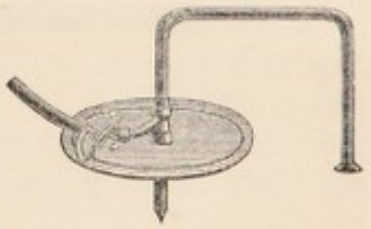

Fig. 58.

Fig. 58 exhibits the mode of the connection of the apparatus with the air-pump. The bulb is placed in the vessel, and distilled water added for the purpose of washing the sediment thoroughly, the water running into the beaker (the vacuum being kept on) for the purpose of drying the precipitate by the

current of air. This may be carried so far as to cause even gelatinous precipitates to shrink together. The spring clamp now being opened, air is admitted to the beaker, and the filtering-tube removed from the crucible as well as from the cover, E F (fig. 56). If the operation has been properly managed, the disc of filter-paper remains on the top of the precipitate, the upper surface of the bulb remains clean, while only a very thin and small ring of the substance adheres to the lower edge of the bulb; this substance is removed by carefully holding a piece of filter-paper flat in the hand and pressing it gently against the bulb; turn the latter slowly so as to rub all the substance on the paper, which, with the substance thus fastened to it, is thrown into the crucible. This having been done, the crucible, covered with its lid, is placed in an air-bath and heated to 105°. At this temperature the precipitate becomes readily and rapidly dry, without any danger of spirting; after which the crucible is ignited, first without the cover, until the very small quantity of paper is consumed, and afterwards with the lid on.

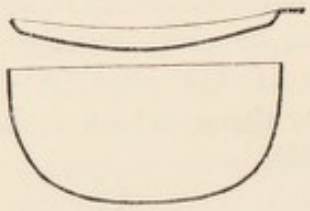


Fig. 59.

Although a bulb of the size above named is sufficiently large for many substances, it is preferable to have another bulb of 3·5 centimetres diameter for use with such gelatinous precipitates as alumina and iron peroxide. Instead of the platinum crucibles in ordinary use, it is for this purpose preferable, though not indispensable, to use a platinum dish and cover, shaped as shown in fig. 59, and weighing about 28 grammes.

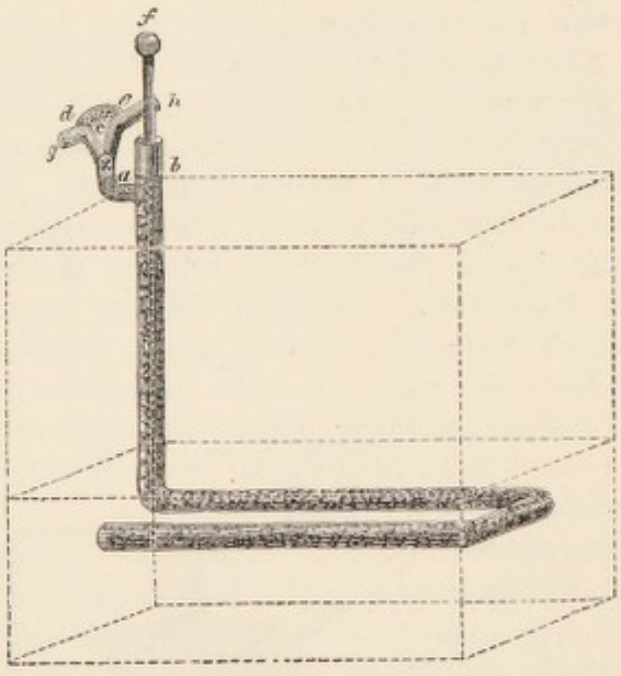


Fig. 60.

As the rapidity of the operations by this method makes it desirable to heat several crucibles at a time to 105°, and since this requires an air-bath with a really good gas-regulator, those hitherto contrived being either of no use or somewhat expensive and too complicated, Dr. Carmichael has contrived the apparatus shown in fig. 60. Anyone who has acquired some practice in glass-blowing may make it for his own use. Take a glass tube 40 centimetres long and 0·6 centimetre interior diameter, bend it as shown in the woodcut so as to admit of two of the bends being placed below the false bottom

of the air-bath, and the third, the vertical bend, to pass through an opening out of the bath, but so as not to touch the metal the bath is made of; at *a* a glass tube of 2 millimetres interior diameter is melted on the wider tube, and shaped as shown at *c*; this narrower tube is branched off into two parts, each so bent as to be on a level together. At *d* and *e* holes are made in these branches in such a manner as to form small nipples towards the outside, which are next nearly closed, and then connected together by means of an indiarubber tube; the lower end of the wide glass tube is sealed, and the top opening closed with a cork, into which, through a carefully made hole, a thin and long glass rod is fitted; the cork should extend to *a b*, so as to exclude air. This contrivance is entirely filled with mercury, and next freed from any adhering air and moisture by heating over a spirit-flame; one of the open tubes at *h* and *g* is in connection with a gas-supply pipe fitted with a tap, the other open glass tube with a burner, while the openings at *d* and *e* are so small that the gas which may pass through them is too minute in quantity to heat the bath to any extent; at the same time, these openings serve to prevent the sudden extinguishing of the flame by the rapid expansion of the mercury.

The apparatus is used in the following manner:—The bath is heated by a gas-burner, until the thermometer connected with the bath indicates nearly the requisite temperature; this having been reached, the glass rod, *f*, is pressed down into the mercury contained in the wider tube, until the mercury at *a* nearly touches the part *c*, which should be made as straight (not rounded) as possible. The sensitiveness of this contrivance depends, of course, upon the quantity of the mercury and its adjustment of surface; but if the apparatus is made with care, according to the directions just described, the bath remains to a fraction of a degree at a constant temperature, even in a draught of air or with a change of pressure of gas. The cooling of the mercury in the narrow tubes prevents oxidation of the metal anywhere in the tube.

The following advantages are obtained by the use of the filtering-bulb:—

1. The decantation of liquids is avoided.

2. The washing, ignition, and allowance for the weight of the filter-ash are entirely dispensed with. For, since the quantity of ash contained in a filter made of the best paper, and of 12 centimetres diameter, amounts to 0·0005 gramme, the ash contained in a disc of filter-paper, as used with this apparatus, would only weigh 0·00002 gramme, and even if the paper were of a commoner quality it would make no difference.

3. The velocity of filtration is very great; the water flowing into the beaker in so uninterrupted a current that it appears as if no paper disc were present. When precipitates are to be filtered off, the velocity

is somewhat less; but it is then far more rapid than by the ordinary plan, and not less rapid than by Bunsen's method.

4. Since the filtering-tube dips under the liquid, no air can pass through the precipitate until it has been completely washed.

5. When a mineral has been dissolved, or when two substances have to be separated from each other, instead of, as is done by the ordinary method, placing them in a beaker to be further treated, the precipitate by this method remains in the crucible, and can be ignited directly after filtration.

6. This apparatus serves as a filtering-stand, and also as a syphon and pipette.

7. The whole apparatus may be readily kept free from dust, and, if required, any gas can be readily admitted to protect a liquid to be filtered from contact with air, while a boiling solution can also be readily filtered.

8. Even so small a quantity of substance as a couple of milligrammes is sufficient for analysis. With so small quantities the entire precipitate remains fixed to the filtering-disc, and may be burnt on the lid of a crucible, while any other very small portion of the substance which may adhere to any part of the apparatus may be readily removed and estimated.

9. The use of this apparatus, and the employment of small quantities of substance for analysis, occupy only about one-third of the time as compared with that required for analyses done by the ordinary plan. As an instance of the advantage of employing this method of analysis, the author quotes the following:—A mixture was taken of magnesia, potassium chloride, and common salt, adding thereto some hydrochloric acid so as to convert the magnesia into chloride, expelling any excess of that acid by a gentle heat. The dry saline mass was redissolved in water, and mercury oxide added. The mass was next gently heated in a covered crucible, until all the mercury was volatilised, and the dry residue again treated with water and filtered by means of the filtering-tube above described, by which operation the magnesia was left behind in the crucible. It was then dried in the air-bath and ignited. The solution of the alkalies was next treated in the usual manner with platinum chloride and alcohol, and the potassium platino-chloride, after having been separated from the liquid by the filtering-tube, dried at 105°. The small filter-paper disc, to which hardly a particle of the salt adhered, was removed, and the potassium platino-chloride, first ignited by itself alone, and afterwards with the addition of the paper disc; the result being that the organic matter of the paper was sufficiently large to cause the reduction of the platinum to the metallic state. The materials left in the crucible were washed with hydrochloric acid to remove any trace of magnesia, and again ignited; the platinum in the filtrate was also reduced to metal, and the sodium chloride present estimated in the usual way,

care being taken to remove and estimate the very small quantity of magnesia by means of sodium phosphate, and to deduct the weight of the magnesia thus estimated from the weight of the sodium chloride.

The results were as follows :—

	Quantities taken.	Quantities found.
Magnesia . . .	0·0690 grm.	0·0688 grm.
Potassium chloride .	0·1873 „	0·1852 „
Sodium chloride . .	0·0876 „	0·0900 „
	0·3439 „	0·3440 „

It appears that the magnesium chloride was completely converted into magnesia again, notwithstanding the small loss of this substance due to the solubility of some of it in the alkalies present; that the quantity of the potassium salt found was deficient is accounted for by the fact that the salt was only washed with dilute alcohol, without any addition of ether to lessen the solubility of the potassium platinochloride. The author twice analysed a portion of a mineral, skolezite, from Scotland, taking in the first case 0·985 gramme of substance, and in the other 0·0807 gramme, the result being that the percentage composition of the substance was found to be :—

	I.	II.
Silica	46·20	46·35
Alumina	26·28	26·21
Lime	9·22	9·17
Soda	5·16	5·10
Water	13·25	13·45
	100·11	100·28

In reference to the difference of the quantity of water, the author observes that the substance had been kept for several months under a desiccator. It is clear that the principle of the apparatus above described may be applied to qualitative analysis, and also in technology on a larger scale, for which purpose a porcelain plate perforated with small holes may be used with a disc of filter-paper.

An Improved Filtering Medium

For the removal of manganese dioxide from the nitric acid, in which solution it has been precipitated by potassium chlorate, a special filter is necessary.

After some experimenting Geo. Wm. Sargent and J. Kirk Faust [1] have adopted the following as giving the most satisfactory results :— A carbon filtering-tube with a stem 5 inches long, and a body $3\frac{1}{2}$ inches long and $1\frac{1}{4}$ inch in diameter, is filled $\frac{1}{4}$ inch with quartz sand, a small piece of glass-wool being used to retain the sand ; over this a thin layer of asbestos is formed by pouring in the asbestos shaken up with water and sucking the bed dry. A little hot dilute nitric acid is

[1] *Chemical News*, April 7, 1899.

poured back and forth through the tube several times, when it is ready for use.

When a heavy precipitate is encountered, the bulb from a syringe is used to force air into the tube and drive the liquid through, care being taken to keep the bulb compressed until removed from the tube.

It has been found that the quickest and best way to wash the manganese dioxide consists in allowing the nitric oxide to run entirely through the filter, then washing all the residue in the beaker into the tube with cold water, and, as soon as the filter is drained, washing out the potassium chloride with hot water. The filter and manganese dioxide are blown out into the beaker, and the dioxide reduced with ferrous sulphate, &c. The sand and asbestos are recovered and used time and again. The washings and nitric acid filtrate are found to be free from manganese.

This sand filter can be used for the removal of ammonium phosphomolybdate from the solution in which it was precipitated. It was found best to place a few pieces of glass rod upon the asbestos to hold it in position when the solution was first being poured upon the filter. With this device the freeing of the precipitate and filter of molybdic acid is more easily and more quickly accomplished than when paper filters were used. The phosphomolybdate has a tendency to creep, and, unless the filter is fitted properly to the funnel, to get into the filtrate. This trouble is avoided by the sand filter.[1] To dissolve the precipitate, the ammonia solution is poured through the filter two or three times, and finally washed out with hot water. A number of determinations, using the sand and paper filters side by side, have been made on the same sample, and the results obtained agreed to a thousandth. It is found best to wash the sand filters, used to catch the ammonium phosphomolybdate, with ammonia as well as with nitric acid, since in the ammonia washings silica and alumina have been found, and these would tend to clog the reductor.



Fig. 61.

Once made up, they stand ready for repeated use. By them one man is able to turn out in one day forty-two phosphorus determinations, every precipitate being washed until the droppings from the tube give no reaction for molybdenum when tested with ammonium sulphide.

The figure shows clearly the manner of making up these filters.

(*A*) In a process described by Isaac B. Cooke, a quantity of carded cotton-wool, so small that the ash in commercial analyses may be generally neglected, will suffice for any ordinary filtration; and a little experience enables the operator, by tight or loose packing, to adapt it to the coarsest or finest precipitate.

[1] *Chemical News*, vol. lxxix. p. 158.

A glass flask, of not more than about 300 c.c. contents, is fitted with a rubber stopper of soft and smooth surface, and of conical shape, so that the small end easily enters the neck of the flask; but the larger end cannot be forced in even under considerable pressure. Through the centre of the stopper a hole is bored to admit of a glass tube of about $\frac{3}{16}$ inch internal diameter. The tube to be inserted should be about 6 inches long; one end being fused to a very small opening, and the other slightly enlarged in funnel form. About 1 inch of the nearly closed end of the tube is passed through the stopper, fitting tightly; and if an inch traverse the stopper 4 inches will be left outside when the stopper is in its place. Into the funnel-shaped mouth of the tube a small quantity of the carded cotton-wool is packed with the tapering end of a wire not having too sharp a point. The cotton-wool should be lightly pressed in at first until it occupies a length of about $\frac{1}{2}$ to $\frac{3}{4}$ inch of the tube, and then may be pressed more tightly at the mouth according to the quality of the precipitate to be filtered off, leaving a spreading brush of about $\frac{3}{4}$ inch length projecting from the end.

To put the instrument into operation a small quantity of distilled water is poured into the flask, sufficient, but not more than sufficient, to quite cover the inner convexity of the bottom. The flask is then placed over the lamp till the water boils freely, and all air is expelled from the flask by steam. During the boiling the stopper should be placed in an inclined position, the short end of the tube resting against the inside of the neck of the flask, so as partially to close it, but leaving space for the air and steam to rush out. Unless the mouth of the flask is thus partially closed during the boiling, a much longer time is required to drive out the air; if quite open a circulation takes place, cold air passing in at one side as steam is driven out at the other.

When steam issues freely past the sides of the stopper, the flask may be taken from the lamp, and the stopper immediately pressed into its place and kept there by pressure until condensation begins. The flask is meantime inverted, and the tube with its brush of cotton-wool plunged into the liquid to be filtered, taking care that the wool is wholly submerged, as, if any portion be left dry protruding from the liquid, air will be drawn through it into the flask. As soon as the liquid is seen to be rising up the tube, the apparatus may be reared against a corner and left to itself.

The filtration will proceed with more or less rapidity in proportion as the cotton-wool is packed lightly or solidly into the tube. When all the liquid has been drawn up, and the air is about to follow, a stream of distilled water from the wash-bottle may be driven upon the precipitate to wash it; and as the last portion of this also passes up the washing can be repeated, and again as often as it is thought necessary. Lastly, the air following will leave the precipitate and the cotton-wool

in a condition almost dry. The contracted orifice of the inner end of the tube secures it also free from liquid.

It is generally advantageous to perform the filtration from a small porcelain evaporating basin of about 2½ inches diameter, supported on a cork ring. The liquid and precipitate can be gradually poured and washed into the basin as the process goes on. When it is completed the flask may be reversed, the stopper gently loosened, and the inner end washed by a stream from the wash-bottle into the flask. The cotton plug must now be carefully taken out by forceps over the evaporating basin, partially wiping the end of the tube in doing so with the clean portion of the plug, and the whole added to the precipitate. The forceps should be carefully wiped with a very small piece of cotton-wool, which may be further used with the forceps to complete the cleaning of the tube, and then also added to the precipitate. The basin, after being rapidly dried over the lamp, is ready for ignition. The precipitate cannot well be separated from the plug without loss; but there are few cases in which it will be injured by being ignited with the same quantity of cotton of which the plug consists, or, at least, in which that injury cannot be remedied by re-ignition after treatment with nitric or sulphuric acid. On cooling, the basin and its contents can be weighed, and, after brushing out the ash, the basin alone; the difference of course being the weight of the ignited ash.

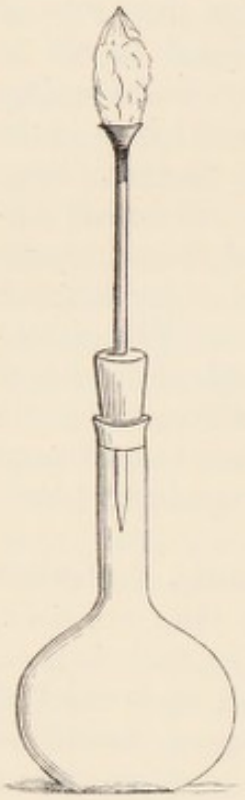


Fig. 62.

A flask of 100 to 150 c.c. capacity is usually sufficient for a filtration; but it is not safe to use one larger than 300 c.c. unless it be of a spherical shape without the flat or concave bottom, as larger ones are not always proof against the pressure. A spherical flask would be better also in respect of requiring a smaller quantity of water to drive out the air, and, therefore, also a shorter time to prepare it. In this case, however, if only a small part of the surface of the bottom is covered with liquid, care is required not to crack the flask during the boiling.

If the stopper be pliable, smooth, and well fitting, no air will pass between it and the neck of the flask during the operation. But the appearance of such leakage is simulated by the renewed boiling of the liquid in the flask in consequence of the diminished pressure. Unless the liquid has been boiled immediately before filtration, bubbles of air will constantly ascend the tube during the process. Yet the vacuum caused by the initial boiling will be so nearly completed that the filtration and washing may be continued if necessary till the body of

the flask is nearly filled with liquid, and on reversion only a portion of the neck will be occupied with air.

When a flask is found unexpectedly not to be large enough to contain all the liquid required by the washing, it is better to suspend the filtration before the flask is full, raising it out of the liquid to allow air to pass up the tube before reversing. The plug will then be in a dry state, and no portion of the liquid will run down the outside of the tube and be lost. Another flask in which the same stopper fits may be prepared by boiling, the tube inserted, and the filtration completed.

Filtration

(*B*) A great number of experiments have been made to shorten filtering operations. Asbestos felt supported on a perforated disc in a funnel throat is always used where possible. By this means finely divided precipitates which need repeated filtering through paper are readily disposed of; but it must be noted that with very fine precipitates, when once the filtration is begun, the funnel must not be allowed to run dry or the process stopped in any other way. Neglect of this precaution often allows the precipitate to pass through. Even if the filtration be stopped by placing the finger over the end of the funnel stem, the precipitate will run through when the filtration is continued. In dark-coloured solutions this point may be easily overlooked, and low carbon percentages in much-worked tungsten and chromium steels are often due to no other cause than this.

Asbestos may be very conveniently replaced by paper pulp, made from the clippings of soft ashless filter-paper. These devices had been used long before the admirable papers of Casamajor [1] were seen. The paper-pulp filter has been much used for separating the manganese oxide after precipitation with bromine and ammonia. The compact precipitate is not brought on to the filter until last. Having sucked the filter dry, it may readily be transferred to a crucible as follows:—Lift the edge of the felt with a forcep leg, then grasp it by its clean underside and lift it bodily into the crucible. A piece of moistened filter-paper, about $\frac{3}{4}$ inch square, laid on the first finger and pressed from the neck to the rim, the other hand meanwhile turning the stem, makes the funnel perfectly clean and involves less trouble than the truncated filter-paper proposed by Casamajor. Unless the felt is laid rather thick or sucked hard, thus more or less impeding the filtration, the impact of the liquid on the new filter disturbs the pulp, and may cause a little precipitate to pass through. This may be obviated by laying a piece of filter-paper the size of a sixpenny piece on the centre of the pulp, and allowing the liquid to strike it. Our experience with felts has led us to adopt them only when the precipitate is crystalline and open, or needs little or no washing.

[1] *Chemical News*, vol. xlvi. p. 8; vol. xxxii. p. 33.

The rapid filtration is largely due to the power the felt has of holding the funnel stem full of water. An ordinary filter-paper acts better when this condition obtains, but it is not always, even when intended, that this happens. With small filters the following plan acts well. Fit and wet the paper as usual, then draw the paper bodily for a little way up one side of the funnel, having previously stopped the stem with the finger. When the stem has filled with water, push the paper down again and remove the finger. The column of water is invariably held with a smooth funnel; a fluted one is not so certain.

Separation and Subsequent Treatment of Precipitates

F. A. Gooch, impressed with the desirability of further improvement in those processes of quantitative analysis which involve the use of dried filters, or the separation of filter and precipitate before ignition, uses a felt of anhydrous asbestos, prepared as follows:—

First.—White, silky, anhydrous asbestos is scraped to a fine short down with an ordinary knife-blade, boiled with hydrochloric acid to remove traces of iron or other soluble matter, washed by decantation, and set aside for use.

Secondly.—A platinum crucible of ordinary size, preferably of the broad low pattern (fig. 63), is chosen, and the bottom (fig. 65) perforated with fine holes (the more numerous and the finer the better) by means of a steel point; or, better still, the bottom may be made of fine platinum gauze. Next a Bunsen funnel of the proper size is selected, and — following Munroe's plan for holding his porous cones—over the top a short piece of rubber tubing is stretched and drawn down until the portion above the funnel arranges itself at right angles to the direction of the stem. Within the opening in the rubber the perforated crucible is fitted as shown in fig. 64, and the funnel is connected with the receiver of a Bunsen pump or other exhausting apparatus in the ordinary manner.



Fig. 63.



Fig. 65.

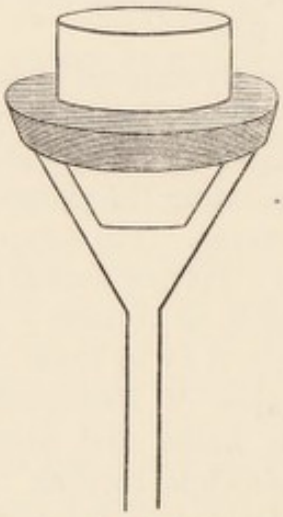


Fig. 64.

To make the asbestos felt, the pressure of the pump is applied and a little of the asbestos prepared as described, and, suspended in water, is poured into the crucible. The rubber and the crucible are held together by the pressure of the vacuum pump with sufficient force to make an air-tight joint; the water is drawn through, and the

asbestos is deposited almost instantly in a close compact layer upon the perforated bottom ; more asbestos (if necessary), in suspension as before, being poured upon the first until the layer becomes sufficiently thick for the purpose for which it is intended. Finally, a little distilled water is drawn through the apparatus to wash away any filaments that might cling to the under side, and the filter is ready for use : the whole process occupying scarcely more time than is necessary to fold and fit an ordinary paper filter to a funnel.

To prepare the filter for the estimation of a precipitate, the crucible, with the felt undisturbed, is removed from the funnel and ignited. In case the precipitate to be subsequently collected must be heated to a very high temperature for a long time, it is better to enclose the perforated crucible with its felt within another crucible ; because in such cases asbestos felt is apt to curl at the edges, and without such precaution some of the precipitate might drop through the perforations and be lost. For drying at low temperatures, however, and even for ordinary ignitions, a second crucible is unnecessary ; but during the ignition of an easily reducible substance care must be taken to prevent the contact of unburnt gas with the perforated bottom.

To perform the filtration, the crucible is replaced in the funnel, the pressure applied, and the process conducted precisely as in an ordinary filtration by the Bunsen pump. It is necessary to observe that the vacuum pump is to be started before pouring the liquid upon the filter. The final drying or ignition, as the case may be, of precipitate and filter is made without difficulty or need of extra precaution.

When turbid liquids are to be filtered, or gelatinous precipitates separated, instead of the perforated crucible it is better to use a platinum cone (figs. 66 and 67), the upper part of foil (to make a tight joint with the rubber fitting of the funnel), the lower of gauze. The method of covering the gauze with felt is identical with that described above. By reason of the larger filtering surface of this apparatus, the tendency to become clogged is, of course, very much diminished. When subjected to prolonged ignition, the gauze cone is enclosed within a crucible or a cone of platinum foil.



Fig. 66.

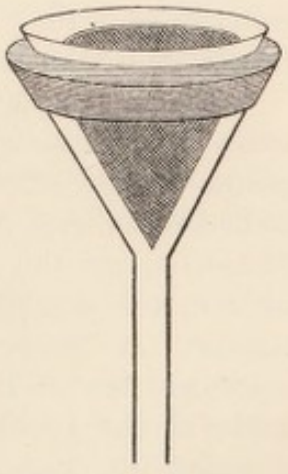


Fig. 67.

In operations in which platinum is liable to receive injury, a porcelain crucible with a perforated bottom may be used ; but recourse to this is rarely necessary, particularly when one may use the gauze cone, protected as it is by asbestos felt ; moreover, the perforation

of porcelain with numerous fine holes is a matter of considerable difficulty and expense.

Asbestos felt may be also used in the process of reverse filtering, it being merely necessary to dip the platinum rose into the asbestos mixture, after starting the vacuum pump, in order to make the felt. The rose, with the felt attached, and the vessel in which the precipitate is collected are to be weighed together, both before and after filtration.

Nothing can be simpler than the whole method of preparation and use of the apparatus which has been described, and its efficiency is extremely great. Clean water may, under the pressure of a Bunsen pump, be passed through a gauze cone coated with asbestos felt, which exposes a filtering surface of 24 square centimetres (nearly the same as that of a paper filter, 8 centimetres in diameter, when folded in the ordinary manner) with ease at the rate of a litre per minute.

When the filtering surface is less, the rapidity of filtration is, of course, somewhat diminished, but always exceeds that of paper of the same dimensions. When the felt is deposited upon gauze, the layer may be surprisingly thin, and yet be efficient enough for all ordinary purposes. If the layer of felt be thick, the filtrate from barium sulphate freshly precipitated in the cold may be made to pass through clear. But the great superiority of asbestos felt lies in its constancy of weight, whether dried at high or low temperatures, the rapidity with which it may be safely and completely dried, and its refractoriness as regards acids (excepting hydrofluoric acid) and alkalies.

A Method of Filtration by Means of Easily Soluble and Easily Volatile Filters

The processes of analysis, in which it is desirable to redissolve precipitates from the filter after washing, or to separate a mixed precipitate into parts by the action of appropriate solvents, are many.

When a complete solution is the object, and the precipitate yields easily to solvents which do not affect paper injuriously, the use of the ordinary filter offers no difficulty. When, however, precipitates are to be treated with reagents which disintegrate paper filters, the case is otherwise, and the attempt to remove by solvents any individual part of a mixed heterogeneous mass upon a filter is always an uncertain matter. As examples of cases of this sort, difficult to deal with, we may take the solution of acid sodic titanate in strong hydrochloric acid; or the purification of baric sulphate from included salts by digestion in strong hydrochloric acid; or the separation of sulphides which are soluble from those which are insoluble in alkaline sulphides; or the washing out of free sulphur from precipitated sulphides by means of carbon disulphide; or the separation of calcic and baric sulphates by the action of sodium hyposulphite. In cases of this nature it is

often convenient to make use of the asbestos filter, but this sometimes has disadvantages. Thus, to recur to the examples just cited, acid sodium titanate may be filtered and washed upon an asbestos filter, and felt and precipitate treated together with hydrochloric acid, but it will be impossible to determine when solution is effected, because of the floating asbestos; and in separating the sulphides it would be necessary to know the weight of the asbestos felt, since it must be weighed finally with the insoluble sulphides, unless removed by a special treatment which involves the solution, filtration, and reprecipitation of the latter.

It is to meet cases like these that F. A. Gooch has sought for a filter which, in the reversal of the ordinary mode of separating filter and precipitate, should dissolve easily in solvents which do not affect the ordinary precipitates met with in analysis. The material which seems best suited to the case—light and fluffy, capable of making secure filters of any desirable degree of porosity, sufficiently insoluble in water and aqueous solution of salts, alkalies, and acids (except strong sulphuric, strong nitric, and glacial acetic acids), easily soluble in naphtha, benzol, carbon disulphide, ether, boiling alcohol, and essential oils, and not too costly—is anthracene.

The mode of preparing and using the filter is simple. Anthracene is slightly moistened with alcohol to make it miscible with water, diluted to the right consistency, and applied to the same apparatus, and in the same way as the emulsion of asbestos which is employed in making asbestos felts; that is to say, enough of the emulsion in water to form a layer of the proper thickness is poured into a perforated crucible, which is held tightly in a packing of rubber tubing stretched over a funnel fitted in the usual manner to a vacuum flask or receiver. After washing with water the filter is ready for use. If the felt happens to be too coarse for the use of the moment, it may be made as close as need be by coating the felt first deposited with a finer emulsion, made by dissolving anthracene in hot alcohol and precipitating with water. When voluminous precipitates are to be filtered, the large perforated cone already described may be substituted with advantage for the crucible; or Cooke's improved form [1] of Carmichael's process of reverse filtration may prove most useful. In using the cone it is well to apply the anthracene in a thick layer.

To remove the anthracene filter from a precipitate it is only necessary to act with the proper solvent. It is usually convenient to stand the crucible containing precipitate and felt in a small beaker, add enough of the solvent, and gently warm until the anthracene dissolves. On the addition of water, or the reagent to work upon the precipitate, the solution of anthracene floats, and nothing remains to obstruct or obscure the action. If the precipitate dissolves entirely, the solution of anthracene may be separated from the aqueous solution by simply

[1] *Proceedings of the American Academy*, vol. xii. p. 124.

pouring the liquid upon a filter previously moistened with water, when the solution in water runs through, and the anthracene and its solvent remain and may be washed indefinitely with water.

If, on the other hand, the case is one of the division of precipitates, the anthracene and its solvent may be made to pass the filter, after the water has run through, by adding a little alcohol to overcome the repulsion between the solution and the water which fills the pores of the filter, the precipitate which stays behind being washed first with a solvent of anthracene, and then, if necessary, with alcohol followed by water ; or, if the vacuum filter be used (either paper or asbestos, according to the circumstances of the case), both liquids leave the precipitate and traverse the filter together.

In general, Dr. Gooch prefers benzol as the solvent for anthracene, but some advantage may be gained in special cases by a proper choice of solvents. Thus, in removing intermixed sulphur from precipitated sulphides, both the anthracene and the sulphur may be dissolved in carbon disulphide in a single operation.

The ready volatility of anthracene, at a temperature very near its melting-point, 213° C., makes it easily separable in cases when to remove it by a solvent is not advisable. The treatment of a solution of anthracene, for example, with strong sulphuric or nitric acid is apt to produce carbonaceous or gummy residues. In such cases it is well either to heat the precipitate and filter directly, or to first remove them from the crucible by means of a solvent for anthracene, then evaporate this, and raise the heat gently until the anthracene has vanished. The purification of precipitated baric sulphate, by dissolving it in hot, strong sulphuric acid, and reprecipitating by dilution, is a case in point, and one, too, in which the reversed filter may be used with great advantage. It may be remarked, in passing, that if one does not happen to possess a platinum rose and does happen to have at disposal a perforated crucible, a very fair reversed filter may be improvised with the crucible, a piece of glass tubing, and a rubber stopper, the last being fitted to the crucible, and the tube passed through nearly to the perforated bottom.

Rapid Separation of Slimy Precipitates

K. Zulkowsky effects this in many cases by shaking up the liquid containing the precipitate with $\frac{1}{3}$ volume of ether. The ether entangles the precipitate and carries it to the surface, so that the clear aqueous solution can be withdrawn. The precipitate is then obtained on allowing the ether to evaporate.

Separation of Minerals for Analysis

E. Sonstadt avails himself for this purpose of their different specific gravities. He prepares a heavy liquid (sp. gr. 3·01) with a solution of mercuric iodide in potassium iodide, by adding alternately

those salts in a dry state to the solution, until no more of either is dissolved. The free iodine which sometimes colours it is then removed by means of a crystal or two of sodium thiosulphate, and the liquid, which possesses a very high density, then presents a light straw colour.

The roughly crushed mineral is thrown into the solution, when any ingredients heavier than 3·01 sink, while the lighter ones float. The solution may be diluted if required. Each class can thus be collected separately, and requires merely to be washed in distilled water.

On the Incineration of Filters

A previous complete drying of the precipitate is not merely a loss of time, but a disadvantage, while introducing the still moist precipitate into the crucible requires the application of a very gentle heat at the outset, and thus ensures the most favourable conditions for the easy and complete incineration of the filter-paper. Precipitates not washed upon the filter-pump can be readily brought to a sufficient degree of dryness if laid for a short time upon blotting-paper or unglazed earthenware.

Dry filters may be also much better incinerated after previous charring at the lowest possible temperature than by rapid carbonisation or direct ignition in the flame. How advantageous it is to char previously very slowly may best be seen on incinerating filters whose contents impede the complete combustion of the paper by the old process—*e.g.* silicic acid, magnesium-ammonio phosphate, &c. Charred paper obtained by rapid heating is deep black and of a silky lustre, while if slowly carbonised it is brownish black, dull, and smoulders away like tinder. Charred paper of the first kind appears under the microscope perfectly amorphous, while the other displays the carbonaceous skeleton of the fibre.

A careful removal of precipitates from the filter—with the exception of cases like zinc and cadmium, where volatile reduction-products may be formed—is quite useless, since the errors which it was hoped to obviate are not really avoided. On incineration with the filter, wet or dry, an error due to reduction may be easily corrected—*e.g.* in barium sulphate with sulphuric acid ; in lead sulphate with nitric and sulphuric acids ; in iron and copper oxides with nitric acid ; in silver chloride with nitric and hydrochloric acids, &c.

Indicators for Alkalinity

(*A*) The comparative sensitiveness of litmus, methyl-orange, phenacetoline and phenol-phthaleine has been carefully studied by R. T. Thomson. In the absence of all interfering agents, litmus and methyl-orange are equally sensitive ; phenacetoline and phenol-phthaleine about five times more sensitive.

If soda exists as hydrate along with sodium carbonate, phenacetoline

and phenol-phthaleine are not suitable, if the proportion of carbonate is large.

For ammonia phenol-phthaleine is useless, as it does not distinctly indicate the end of the reaction.

In the estimation of alkalies existing as carbonates and bicarbonates, the well-known fact is mentioned that litmus cannot be used for the estimation of ammonia in the commercial carbonate without adding excess of acid, boiling to expel carbonic acid, and titrating back with an alkali. The same holds good for phenacetoline. Methyl-orange appears to have given an apparent excess of ammonia. Phenol-phthaleine is useless for ammonium carbonate, and requires tedious boiling with the carbonates of the fixed alkalies.

In presence of alkaline sulphates, nitrates, and chlorides, litmus and phenacetoline are as delicate as in their absence. With methyl-orange a greater quantity of normal acid is needed to bring out the full pink colour than if distilled water only were present. Phenol-phthaleine is unaffected by the above-named salts in case of potash and soda, but ammonia and its salts must be carefully excluded if this indicator is to be used.

If the alkaline sulphites are present, the results given by all the indicators are vitiated.

Sodium thiosulphate is neutral to all the indicators.

With sodium sulphide, litmus, methyl-orange and phenacetoline gave accordant results; phenol-phthaleine showed one half too little Na_2S, unless boiled, when it approached the truth.

If alkaline phosphates were present, methyl-orange gave results slightly higher and nearer the truth than litmus, the end of the reaction being more distinct. Phenol-phthaleine cannot be depended upon. If phenacetoline is used, the normal acid must be added until a permanent colour is produced, when the results agree with those obtained with litmus.

If sodium silicate is present, litmus, methyl-orange and phenacetoline give results which do not materially differ. With phenacetoline the end reaction is indistinct. Phenol-phthaleine gives results considerably too low.

With sodium aluminate litmus gives too high a result, and an indistinct termination: with methyl-orange the result is much too high, while phenacetoline and phenol-phthaleine give a correct estimation.

Potassium nitrite is neutral to litmus, phenacetoline, and phenol-phthaleine; methyl-orange is not admissible.

For the estimation of soda in borax, methyl-orange shows a correct result, and the end of the reaction is quite distinct. With litmus and phenacetoline the end is indistinct, and phenol-phthaleine is utterly useless.

On the estimation of the mineral acids with a caustic alkali, it need

only be said that ammonia must not be used with phenol-phthaleine. Sodium carbonate can be used in the cold with methyl-orange. If phenacetoline is to be employed, a little carbonate must be used along with the caustic alkali.

For free oxalic acid, litmus and phenol-phthaleine give distinct and concordant results, while methyl-orange and phenacetoline cannot be recommended.

For free acetic acid, methyl-orange and phenacetoline are not well adapted. With litmus the end of the reaction is not easily recognised. Phenol-phthaleine works admirably.

For tartaric acid the results are similar, phenol-phthaleine showing the most distinct reaction.

With citric acid, limejuice, &c., the case is similar, methyl-orange and phenacetoline being useless, and phenol-phthaleine giving a sharper end reaction than litmus.

(*B*) For estimating caustic alkalies in presence of alkaline carbonates, and quicklime in presence of calcium carbonate, Dr. Lunge recommends a method first suggested by Degener.

The solution of lime is coloured with phenacetoline, and normal acid is dropped in as long as the yellowness produced by each drop at once gives place to redness. If this change does not occur for a few seconds, the burette is read off, and two more drops of acid are added. If the liquid remains yellow, the former reading was correct; but if it becomes red, the addition of the acid must be continued until a permanent yellow colouration is established.

The estimation of caustic soda is effected directly by titration with acid, using phenacetoline as indicator. As soon as the liquid remains of a faint rose colour all the sodium hydroxide is saturated, and only the carbonate remains. If more acid is added, the yellowish-red colouration changes suddenly to a golden yellow. At this point the carbonate also is saturated. The process is most suitable for caustic lyes which contain moderately large proportions of carbonate. Ammonia behavés differently from caustic soda, and is at once reddened by phenacetoline.

Dr. Lunge recommends practice with this indicator with liquids of known composition, so as to acquire a knowledge of the correct shade of colour.

Ultramarine Test-Paper.—The great sensitiveness of artificially made ultramarine for even very weak acids has been turned to account by applying that pigment to prepare a test-paper especially suited for the rapid detection of the presence of free acids in such salts as aluminium sulphate, alum, and other similar compounds. The ultramarine intended for this use should be that known commercially as No. 1; it should first be mixed with some water, collected on a filter, and then thoroughly washed with some boiling distilled water, and afterwards incorporated with a mucilage made of 1 part of selected

Irish moss, previously washed with cold water, boiled with about 30 parts of distilled water; the pigment thus obtained is uniformly painted over best filter-paper, and, after drying, cut up into strips, as is usual for litmus-paper, and preserved in a glass-stoppered bottle. In order to test the ultramarine, it is necessary to prepare a perfectly neutral alum in the following manner. Alum of commerce, by preference potash alum, is dissolved in from 8 to 10 times its weight of boiling water, and this solution is poured into twice its bulk of alcohol at 80 per cent. The alum separated after complete cooling is collected, redissolved in boiling water, and the solution again poured into the same quantity of fresh alcohol of the same strength; the alum which separates on cooling is collected on a filter, and, after having been washed with alcohol, dissolved in water; a drop or two of this solution should not discolour the ultramarine, while its almost instantaneous discolouration should follow on its being touched with a drop or two of very dilute sulphuric acid, 1 part of strong acid to from 50 to 60 parts of distilled water.

Application of Hydrogen Peroxide in Chemical Analysis

The behaviour of hydrogen peroxide with ammonium sulphide, or of hydrogen sulphide with ammoniacal hydrogen peroxide, may be used qualitatively for the detection of these compounds, and quantitatively for estimating hydrogen sulphide, whether gaseous or in solution, and for estimating the sulphur or the metal in metallic sulphides. In cases where the sulphide can be decomposed by the direct action of hydrogen peroxide in presence of ammonia, it takes place in this manner; in other cases, as in the sulphides which on heating with hydrochloric acid evolve definite quantities of hydrosulphuric acid, it takes place by conversion into sulphuric acid or barium sulphate. Just as hydrogen sulphide or metallic sulphides are oxidised to sulphuric acid or to sulphates, sulphurous acid and sulphites are oxidised to sulphuric acid or sulphates. These reactions may be utilised in various directions.

Several metallic sulphides are completely oxidised by ammoniacal hydrogen peroxide without the formation of precipitates, as the arsenic, copper, zinc, and thallium sulphides. After the expulsion of the ammonia all the copper is deposited by a copper solution as a dirty green precipitate, not changed by ignition. From the zinc solution only a part of the zinc is separated as a white deposit. On the action of hydrogen peroxide upon antimony trisulphide a part of the antimony separates as a white precipitate, while the liquid contains all the sulphur as sulphuric acid. Tin sulphide is decomposed in a similar manner, oxide being deposited and the sulphur oxidised to sulphuric acid. With the other metallic sulphides the behaviour of hydrogen peroxide is very various. It attacks mercury sulphide, which is scarcely affected

by nitric acid, very energetically. After the expulsion of the mercury there remains a spongy precipitate which settles quickly, dissolves in hydrochloric acid, and is converted into a white powder by the action of nitric acid. After the conversion of mercury sulphide by the action of hydrogen peroxide, no mercury can be detected in the filtrate. Cadmium sulphide is decomposed with formation of a yellowish-white precipitate, easily soluble in hydrochloric acid. When the oxidation is completed a part of the cadmium remains in the filtrate as sulphate.

Certain metallic sulphides, the solutions of which in acids are precipitable by ammonia, are decomposed by hydrogen peroxide with formation of sulphuric acid and separation of hydroxides; thus iron sulphide, which is oxidised as just mentioned, and manganese sulphide, which is quickly and completely decomposed with formation of sulphuric acid and separation of a mixture of hydrated peroxide and oxide. On heating cobalt sulphide with ammoniacal hydrogen peroxide there is first formed soluble cobalt sulphate, which on prolonged heating is further attacked, with formation of a dirty brown precipitate. Nickel sulphide is decomposed in the same manner, with formation of a green precipitate which does not contain all the nickel. Silver and bismuth sulphides are not attacked by ammoniacal hydrogen peroxide; lead sulphide is readily converted into sulphate.

The property of hydrogen peroxide in alkaline solution, of easily and completely oxidising hydrogen sulphide to sulphuric acid, may be used, in the first place, for the estimation of hydrochloric, hydrobromic, and hydriodic acids in liquids containing hydrogen sulphide. These estimations have occasioned much trouble to analysts.

From the estimation of hydrochloric acid along with hydrogen sulphide an ammoniacal solution of hydrogen peroxide is added, and the mixture is boiled until no more bubbles of oxygen rise up. Nitric acid and silver nitrate are then added, and the silver chloride is estimated in the usual manner.

For hydriodic acid in presence of hydrogen sulphide the procedure is similar, but the hydrogen peroxide is used mixed not with ammonia, but with sodium carbonate. The mixture is boiled as before, and silver nitrate is added, and nitric acid until a faintly acid reaction is produced.

In estimating hydrobromic acid under similar circumstances the process is exactly the same as for hydriodic acid.

In the metallic sulphides capable of direct oxidation by hydrogen peroxide the quantity of metal can be calculated from the sulphuric acid formed. This method is applicable to the sulphur compounds of arsenic, antimony, zinc, copper, and cobalt. The sulphide is dissolved in ammonia, treated with sufficient hydrogen peroxide, boiled to expel excess, the liquid is acidulated with hydrochloric acid, and the sulphuric acid precipitated with barium chloride.

Antimony trisulphide is treated exactly like arsenic trisulphide:

indicated by the accompanying table. It is given here to illustrate the adaptability of some of the well-known but more positive and satisfactory tests for the several metals.

Precipitate A contains iron, manganese, cobalt, and nickel.

(*a*) Test for iron by dissolving a small portion of the precipitate in dilute hydrochloric acid and adding potassium thiocyanate.

The blood-red colouration is due to ferric thiocyanate.

(*b*) For manganese, to 5 c.c. of water add 5 c.c. concentrated nitric acid and 5 to 10 grammes Pb_3O_4. Stir into the warm mixture a little of the precipitate and let stand. A purple solution is permanganic acid.

(*c*) In absence of iron or manganese, stir a little of the precipitate into dilute hydrochloric acid, and add solution of potassium iodide and starch. In presence of iron and manganese use the bead test.

(*d*) Boil some of the precipitate with bromine water till all bromine is expelled, add water and solution of potassium iodide and starch, $Ni(OH)_3 + KI = Ni(OH)_2 + KOH + I$, imparting the blue to the solution.

Solution A contains all the aluminium, zinc, and chromium. The yellow colour is evidence of chromium. Acidify with hydrochloric acid, boil, and add ammonium hydroxide.

Precipitate B consists of aluminium hydroxide, and any chromium hydroxide that may have escaped oxidation. Dissolve in nitric acid, and repeat the precipitation with sodium peroxide, or apply the blowpipe and cobalt test for aluminium.

Solution B contains zinc and chromium.

(*a*) Test for zinc by adding to a portion a few drops of potassium ferrocyanide. A heavy white precipitate indicates zinc.

(*b*) If further verification of chromium is needed, make the solution acid with hydrochloric acid, and boil with a little alcohol added. The chromium reverts to the green chromic chloride.

In the presence of phosphates the method so far employed has been as follows:—Upon dissolving the precipitate from the ammonium sulphide in concentrated nitric acid, a very little of the solution is tested for phosphoric acid in the usual manner. If present, granulated tin is added and the boiling continued. Filter from the insoluble tin phosphate, make ammoniacal, re-precipitate with ammonium sulphide, and proceed as with phosphoric acid absent. Any method not involving the use of tin, and depending upon the non-formation of the phosphates of iron, manganese, and nickel, is as yet unsatisfactory. Having removed the barium and strontium with sulphuric acid before the precipitation with ammonium sulphide, the oxidation and precipitation by means of sodium peroxide may be performed as usual; but before filtering, the solution is made acid with acetic acid, and boiled a

little further and filtered. The filtrate now may contain, besides the aluminium, zinc, and chromium, the nickel which is readily soluble in acetic acid, and the calcium and magnesium which have been brought along by means of the phosphoric acid. A little of the cobalt, however, dissolves with the acetic acid, and a solvent has not been found thus far for the calcium phosphate and nickel hydroxide that will not dissolve traces of the other three metals of the precipitate.

The precipitate obtained in the ordinary method by means of ammonium hydroxide and ammonium sulphide contains, as hydroxides and sulphides, iron, manganese, cobalt, nickel, aluminium, zinc, and chromium, and is brought into solution by means of 10 to 15 c.c. of concentrated nitric acid with heat. Nearly neutralise with sodium hydroxide, then sift in slowly (with stirring) sodium peroxide in excess. Boil.

On the Correct Adjustment of Chemical Weights

The following description of the method adopted for adjusting a set of platinum weights is taken from the author's Memoir on the Atomic Weight of Thallium.[1]

A set of weights as ordinarily supplied by even the best instrument-makers is never absolutely exact; however carefully they may be adjusted, the pieces of metal which respectively represent 1000 grains, 100 grains, 10 grains, &c., are only more or less approximations to the true weights. In most chemical analyses the error arising from such inaccuracies in the weights used is so small, in comparison to errors of manipulation or to imperfections inherent in the chemical processes adopted, that it may generally be disregarded; but when the chemist has for his object the estimation of an atomic weight, or is engaged in other researches demanding the highest refinement of accuracy which chemistry and physics can supply, then he is bound to neglect no correction which will increase the precision of the results. That chemists whose well-trained reasoning powers allow them to take for granted nothing which is not capable of experimental verification, and who insist upon the utmost attainable precision in their balances, should, as a rule, neglect the probable errors which the inaccuracies of their weights may introduce, is somewhat inconsistent.

The weights employed in the experiments were of platinum. The platinum was quite pure; it was fused, cast, and then well hammered. The weights were adjusted by myself during May, June, July, and August, 1864: they were first roughly adjusted, and then the specific gravity of each weight was taken. The weights were heated to redness in a bath of magnesia previous to ascertaining their specific gravity. The density of the larger weights was ascertained to the second place of decimals, and that of the smaller ones to the first place. The record

[1] *Phil. Trans.* 1873, p. 277.

change its weight. Its surface does not become rough by crystallisation, or from little sand and dust particles which, being projected on the soft, white-hot metal, stick to it and make it often heavier.

Professor Brauner has used the same crucibles for the last twenty years, and they look like new to-day, and, what is more important, they do not leak, whereas crucibles which are heated directly over the blast invariably do so after a few months' use, so that they become unfit for any kind of exact work.

Analysis of the Gold and Platinum Salts of Organic Bases

C. Scheibler dissolves a weighed quantity of the acid or platinum salt in water, or, if it does not happen to be readily soluble, keeps it suspended therein, and places it in contact with metallic magnesium, whereby the metals gold and platinum are separated, and hydrogen is at the same time evolved. This operation is carried on at the ordinary temperature, or, if the salts are difficultly soluble, on a water-bath; the liquid may be acidified, but not with hydrochloric acid, since the object often may be to estimate chlorine also. The ribbon-like magnesium wire met with in commerce is sufficiently pure for this purpose. The gold and platinum separated during this operation are, by means of careful decantation, freed from the liquid wherein they are immersed, and next transferred to a filter and washed, first with distilled water and next, after the filtrates intended for the estimation of chlorine have been set aside, with dilute hydrochloric acid, in order thereby to remove any excess of magnesium or any magnesia which might remain mixed with or adherent to these metals; after having been well purified and dried the metals are ignited and weighed. The results obtained by this method are very correct.

To Prevent the Bumping of Boiling Liquids

(*A*) In cases where the introduction of any foreign matter into the liquid about to be distilled is undesirable, Dr. Hugo Müller, F.R.S., introduces through the cork in the tubulure of the retort a glass tube, which is drawn out to a long capillary tube and pressed tightly to the bottom of the retort. The upper end of the glass tube is connected, by means of an indiarubber tube, with a generator of carbonic acid, or hydrogen, or a gas-holder containing air, and while the distillation is going on, one of these gases is passed in a slow but continuous current through the liquid. Under these conditions all bumping is avoided, and the distillation proceeds with the utmost facility.

(*B*) For ordinary purposes, however, it is still more convenient to introduce into the liquid about to be distilled a small fragment of sodium amalgam or, in cases where the liquid is acid, a small piece of sodium-tin. Methylic alcohol is well known to be one of the most difficult liquids to distil; yet, on the introduction of a minute piece of

sodium amalgam or sodium-tin, it can be distilled without the slightest inconvenience. On one occasion Dr. Müller found that more than 400 grammes of methylic alcohol distilled over with perfect steadiness, and without exhausting the activity of a fragment of sodium-tin weighing not more than 0·06 gramme.

It is, perhaps, hardly necessary to mention that the action of sodium amalgam and sodium-tin is due to a minute but continuous disengagement of hydrogen taking place during the process of distillation.

New Form of Water-bath Regulator

H. Stafford Hatfield [1] has devised a simple regulator for maintaining for some time without attention a constant level of liquid in a water-bath. Some form of syphon is usually employed, connected with a

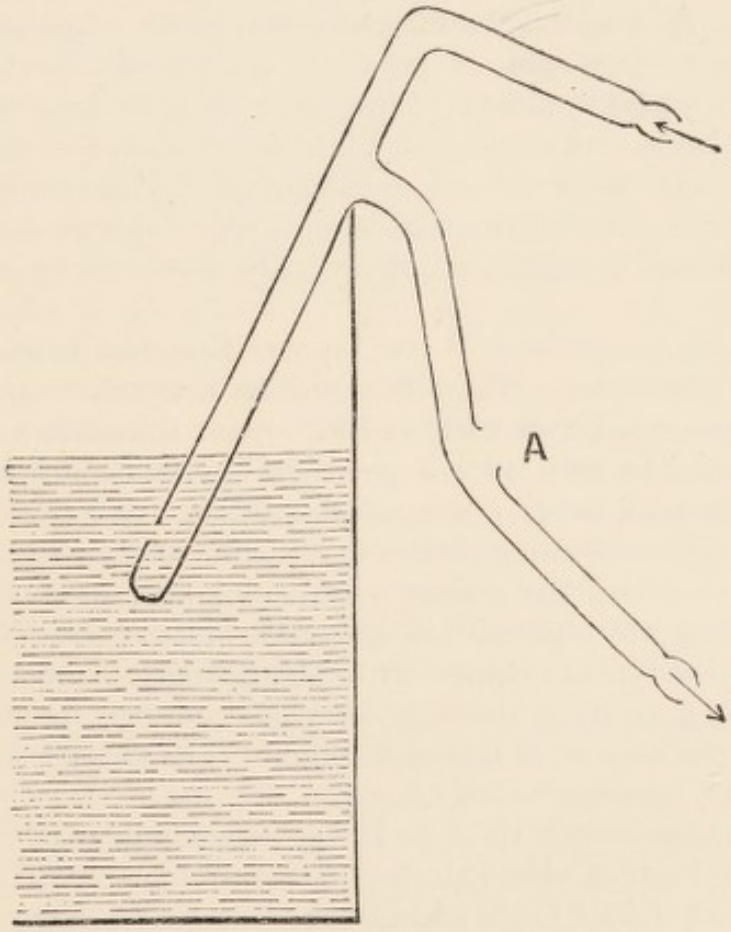


Fig. 68.

reservoir, maintained at constant level by inflow and outflow of water. But all such regulators cease to work in a short time if ordinary tap-water is used, because the heating of the inflowing water during its passage down the syphon-tube fills the latter with air, and so the supply ceases, unless an air-collector of considerable capacity is sealed on at the highest point of the syphon.

[1] *Chemical News*, Feb. 9, 1900.

Fig. 68 (page 679) illustrates a form of apparatus which renders unnecessary a reservoir, and which is not stopped in its action by air-bubbles. The supply-tube bifurcates, and one limb dips under the liquid in the bath. The other is opened to the air at A. The water in the bath will keep at the level of A, or slightly above it; the excess of level being due to the force necessary to divert the stream of water. All the tubes must be full of water, but air-bubbles on rising are immediately swept away by the current of water, which must be sufficient to do this properly, but need not be great. The water must leave the sides of the glass at A. The tubes may be bent to fit any particular form of vessel.

Thioacetic Acid

Robert Schiff[1] has proposed the use of thioacetic acid to replace in analytical operations the unpleasant and tedious use of sulphuretted hydrogen. He prepares the thioacetic acid in the following manner:—

One part by weight of powdered phosphorus pentasulphide is mixed with ½ part by weight of fragments of glass (not too small) and 1 part of glacial acetic acid, and the mass is placed in a glass vessel fitted with a thermometer and an ascending condenser, and heated upon the wire gauze with a luminous flame. The reaction begins without any troublesome tumefaction, and is easily regulated by means of the flame.

When the temperature of the vapours has risen to about 103°, the process is interrupted. The yellow product is rectified, and the portion which passes over between 92° and 97°—pure thioacetic acid—is used, either in the free state as a 6 per cent. aqueous solution, or as a salt in a 30 per cent. feebly ammoniacal solution. We thus obtain pure thioacetic acid amounting almost to one-third of the acetic acid used. For each operation the author used in a 2-litre flask 300 grammes phosphorus pentasulphide, 150 grammes broken glass, 300 grammes glacial acetic acid, and obtained 97 to 100 grammes of rectified thioacetic acid. This quantity, which does not require an hour to prepare, forms 300 cubic centimetres of thioacetic solution, and suffices for more than 150 ordinary qualitative operations.

In the glass vessels there is left a hard black mass, which can be removed by heating with soda-lye. To save the trouble of cleansing, the well-known wine-flasks common in Tuscany may be used. They are made of good thin green glass, and contain 2¼ to 2½ litres. Cut off two-thirds of the neck, melt off the aperture, inserting it in an ascending T-tube. When the reaction is completed the flask is thrown away.

All the operation is performed under a good draught-hood with a large flame burning in order to burn all escaping gases of an evil odour.

[1] *Chemical News*, Aug. 9, 1895.

This thioacetic method is important for the qualitative and quantitative recognition of arsenic in chemico-legal investigations. If a hydrochloric solution of arsenious or arsenic acid is boiled with thioacetate for about a minute, when the liquid is cold the arsenic is found to have been quantitatively precipitated from the clear liquid.

The difficulty of maintaining a long-continued current of hydrogen sulphide, absolutely free from arsenic—as required for judicial purposes —is well known. On the contrary, rectified thioacetic acid is always absolutely free from arsenic.

Liquid Baths for Melting-point Determinations

A mixture prepared by boiling together for five minutes 7 parts by weight of sulphuric acid (sp. gr. 1·84) and 3 parts by weight of potassium sulphate remains a transparent liquid at ordinary temperatures, and can be heated up to 325° without boiling. Such a mixture has been used by Heyward Scudder [1] as a liquid bath for melting-point determinations. If the proportions are changed to 6 parts by weight of acid and 4 parts of the sulphate, the mixture forms a soft mass at ordinary temperatures (though after boiling and then cooling down it will usually remain liquid for half an hour or more), melting from 60° to 100° and boiling above 365°. Acid potassium sulphate can be used instead of potassium sulphate. In this case the amount should be calculated to give the same ratio of potassium sulphate to sulphuric acid.

These mixtures are self-clearing and remain permanently white (turning slightly yellowish at about 230°) unless much organic matter gets in. They can be cleared, if brown, by boiling with a few drops of concentrated nitric acid or with a small crystal of potassium nitrate. The vapour is so slightly acid that the capillary can always be fastened to the thermometer by a rubber band, provided the band is 1 to 2 centimetres above the surface of the bath. Platinum wire need never be used. In preparing the bath, after the potassium sulphate has melted, the two layers should be mixed, or explosive boiling may occur.

Most melting-points given accurately are below 325°. The first mixture is therefore suitable for all ordinary purposes. It does not have to be renewed frequently, as does the ordinary sulphuric acid bath, nor does it become permanently discoloured as does paraffin after short use, even though prepared by distillation under diminished pressure.

If the bath has solidified (which happens sometimes under unknown conditions, though very rarely), boiling for a minute or two will bring it back to its original condition. If it has not been used for a number of weeks, it should be boiled for a minute or two before using for temperatures above 300°.

For temperatures from 360° to 600° Booth has found that the most satisfactory bath is fused zinc chloride. This melts to a clear

[1] *Chemical News*, Aug. 28, 1903.

transparent liquid at about 250°. After use it must be poured out on a tile while liquid, since it expands on solidification, and will crack any flask or beaker in which it is allowed to grow cold. It can be cleared from organic impurities by heating with a small crystal of potassium nitrate. Unless the zinc chloride used is pure, the bath will gradually become opaque after a short time, and cannot be made transparent again.

The temperatures given here are uncorrected. They were obtained in a melting-point apparatus made by inserting a test-tube in a round-bottom flask (150 to 250 cubic centimetres). The bottom of the tube is about 1 centimetre from the bottom of the flask. The bath is placed both in the test-tube and in the flask. In this apparatus fresh sulphuric acid (sp. gr. 1·84) can be used up to 280° to 300°. In using the sulphate mixtures, if the upper part of the tube becomes cloudy from a film of solid, it can be cleared by boiling with a little concentrated nitric acid. In using such an apparatus it is not safe to heat it much above the temperatures given here for the various baths, since the boiling is apt to start very violently. It is safe to heat it till large bubbles begin to rise moderately frequently.

When these baths are used in open beakers, it is not possible with sulphuric acid or the sulphate mixtures to obtain temperatures as high as those previously mentioned, without having disagreeable amounts of acid vapour given off. The zinc chloride bath can be used in a beaker up to about 600°.

The sulphate mixtures seem to contain some compound in a persistent state of supersaturation. Although possessed of considerable oxidising power when hot, it is a curious fact that they are markedly less caustic than hot concentrated sulphuric acid when dropped on the skin.

The Use of Sodium Peroxide in Analysis

Hempel, Spuller, Kalman, and Poleck [1] have investigated the oxidising properties of sodium peroxide. This reagent, exceedingly rich in oxygen, is more suitable than any other substance for oxidations at a red-heat.

If we mix chromiferous or manganiferous substances with about twice their weight of the peroxide, and heat on sheet-silver or platinum, the mixture becomes almost immediately deep yellow or green. Tungsten mineral, if mixed with 4 parts of the peroxide, gives in a few minutes a melt from which sodium tungstate can be easily extracted on treatment with water.

Titaniferous iron ore can be opened up in a very short time by mixture with 4 parts of sodium peroxide, and fusion in a silver crucible. The melt is extracted with hot water; the precipitate, containing ferric oxide and the titanic acid, is placed without washing in a

[1] *Chemical News*, May 17, 1895.

platinum crucible along with concentrated sulphuric acid, which is evaporated down to a slight residue. Hence we obtain all the titanic acid in solution if the liquid, when quite cold, is poured into a large quantity of cold water. If the solution is not perfectly clear it is filtered, and then the titanic acid is separated as usual by prolonged ebullition, with the introduction of sulphurous acid.

Sulphur compounds are oxidised with explosive violence. For determining sulphur Hempel uses, to 1 part of the substance in question, 2 parts soda and 4 parts of peroxide, and melts the mixture in a silver crucible. The chief part of the melt is conveniently poured into a capsule of silver, nickel, or platinum, standing in cold water. It is filtered, acidified with hydrochloric acid, and precipitated with barium chloride.

For the complete analysis of blende and galena it is also recommended to open up with sodium peroxide, since the iron is at once separated as oxide, while lead and zinc pass into the alkaline liquid.

Spuller and Kalman have also made experiments which lead to analytical methods. They have successfully oxidised with sodium peroxide ferrochrome, chrome-steels, chrome-iron ore, and sulphur ores.

The experiments of Poleck are also interesting. While a great number of organic liquids—glacial acetic acid, benzaldehyde, ether, &c.—are at once ignited, ethylic alcohol behaves quite differently; substances dissolved in alcohol can be easily oxidised by sodium peroxide. Iodine was oxidised to periodic acid, lead to sodium orthoplumbate. On the other hand, salts of silver and mercury, as also potassium permanganate, were reduced.

Sodium Peroxide as a Third Group Reagent

Sodium peroxide as a reagent has properties of a very unusual and striking character. These properties are no less valuable than peculiar, and indicate for this substance a prominent place in analytical work. S. W. Parr [1] has described the advantages and adaptability of sodium peroxide to qualitative analysis.

In the ordinary procedure for the separation of the metals the greatest difficulty arises in the third or iron group. These complications may be briefly enumerated as follows:—

(*a*) The separation of zinc in the presence of chromium.

(*b*) The unsatisfactory separation of cobalt and nickel from the other members of the group by the action of dilute hydrochloric acid on their sulphides.

(*c*) The variations arising from the presence of phosphates, &c.

It is not necessary to enlarge upon these difficulties. The one most commonly ignored in methods is usually outlined, and yet a very serious obstacle is the one designated under (*a*). Zinc and chromium

[1] *Chemical News*, April 23, 1897.

enter into a combination which, to a very large extent, resists the action of ammonia and ammonium salts. The use of barium carbonate to obviate this difficulty is cumbersome. By use of sodium peroxide we may oxidise the chromic compounds present to sodium chromate, and thus completely eliminate it as a factor in any precipitation likely to be employed, excepting of course such as would involve a reduction and return to the condition of a chromic salt.

The method of procedure is as follows :—The solution should be slightly acid. A small porcelain spoonful of the peroxide is slowly sifted in with constant stirring. The solution is then heated to complete the decomposition of the peroxide, and finally boiled for some minutes after the oxygen seems to be all driven off. The completeness of the oxidation may be easily tested by filtering from any insoluble constituents, acidifying, boiling, and making ammoniacal. A precipitate may be alumina or chromium oxide. Filter and wash free from all sodium chromate, redissolve in a little nitric acid, and treat as before with a small amount of sodium peroxide. A yellow colouration is due to the chromium which escaped oxidation by the first treatment. However, if properly conducted, the first operation should be complete. Similarly, the insoluble residue on the filter, if suspected of being a zinc-chromium compound, may be washed free from chromate, dissolved in dilute nitric acid, and treated again with the peroxide. The only condition so far governing the completeness of the transformation to the chromate form is the necessity of starting the oxidation with the chromium entirely in solution. Precipitated chromium hydroxide will undergo this transformation, but less readily, and especially if the precipitate is the double one of zinc and chromium.

Hence the advisability of beginning the oxidation with the solution containing some free acid, preferably nitric. The quantity of free acid is immaterial, less than 1 cubic centimetre being sufficient. It should be noted, however, that the amount of sodium peroxide should cause the solution to pass quite beyond the neutral condition, since the oxidation is only partial while in the acid state. It might be expected that the moment the addition of sodium peroxide passed the neutral point the precipitation of chromium would commence, and the completeness of the oxidation be lessened in consequence ; but this has not been found to be the case. The oxidising action of the peroxide is so pronounced that it precedes the precipitating action, hence the reason for using the dry sodium peroxide. A cold saturated solution of the peroxide will operate but incompletely. Hydrogen peroxide will also act similarly, but even less completely than the solution of sodium peroxide. For obvious reasons, also, the operation is performed on the solution before heating, and it is better to shake the powder in gradually than to drop the reagent in at once.

We are ready now to note the effect of such treatment as above indicated, upon the other members of this group, assuming that any or

all may be present, including cobalt and nickel. The results are as follows :—

(*a*) Aluminium compounds are in solution in the form of sodium aluminate, not different from the ordinary result from using sodium hydroxide in excess. It is assumed, of course, that the sodium peroxide has exceeded the free acid in sufficient amount to provide sodium hydroxide in excess.

(*b*) Zinc is similarly in solution as zincate.

(*c*) Iron precipitates as a very dense, reddish-brown precipitate, the exact composition of which is not quite known. The precipitation is complete, no re-solution being effected upon boiling. The filtration is performed with great facility. The precipitate is almost insoluble in concentrated nitric acid ; soluble in dilute acids on heating. If phosphates are present none are precipitated with the iron, but all pass through and are found in the filtrate.

(*d*) Manganese behaves exactly as iron, precipitating presumably as the hydrated dioxide, MnO_2xH_2O, having all the properties of that compound as to colour, solubilities, &c. Similarly also, phosphates are not precipitated. It should further be noted that from this precipitate can most readily be obtained the delicate test for the presence of manganese by formation of permanganic acid by means of nitric acid and lead peroxide or Pb_3O_4.

(*e*) Cobalt precipitates also a black hydrated cobaltic oxide with solubilities the same as in the case of iron and manganese. No phosphate is precipitated with the cobalt. The precipitate, in conjunction with dilute acid and potassium iodide, liberates free iodine, imparting an intense blue to starch solution. This latter property, however, is common to the precipitates of iron and manganese under (*c*) and (*d*).

(*f*) Nickel precipitates, as the ordinary green nickelous hydroxide, $Ni(OH)_2$, easily soluble in acid, either concentrated or dilute. As to phosphates, in the case of nickel, if present in large amounts, small quantities are found in the precipitated nickel. A re-solution and re-precipitation with sodium peroxide, however, eliminates all the phosphate from the precipitate. The behaviour of nickel in thus precipitating as the nickelous compound indicates for its higher form of oxidation a less degree of stability than exists in the case of cobalt. This property suggests the readiest and most delicate method for the detection of nickel, even in the presence of the three precipitates enumerated above, thus :—Boiling this precipitate of nickel with bromine water converts it at once into the black nickelic hydroxide, which has the property of decomposing potassium iodide with water alone, no acid being required, as in the case of iron, manganese, and cobalt. It is necessary, of course, to boil off the free bromine, which is readily accomplished. The action upon a potassium iodide starch solution is very marked.

The above facts suggest a method for the iron group which is

indicated by the accompanying table. It is given here to illustrate the adaptability of some of the well-known but more positive and satisfactory tests for the several metals.

Precipitate A contains iron, manganese, cobalt, and nickel.

(*a*) Test for iron by dissolving a small portion of the precipitate in dilute hydrochloric acid and adding potassium thiocyanate.

The blood-red colouration is due to ferric thiocyanate.

(*b*) For manganese, to 5 c.c. of water add 5 c.c. concentrated nitric acid and 5 to 10 grammes Pb_3O_4. Stir into the warm mixture a little of the precipitate and let stand. A purple solution is permanganic acid.

(*c*) In absence of iron or manganese, stir a little of the precipitate into dilute hydrochloric acid, and add solution of potassium iodide and starch. In presence of iron and manganese use the bead test.

(*d*) Boil some of the precipitate with bromine water till all bromine is expelled, add water and solution of potassium iodide and starch, $Ni(OH)_3 + KI = Ni(OH)_2 + KOH + I$, imparting the blue to the solution.

Solution A contains all the aluminium, zinc, and chromium. The yellow colour is evidence of chromium. Acidify with hydrochloric acid, boil, and add ammonium hydroxide.

Precipitate B consists of aluminium hydroxide, and any chromium hydroxide that may have escaped oxidation. Dissolve in nitric acid, and repeat the precipitation with sodium peroxide, or apply the blowpipe and cobalt test for aluminium.

Solution B contains zinc and chromium.

(*a*) Test for zinc by adding to a portion a few drops of potassium ferrocyanide. A heavy white precipitate indicates zinc.

(*b*) If further verification of chromium is needed, make the solution acid with hydrochloric acid, and boil with a little alcohol added. The chromium reverts to the green chromic chloride.

In the presence of phosphates the method so far employed has been as follows:—Upon dissolving the precipitate from the ammonium sulphide in concentrated nitric acid, a very little of the solution is tested for phosphoric acid in the usual manner. If present, granulated tin is added and the boiling continued. Filter from the insoluble tin phosphate, make ammoniacal, re-precipitate with ammonium sulphide, and proceed as with phosphoric acid absent. Any method not involving the use of tin, and depending upon the non-formation of the phosphates of iron, manganese, and nickel, is as yet unsatisfactory. Having removed the barium and strontium with sulphuric acid before the precipitation with ammonium sulphide, the oxidation and precipitation by means of sodium peroxide may be performed as usual; but before filtering, the solution is made acid with acetic acid, and boiled a

little further and filtered. The filtrate now may contain, besides the aluminium, zinc, and chromium, the nickel which is readily soluble in acetic acid, and the calcium and magnesium which have been brought along by means of the phosphoric acid. A little of the cobalt, however, dissolves with the acetic acid, and a solvent has not been found thus far for the calcium phosphate and nickel hydroxide that will not dissolve traces of the other three metals of the precipitate.

The precipitate obtained in the ordinary method by means of ammonium hydroxide and ammonium sulphide contains, as hydroxides and sulphides, iron, manganese, cobalt, nickel, aluminium, zinc, and chromium, and is brought into solution by means of 10 to 15 c.c. of concentrated nitric acid with heat. Nearly neutralise with sodium hydroxide, then sift in slowly (with stirring) sodium peroxide in excess. Boil.

On the Correct Adjustment of Chemical Weights

The following description of the method adopted for adjusting a set of platinum weights is taken from the author's Memoir on the Atomic Weight of Thallium.[1]

A set of weights as ordinarily supplied by even the best instrument-makers is never absolutely exact; however carefully they may be adjusted, the pieces of metal which respectively represent 1000 grains, 100 grains, 10 grains, &c., are only more or less approximations to the true weights. In most chemical analyses the error arising from such inaccuracies in the weights used is so small, in comparison to errors of manipulation or to imperfections inherent in the chemical processes adopted, that it may generally be disregarded; but when the chemist has for his object the estimation of an atomic weight, or is engaged in other researches demanding the highest refinement of accuracy which chemistry and physics can supply, then he is bound to neglect no correction which will increase the precision of the results. That chemists whose well-trained reasoning powers allow them to take for granted nothing which is not capable of experimental verification, and who insist upon the utmost attainable precision in their balances, should, as a rule, neglect the probable errors which the inaccuracies of their weights may introduce, is somewhat inconsistent.

The weights employed in the experiments were of platinum. The platinum was quite pure; it was fused, cast, and then well hammered. The weights were adjusted by myself during May, June, July, and August, 1864: they were first roughly adjusted, and then the specific gravity of each weight was taken. The weights were heated to redness in a bath of magnesia previous to ascertaining their specific gravity. The density of the larger weights was ascertained to the second place of decimals, and that of the smaller ones to the first place. The record

[1] *Phil. Trans.* 1873, p. 277.

of the final adjustment of these weights will be sufficient to show the method adopted.

In taking the specific gravity of the weights, the distilled water was contained in a glass beaker of about 250 cubic inches capacity. Each weight was suspended by a fine platinum wire to be attached to the pan of the balance. With this wire affixed the weight was introduced into a small glass vessel filled with water, and heated over a spirit-lamp to the boiling-point. When all the air-bubbles had been expelled by this process, the small jar containing the weight was lowered into the water in the beaker, the weight, on removing the small jar, being perfectly free from any adhering bubbles of air. After the temperature had sunk to the proper point, the specific gravity was taken.

The 1000-grain weight was selected as the standard; for in nearly every process in which weights are used in chemistry, the object is not to ascertain the *absolute* weight of a substance in terms of a grain or gramme, but to estimate its *relative* weight in comparison with that which it possessed at some other time before it was submitted to certain analytical or synthetical operations. If the weighings are performed with the same weights, it does not at all matter whether the weights are absolutely of the value which they profess to be; but it is very important that they should bear a known proportion to each other. This must be understood as referring only to ordinary chemical research in synthesis or analysis. In many physical investigations it is of great importance that the 1000-grain weight should really represent 1000 normal grains, or that its deviation from that value should be accurately estimated; but I confess I do not know where a standard weight suitable for such a comparison is to be met with. The weights at first tried were far from accurate among themselves. I accordingly ascertained their errors by the method described below, and then adjusted them myself according to the corrections thus found necessary. The residual errors in the weights were then finally taken in the following manner.

The balance being brought into equilibrium and the temperature and barometrical pressure carefully noted, the 1000-grain weight was placed in the left pan, and in the right the 600, the 300, and the 100 grain weights. It was now found that, to bring the balance back to equilibrium, a slight additional weight had to be placed on the right side to supplement the three weights already in that pan. This was noted. The weights were then removed to the opposite sides, the 1000-grains being on the right and the three smaller weights on the left. It was now found that a small weight had to be subtracted from the side carrying the three weights in order to produce equilibrium. The weights were removed and interchanged in this manner ten times, so as to eliminate, as far as possible, the errors arising from observation, or the unequal expansion by heat of the arms of the balance;

and by applying the method of least squares to the results obtained, the following equation was arrived at :—

$$(1000) = (600) + (300) + (100) + 0{\cdot}01 \quad . \quad . \quad . \quad a,$$

the figures within parentheses representing the nominal value of the actual pieces of platinum stamped 1000, 600, 100 grains, &c.

In a similar manner the values of the remaining weights were ascertained ; thus :—

$(600) = (300) + (200) + (100)$	$+$	$0{\cdot}00777$	$b.$
$(300) = (200) + (100)$	$+$	$0{\cdot}00991$	$c.$
$(200) = (100) + (60) + (30) + (10)$	$+$	$0{\cdot}01577$	$d.$
$(100) = (60) + (30) + (10)$	$-$	$0{\cdot}00030$	$e.$
$(60) = (30) + (20) + (10)$	$-$	$0{\cdot}00522$	$f.$
$(30) = (20) + (10)$	$+$	$0{\cdot}00154$	$g.$
$(20) = (10) + (6) + (3) + (1)$	$+$	$0{\cdot}00355$	$h.$
$(10) = (6) + (3) + (1)$	$+$	$0{\cdot}00052$	$i.$
$(6) = (3) + (2) + (1)$	$-$	$0{\cdot}00102$	$j.$
$(3) = (2) + (1)$	$+$	$0{\cdot}00165$	$k.$
$(2) = (1) + (\cdot6) + (\cdot3) + (\cdot1)$	$-$	$0{\cdot}00312$	$l.$
$(1) = (\cdot6) + (\cdot3) + (\cdot1)$	$-$	$0{\cdot}00508$	$m.$
$(\cdot6) = (\cdot3) + (\cdot2) + (\cdot1)$	$-$	$0{\cdot}00260$	$n.$
$(\cdot3) = (\cdot2) + (\cdot1)$	$+$	$0{\cdot}00225$	$o.$
$(\cdot2) = (\cdot1) + (\cdot06) + (\cdot03) + (\cdot01)$	$-$	$0{\cdot}00100$	$p.$
$(\cdot1) = (\cdot06) + (\cdot03) + (\cdot01)$	$-$	$0{\cdot}00802$	$q.$
$(\cdot06) = (\cdot03) + (\cdot02) + (\cdot01)$	$-$	$0{\cdot}00607$	$r.$
$(\cdot03) = (\cdot02) + (\cdot01)$	$-$	$0{\cdot}00642$	$s.$
$(\cdot02) = (\cdot01) + (\cdot01r'')$ [1]	$-$	$0{\cdot}00118r'$	$t.$
$(\cdot01) = (\cdot01r'')$	$+$	$0{\cdot}00413r'$	$u.$
$(\cdot01) = (\cdot01r')$	$+$	$0{\cdot}00410r''$	$v.$

We have now the data for ascertaining the absolute values of the weights in terms of the (1000) weight taken as standard. Adding the equations a and b gives

$$(1000) = 2(300) + (200) + 2(100) + 0{\cdot}01777.$$

Multiplying equation c by 2 gives

$$2(300) = 2(200) + 2(100) + 0{\cdot}01982.$$

Subtracting e from d gives

$$(200) = 2(100) + 0{\cdot}01607.$$

Now by $(a+b)+2c+3(d-e)$ we get

$$(1000) = 10(100) + 0{\cdot}01777 + 0{\cdot}01982 + 0{\cdot}04827 ;$$

$$\therefore (1000) = 10(100) + 0{\cdot}0858 ;$$

$$\therefore \tfrac{(1000)}{10} = (100) + 0{\cdot}00858 ;$$

$$\therefore (100) = 100 - 0{\cdot}00858 ;$$

$$\therefore (100) = 99{\cdot}991420 \text{ grains} \quad . \quad . \quad . \quad A\,[2]$$

[1] r', r'' represent riders, two of which were adjusted in this manner.

[2] Although these decimals are carried to the sixth place, the balance would not indicate beyond the fourth place. By taking the mean of ten interchanged weighings, I could obtain a fifth place. The calculated values of the weights were carried to a sixth decimal, in order to avoid inaccuracy in the fourth and fifth places when several values were summed.

Substituting this value for the (100) weight, we get from equation *e*,

$$99{\cdot}991420 = (60) + (30) + (10) - 0{\cdot}00030\,;$$
$$\therefore\ (60) + (30) + (10) = 99{\cdot}991720 \quad . \quad . \quad \text{B.}$$

From equation *d* we therefore get

$$(200) = 99{\cdot}99142 + 99{\cdot}99172 + 0{\cdot}01577\,;$$
$$\therefore\ (200) = 199{\cdot}99891 \quad . \quad . \quad . \quad . \quad \text{C.}$$

From equation *c* we get

$$(300) = 199{\cdot}998910 + 99{\cdot}991420 + 0{\cdot}00991\,;$$
$$\therefore\ (300) = 300{\cdot}000240 \quad . \quad . \quad . \quad . \quad \text{D.}$$

From equation *b* we get

$$(600) = 300{\cdot}000240 + 199{\cdot}998910 + 99{\cdot}991420 + 0{\cdot}00777\,;$$
$$\therefore\ (600) = 599{\cdot}998340 \quad . \quad . \quad . \quad . \quad \text{E.}$$

Again, adding *e* and *f*,

$$(100) = 2(30) + (20) + 2(10) - 0{\cdot}00552\,;$$

$\therefore$ from A,

$$99{\cdot}991420 = 2(30) + (20) + 2(10) - 0{\cdot}00552.$$

Multiplying *g* by 2,

$$2(30) = 2(20) + 2(10) + 0{\cdot}00308.$$

Subtracting *i* from *h*,

$$(20) = 2(10) + 0{\cdot}00303.$$

By adding *e*, *f*, twice *g*, and thrice the last equation, we get

$$99{\cdot}99142 = 10(10) + 0{\cdot}000665\,;$$
$$\therefore\ (10) = 9{\cdot}998477\,. \quad . \quad . \quad . \quad . \quad \text{F.}$$

From equation *i* we get

$$9{\cdot}998477 = (6) + (3) + (1) + 0{\cdot}00052\,;$$
$$\therefore\ (6) + (3) + (1) = 9{\cdot}997957 \quad . \quad . \quad . \quad \text{G.}$$

Substituting these values in *h*, we get

$$(20) = 9{\cdot}998477 + 9{\cdot}997957 + 0{\cdot}00355\,;$$
$$\therefore\ (20) = 19{\cdot}999984 \quad . \quad . \quad . \quad . \quad \text{H.}$$

From *g* we get

$$(30) = 19{\cdot}999984 + 9{\cdot}998477 + 0{\cdot}00154\,;$$
$$\therefore\ (30) = 29{\cdot}999991 \quad . \quad . \quad . \quad . \quad \text{I.}$$

From *f* we get

$$(60) = 29{\cdot}999991 + 19{\cdot}999984 + 9{\cdot}998477 - 0{\cdot}00522\,;$$
$$\therefore\ (60) = 59{\cdot}993232 \quad . \quad . \quad . \quad . \quad \text{J.}$$

Again, adding *i* and *j*,

$$(10) = 2(3) + (2) + 2(1) - 0{\cdot}00050.$$

Multiplying *k* by 2,

$$2(3) = 2(2) + 2(1) + 0{\cdot}00330.$$

Subtracting m from l,

$(2) = 2(1) + 0{\cdot}001960.$

Then $(i+j)+2k+3(l-m)$ gives

$(10) + 10(1) + 0{\cdot}00868;$

$\therefore\ 9{\cdot}998477 = (10)1 + 0{\cdot}00868;$

$\therefore\ 0{\cdot}9998477 = (1) + 0{\cdot}000868;$

$\therefore\ (1) = 0{\cdot}9989797 \quad . \quad . \quad . \quad . \quad . \quad \text{K.}$

From equation m we have

$0{\cdot}9989797 = (\cdot6) + (\cdot3) + (\cdot1) - 0{\cdot}00508;$

$\therefore\ (\cdot6) + (\cdot3) + (\cdot1) = 1{\cdot}0040597 \quad . \quad . \quad \text{L.}$

From l,

$(2) = 0{\cdot}9989797 + 1{\cdot}0040597 - 0{\cdot}00312;$

$\therefore\ (2) = 1{\cdot}9998394 \quad . \quad . \quad . \quad . \quad \text{M.}$

From k,

$(3) = 1{\cdot}9998394 + 0{\cdot}9989797 + 0{\cdot}00165;$

$\therefore\ (3) = 3{\cdot}0004691 \quad . \quad . \quad . \quad . \quad \text{N.}$

From j,

$(6) = 3{\cdot}0004691 + 1{\cdot}9998394 + 0{\cdot}9989797 - 0{\cdot}00102$

$\therefore\ (6) = 5{\cdot}9982682 \quad . \quad . \quad . \quad . \quad \text{O.}$

Again, adding m and n,

$(1) = 2(\cdot3) + (\cdot2) + 2(\cdot1) - 0{\cdot}00768.$

Multiplying o by 2, we get

$2(\cdot3) = 2(\cdot2) + 2(\cdot1) + 0{\cdot}0045.$

Subtracting q from p,

$(\cdot2) = 2(\cdot1) + 0{\cdot}00702.$

Then $(m+n)+2o+3(p-q)$ gives

$(1) = 10(\cdot1) + 0{\cdot}01788;$

$\therefore\ 0{\cdot}9989797 = 10(\cdot1) + 0{\cdot}01788;$

$\therefore\ 0{\cdot}09989797 = (\cdot1) + 0{\cdot}001788;$

$\therefore\ (\cdot1) = 0{\cdot}09810997 \quad . \quad . \quad . \quad . \quad \text{P.}$

From q we get

$0{\cdot}09810997 = (\cdot06) + (\cdot03) + (\cdot01) - 0{\cdot}00802;$

$\therefore\ (\cdot06) + (\cdot03) + (\cdot01) = 0{\cdot}10612997 \quad . \quad \text{Q.}$

From p,

$(\cdot2) + 0{\cdot}09810997 + 0{\cdot}10612997 - 0{\cdot}0010;$

$\therefore\ (\cdot2) = 0{\cdot}20323994 \quad . \quad . \quad . \quad . \quad \text{R.}$

From o,

$(\cdot3) = 0{\cdot}20323994 + 0{\cdot}09810997 + 0{\cdot}00225$

$\therefore\ (\cdot3) = 0{\cdot}30359991 \quad . \quad . \quad . \quad . \quad \text{S.}$

From n we get

$(\cdot6) = 0{\cdot}30359991 + 0{\cdot}20323994 + 0{\cdot}09810997 - 0{\cdot}0026;$

$\therefore\ (\cdot6) = 0{\cdot}60234982 \quad . \quad . \quad . \quad . \quad \text{T.}$

Again, adding q and r,

$$(\cdot1) = 2(\cdot03) + (\cdot02) + 2(\cdot01) - 0\cdot01409.$$

Multiplying s by 2, we get

$$2(\cdot03) = 2(\cdot02) + 2(\cdot01) - 0\cdot01284.$$

Subtracting u from t,

$$(\cdot2) = 2(\cdot01) - 0\cdot00531.$$

Then $(q+r)+2s+3(t-u)$ gives

$$(\cdot1) = 10(\cdot01) - 0\cdot04286\ ;$$
$$\therefore\ 0\cdot09810997 = 10(\cdot01) - 0\cdot04286\ ;$$
$$\therefore\ 0\cdot009810997 = (\cdot01) - 0\cdot004286\ ;$$
$$\therefore\ (\cdot01) = 0\cdot014096997 \quad . \quad . \quad . \quad \text{U.}$$

From u we get

$$0\cdot014096997 = (\cdot01r'') + 0\cdot00413,$$
$$\therefore\ (\cdot01r'') = 0\cdot009966997 \quad . \quad . \quad . \quad \text{V.}$$

From t we get

$$(\cdot02) = 0\cdot014096997 + 0\cdot009966997 - 0\cdot00118,$$
$$\therefore\ (\cdot02) = 0\cdot022883994 \quad . \quad . \quad . \quad \text{W.}$$

From s we get

$$(\cdot03) = 0\cdot022883994 + 0\cdot014096997 - 0\cdot00642,$$
$$\therefore\ (\cdot03) = 0\cdot030560991 \quad . \quad . \quad . \quad \text{X.}$$

From r we get

$$(\cdot06) = 0\cdot030560991 + 0\cdot22883994 + 0\cdot014096997 - 0\cdot00607,$$
$$\therefore\ (\cdot06) = 0\cdot061471982 \quad . \quad . \quad . \quad \text{Y.}$$

From v we get

$$0\cdot014096997 = (\cdot01r') + 0\cdot0041,$$
$$\therefore\ (\cdot01r') = 0\cdot009996997 \quad . \quad . \quad . \quad \text{Z.}$$

The value of the weights thus given was, however, their weight in air of the ordinary pressure; it became therefore necessary to ascertain their value in a vacuum. All bodies displace a bulk of air equal to their own volume, and the weight of this air is of course greater as their specific gravity diminishes. In delicate investigations this loss of weight is important. The reduction of the platinum weights to their true value *in vacuo* was calculated by the following formula:—

Let W = weight in air,
w = „ „ water,
a = specific gravity of air as compared with water;

then

$$x, \text{ or weight } in\ vacuo, = \frac{W - aw}{1 - a},$$

where

$$a = 0\cdot001225, \text{ and}$$
$$1 - a = 0\cdot998775.$$

The following table shows the final results of these adjustments :—

Nominal Value of Weights	True Value in Air at 30 in.,[1] 62° F.	Weight of Air displaced	Volume in Water of Maximum Density
grs.	grs.	gr.	grs.
1000·00	1000·000000	0·058271	47·5100
600·00	599·998340	0·035533	28·9700
300·00	300·000240	0·017501	14·2700
200·00	199·998910	0·011664	9·5100
100·00	99·991420	0·005887	4·8000
60·00	59·993232	0·003483	2·8400
30·00	29·999991	0·001668	1·3600
20·00	19·999984	0·001104	0·9000
10·00	9·998477	0·000490	0·4000
6·00	5·998268	0·000355	0·2900
3·00	3·000469	0·000171	0·1400
2·00	1·999839	0·000113	0·1000
1·00	0·998980	0·000055	0·0400
0·60	0·602350	0·000035	0·0300
0·30	0·303600	0·000017	0·0200
0·20	0·203240	0·000011	0·0100
0·10	0·098110	0·000005	0·0040
0·06	0·061472	0·000003	0·0030
0·03	0·030561	0·000002	0·0020
0·02	0·022884	0·000001	0·0010
0·01	0·014097	0·000001	0·0004
0·01′	0·009997	0·000001	0·0004
0·01″	0·009967	0·000001	0·0004

The value of each weight in air, plus the weight of air displaced, is the weight *in vacuo*.

Having ascertained their true value, the weights were carefully preserved ; and as, being of platinum, there is no accumulation of tarnish on their surface, and as they are lifted with ivory-tipped forceps to prevent wear, they have shown up to the present time, whenever compared, absolutely no alteration.

[1] The cistern of the barometer was 115 feet above the approximate mean water-level at Somerset House.

CHAPTER XV

USEFUL TABLES

Conversion of Centigrade and Fahrenheit Degrees

$1°$ C. $= 1{\cdot}8°$ F. $= \frac{9}{5}°$ F. $\quad 1°$ C. $\times \frac{9}{5} = 1°$ F. $\quad 1°$ F. $\times \frac{5}{9} = 1°$ C.

To convert Fahrenheit into Centigrade—Subtract 32 from the original number, and divide the remainder by 1·8, thus: 176° F.— $32 \div 1{\cdot}8 = 80°$ Cent.

To convert Centigrade into Fahrenheit, multiply by 1·8, add 32 to the product, thus: 80° Cent. $\times$ 1·8 + 32 = 176° F.

With the aid of a scale like the accompanying one,[1] thermometric degrees may be converted from one to the other with the greatest accuracy without making any calculations.

A simple inspection of the diagram will suffice to show the principle upon which the scale is constructed. Each degree Fahrenheit is divided into 5 parts, and each degree Centigrade into 9 parts, which are intended to represent fractions of a degree; the degrees themselves being numbered consecutively from the freezing-point of each thermometer upwards.

A few examples will best explain the use of this scale. Suppose the temperature of a body to be 40° F. and it is required to know what degree that is on the Centigrade scale. By looking for the next degree Centigrade above 40° F. on the scale, it is found to be 4, and 4 of the small divisions after it; 40° F. are therefore equivalent to 4·4° C., or, repeating the decimal figure for greater accuracy, 4·44° C.

When Centigrade degrees have to be reduced to degrees of Fahrenheit, the decimal figures of the latter must be doubled to obtain the correct answer. For example, it is required to represent 3° C. by their Fahrenheit equivalent; referring to the scale we find the next degree Fahrenheit above 3° C. to be 37·2°, and doubling the decimal figure we have the correct answer 37·4° F. Again, taking the outer columns of figures at the same place, we find 43° C. corresponding to 109·4° F.

[1] By Mr. Birney.

Fahrenheit.				Centigrade or Celsius.			
140	104	68	32	0	20	40	60
141	105	69	33				
142	106	70	34	1	21	41	61
143	107	71	35				
144	108	72	36	2	22	42	62
145	109	73	37				
146	110	74	38	3	23	43	63
147	111	75	39				
148	112	76	40	4	24	44	64
149	113	77	41				
150	114	78	42	5	25	45	65
151	115	79	43				
152	116	80	44	6	26	46	66
153	117	81	45				
154	118	82	46	7	27	47	67
155	119	83	47				
156	120	84	48	8	28	48	68
157	121	85	49				
158	122	86	50	9	29	49	69
159	123	87	51				
160	124	88	52	10	30	50	70
161	125	89	53				
162	126	90	54	11	31	51	71
163	127	91	55				
164	128	92	56	12	32	52	72
165	129	93	57				
166	130	94	58	13	33	53	73
167	131	95	59				
168	132	96	60	14	34	54	74
169	133	97	61				
170	134	98	62	15	35	55	75
171	135	99	63				
172	136	100	64	16	36	56	76
173	137	101	65				
174	138	102	66	17	37	57	77
175	139	103	67				
				18	38	58	78
				19	39	59	79

Tables for the Mutual Conversion of French and English Weights and Measures

The equivalents in one system of the weights and measures of the other system can readily be found by means of the following tables. By changing the position of the decimal point, the tables are available for all decimal multiples and subdivisions of these quantities; for instance, in order to find the part of a gramme which corresponds to 0·1, 0·01, 0·001, &c., of a grain, it is necessary to advance the decimal point one, two, or three places to the left. In the same manner it is advanced to the right for the purpose of finding the grammes corresponding to 10, 100, 1000, &c., grains.

For example :—In the table for the conversion of grammes into grains, it is required to find the equivalent in grains of 6·4431 grammes.

From number 6 (without altering the place of the decimal point)	92·6304
[1] From number 4 (advancing the decimal point one place to the left)	6·1753
[1] From number 4 (advancing the decimal point two places to the left)	0·6175
[1] From number 3 (advancing the decimal point three places to the left)	0·0463
[1] From number 1 (advancing the decimal point four places to the left)	0·0015
Therefore 6·4431 grammes are equal to . . .	99·4710 grains

Grammes into Grains.

Grammes	Grains	Grammes	Grains	Grammes	Grains
1 =	15·4384	4 =	61·7536	7 =	108·0688
2 =	30·8768	5 =	77·1920	8 =	123·5072
3 =	46·3152	6 =	92·6304	9 =	138·9456

Grains into Grammes.

Grains	Grammes	Grains	Grammes	Grains	Grammes
1 =	0·06477	4 =	0·25908	7 =	0·45339
2 =	0·12954	5 =	0·32385	8 =	0·51816
3 =	0·19431	6 =	0·38862	9 =	0·58293

Pounds into Kilogrammes.

Pounds	Kilogrammes	Pounds	Kilogrammes	Pounds	Kilogrammes
1 =	0·4534148	4 =	1·8136592	7 =	3·1739036
2 =	0·9068296	5 =	2·2670740	8 =	3·6273184
3 =	1·3602444	6 =	2·7204888	9 =	4·0807332

Kilogrammes into Pounds.

Kilogrammes	Pounds	Kilogrammes	Pounds	Kilogrammes	Pounds
1 =	2·205486	4 =	8·821944	7 =	15·438402
2 =	4·410972	5 =	11·027430	8 =	17·643888
3 =	6·616458	6 =	13·232916	9 =	19·849374

Inches into Centimetres.

Inches	Centimetres	Inches	Centimetres	Inches	Centimetres
1 =	2·539954	4 =	10·1598	7 =	17·7797
2 =	5·079900	5 =	12·6998	8 =	20·3196
3 =	7·619900	6 =	15·2397	9 =	22·8596

[1] In almost every case when the decimal point is moved to the left, the last figures may be omitted without introducing any appreciable error.

Centimetres into Inches.

Centimetres		Inches	Centimetres		Inches	Centimetres		Inches
1	=	0·3937079	4	=	1·5748316	7	=	2·7559553
2	=	0·7874158	5	=	1·9685395	8	=	3·1496632
3	=	1·1811237	6	=	2·3622474	9	=	3·5433711

Feet into Metres.

Feet		Metres	Feet		Metres	Feet		Metres
1	=	0·3047945	4	=	1·2197680	7	=	2·1335614
2	=	0·6095890	5	=	1·5239724	8	=	2·4383559
3	=	0·9143835	6	=	1·8287669	9	=	2·7431504

Metres into Feet.

Metres		Feet	Metres		Feet	Metres		Feet
1	=	3·2808992	4	=	13·1235968	7	=	22·9662944
2	=	6·5617984	5	=	16·4044960	8	=	26·2471936
3	=	9·8426976	6	=	19·6853952	9	=	29·5280928

Miles into Kilometres.

Miles		Kilometres	Miles		Kilometres	Miles		Kilometres
1	=	1·6093	4	=	6·4373	7	=	11·2652
2	=	3·2186	5	=	8·0466	8	=	12·8745
3	=	4·8279	6	=	9·6559	9	=	14·4838

Kilometres into Miles.

Kilometres		Miles	Kilometres		Miles	Kilometres		Miles
1	=	0·62138	4	=	2·48552	7	=	4·34966
2	=	1·24276	5	=	3·10690	8	=	4·97104
3	=	1·86414	6	=	3·72828	9	=	5·59242

Square Feet into Square Metres.

Sq. Feet		Sq. Metres	Sq. Feet		Sq. Metres	Sq. Feet		Sq. Metres
1	=	0·0929	4	=	0·3716	7	=	0·6503
2	=	0·1858	5	=	0·4645	8	=	0·7432
3	=	0·2787	6	=	0·5574	9	=	0·8361

Square Metres into Square Feet.

Sq. Metres		Sq. Feet	Sq. Metres		Sq. Feet	Sq. Metres		Sq. Feet
1	=	10·7698	4	=	43·0792	7	=	75·3886
2	=	21·5396	5	=	53·8490	8	=	86·1584
3	=	32·3094	6	=	64·6188	9	=	96·9282

Cubic Feet into Cubic Metres.

Cub. Feet		Cub. Metres	Cub. Feet		Cub. Metres	Cub. Feet		Cub. Metres
1	=	0·028314	4	=	0·113256	7	=	0·198198
2	=	0·056628	5	=	0·141570	8	=	0·226512
3	=	0·084942	6	=	0·169884	9	=	0·254826

Cubic Metres into Cubic Feet.

Cub. Metres		Cub. Feet	Cub. Metres		Cub. Feet	Cub. Metres		Cub. Feet
1	=	35·3171	4	=	141·2684	7	=	247·2197
2	=	70·6342	5	=	176·5855	8	=	282·5368
3	=	105·9513	6	=	211·9026	9	=	317·8539

Long Tons into Tonnes of 1000 *Kilos.*

Long Tons		Tonnes of 1000 Kilos.	Long Tons		Tonnes of 1000 Kilos.	Long Tons		Tonnes of 1000 Kilos.
1	=	1·015649	4	=	4·062596	7	=	7·109543
2	=	2·031298	5	=	5·078245	8	=	8·125192
3	=	3·046947	6	=	6·093894	9	=	9·140841

Pounds per Square Inch into Kilogrammes per Square Centimetre.

Pounds per Sq. Inch		Kilos. per Sq. Centim.	Pounds per Sq. Inch		Kilos. per Sq. Centim.	Pounds per Sq. Inch		Kilos. per Sq. Centim.
1	=	0·0702774	4	=	0·2811096	7	=	0·4919418
2	=	0·1405548	5	=	0·3513870	8	=	0·5622192
3	=	0·2108322	6	=	0·4216644	9	=	0·6324966

Kilogrammes per Square Millimetre into Pounds per Square Inch.

Kilos. per Sq. Millim.		Pounds per Sq. Inch	Kilos. per Sq. Millim.		Pounds per Sq. Inch	Kilos. per Sq. Millim.		Pounds per Sq. Inch
1	=	1425·45	4	=	5701·80	7	=	6978·15
2	=	2850·90	5	=	7127·25	8	=	11403·60
3	=	4276·35	6	=	8552·70	9	=	12829·05

Relative Values of French and English Weights and Measures.

Weights.

Milligramme	=	0·015438395	troy grain
Centigramme	=	0·15438395	,, ,,
Décigramme	=	1·5438395	,, ,,
Gramme	=	15·438395	,, ,,
,, ...	=	0·643	pennyweight
,, ...	=	0·03216	oz. troy
,, ...	=	0·03527	oz. avoirdupois
Décagramme	=	154·38395	troy grains
,, ...	=	5·64	drams avoirdupois
Hectogramme	=	3·2154	ozs. troy
,, ...	=	3·527	ozs. avoirdupois
Kilogramme	=	2·6803	lbs. troy
,, ...	=	2·205486	lbs. avoirdupois
Myriagramme	=	26·803	lbs. troy
,, ...	=	22·05486	lbs. avoirdupois
Quintal métrique . . .	=	100 kilos.	= 220·5486 lbs. avoir.
Tonne , ...	=	1000 ,,	= 2205·486 ,,

Different authors give the following values for the gramme:—

Gramme	= 15·44402	troy grains
,,	= 15·44242	,,
,,	= 15·4402	,,
,,	= 15·43839	,,
,,	= 15·433159	,,
,,	= 15·43235	,,

Avoirdupois.

Long ton = 20 cwt. = 2240 lbs.	= 1015·649	kilogrammes
Short ton (2000 lbs.) . .	= 906·8296	,,
Hundredweight (112 lbs.) .	= 50·78245	,,
Quarter (28 lbs.) . . .	= 12·6956144	,,
Pound = 16 ozs. = 7000 grs.	= 453·4148	grammes
Ounce = 16 drams = 437·5 grs.	= 28·3375	,,
Dram = 27·344 grains	= 1·77108	gramme
Grain	= 0·064773	,,

Troy (Precious Metals).

Pound = 12 ozs.	= 5760 grs.	= 373·096	grammes
Ounce = 20 dwts.	= 480 ,,	= 31·0913	,,
Pennyweight .	= 24 ,,	= 1·55457	gramme
Grain		= 0·064773	,,

Troy (Pharmacy).

Ounce	= 8 drams	= 480 grs.	= 31·0913	grammes
Dram	= 3 scruples	= 60 ,,	= 3·8869	,,
Scruple	. .	= 20 ,,	= 1·29546	gramme

Measures of Length.

Millimetre	=	0·03937	inch
Centimetre	=	0·393708	,,
Decimetre	=	3·937079	inches
Metre	=	39·37079	,,
,,	=	3·2808992	feet
,,	=	1·093633	yard
Inch ($\frac{1}{36}$th yard) . . .	=	2·539954	centimetres
Foot ($\frac{1}{3}$rd yard) . . .	=	3·0479449	decimetres
Yard	=	0·91438348	metre
Mile (1760 yards) . . .	=	1609·6149	metres

Superficial Measures.

Square millimetre	=	$\frac{1}{645}$th of a square inch	
,, ,, ...	=	0·00155 ,,	,,
,, centimetre	=	0·155086 ,,	,,
,, decimetre	=	15·5086 ,,	inches
,, ,, ...	=	0·10769 ,,	foot
,, metre or centiare . . .	=	1550·86 ,,	inches
,, ,, . . .	=	10·7698 ,,	feet
,, ,, . . .	=	1·196033 ,,	yard
Are	=	1076·98 ,,	feet
,, ...	=	119·6033 ,,	yards
,, ...	=	0·098845 ,,	rood

Hectare	=	11960·33	square yards
,,	=	2·471143	,, acres
Square inch	=	645·169201	,, millimetres
,, ,,	=	6·45109	,, centimetres
,, foot	=	9·2903	,, decimetres
,, yard	=	0·836097	,, metre
Acre (4840 square yards)	=	0·404671	,, hectare

Measures of Capacity.

Cubic millimetre	=	0·000061029	cubic inch
,, centimetre	=	0·061029	,, ,,
10 cubic centimetres	=	0·61029	,, ,,
100 ,, ,,	=	6·10295	,, inches
1000 ,, ,, or litre	=	61·0295688	,, ,,
,, ,, ,, ,,	=	1·760773	imperial pint
,, ,, ,, ,,	=	0·2200967	,, gallon
Decalitre	=	610·295688	cubic inches
,,	=	2·2009668	imp. gallons
Hectolitre	=	3·5317	cubic feet
,,	=	22·009668	imp. gallons
Cubic metre	=	1·308	cubic yard
,, ,,	=	35·3171	,, feet

Cubic inch = 16·3855 cubic centimetres
,, foot = 28·3159 ,, decimetres
,, yard = 0·764520696 ,, metre

British Imperial Measures.

Pint ($\frac{1}{8}$ gallon)	=	0·567932	litre
Quart ($\frac{1}{4}$,,)	=	1·135864	,,
Imperial gallon	=	4·54345797	litres

Weight of Water, &c.

1 cubic inch	252·45 grs.
1 pint (= 34·65 cubic inches)	1·25 lb.
1 cubic foot (= 6·25 galls., or 1000 ozs.)	62·50 lbs.
1 gallon (= 277·274 cubic inches)	10·00 lbs.
1·8 cubic foot	1 cwt.
35·84 cubic feet	1 ton
11·20 gallons	1 cwt.
224·0 ,,	1 ton

A cubic inch of mercury = 3425·25 grains.

Coins as Weights.

20 grains =	1 threepenny piece
40 grains =	1 sixpence
80 grains =	1 shilling
100 grains =	1 shilling and 1 threepenny piece
200 grains =	1 half-crown
$\frac{1}{4}$ ounce (not quite) =	1 halfpenny and 1 threepenny piece
$\frac{1}{2}$ ounce (and a trifle more) =	2 shillings and 1 sixpence
1 ounce =	3 pence

Baumé's Hydrometer

The following tables give the comparison of the degrees of Baumé's hydrometer with the specific gravity :—

Table for Liquids Heavier than Water.

Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity
0	1·000	26	1·206	52	1·520
1	1·007	27	1·216	53	1·535
2	1·013	28	1·226	54	1·551
3	1·020	29	1·236	55	1·567
4	1·027	30	1·246	56	1·583
5	1·034	31	1·256	57	1·600
6	1·041	32	1·267	58	1·617
7	1·048	33	1·277	59	1·634
8	1·056	34	1·288	60	1·652
9	1·063	35	1·299	61	1·670
10	1·070	36	1·310	62	1·689
11	1·078	37	1·322	63	1·708
12	1·086	38	1·333	64	1·727
13	1·094	39	1·345	65	1·747
14	1·101	40	1·357	66	1·767
15	1·109	41	1·369	67	1·788
16	1·118	42	1·382	68	1·809
17	1·126	43	1·395	69	1·831
18	1·134	44	1·407	70	1·854
19	1·143	45	1·421	71	1·877
20	1·152	46	1·434	72	1·900
21	1·160	47	1·448	73	1·924
22	1·169	48	1·462	74	1·949
23	1·178	49	1·476	75	1·974
24	1·188	50	1·490	76	2·000
25	1·197	51	1·505		

Table for Liquids Lighter than Water.

Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity
10	1·000	27	0·896	44	0·811
11	0·993	28	0·890	45	0·807
12	0·986	29	0·885	46	0·802
13	0·980	30	0·880	47	0·798
14	0·973	31	0·874	48	0·794
15	0·967	32	0·869	49	0·789
16	0·960	33	0·864	50	0·785
17	0·954	34	0·859	51	0·781
18	0·948	35	0·854	52	0·777
19	0·942	36	0·849	53	0·773
20	0·936	37	0·844	54	0·768
21	0·930	38	0·839	55	0·764
22	0·924	39	0·834	56	0·760
23	0·918	40	0·830	57	0·757
24	0·913	41	0·825	58	0·753
25	0·907	42	0·820	59	0·749
26	0·901	43	0·816	60	0·745

Table of Atomic Weights

COMPILED BY THE INTERNATIONAL COMMITTEE

Name	Symbol	O=16	H=1
Aluminium	Al	27·1	26·9
Antimony	Sb	120·2	119·3
Argon	A	39·9	39·6
Arsenic	As	75·0	74·4
Barium	Ba	137·4	136·4
Bismuth	Bi	208·5	206·9
Boron	B	11·0	10·9
Bromine	Br	79·96	79·36
Cadmium	Cd	112·4	111·6
Cæsium	Cs	132·9	131·9
Calcium	Ca	40·1	39·7
Carbon	C	12·00	11·91
Cerium	Ce	140·25	139·2
Chlorine	Cl	35·45	35·18
Chromium	Cr	52·1	51·7
Cobalt	Co	59·0	58·55
Columbium	Cb	94	93·3
Copper	Cu	63·6	63·1
Erbium	Er	166	164·8
Fluorine	F	19	18·9
Gadolinium	Gd	156	154·8
Gallium	Ga	70	69·5
Germanium	Ge	72·5	72
Glucinum	Gl	9·1	9·03
Gold	Au	197·2	195·7
Helium	He	4	4
Hydrogen	H	1·008	1·000
Indium	In	115	114·1
Iodine	I	126·97	126·01
Iridium	Ir	193·0	191·5
Iron	Fe	55·9	55·5
Krypton	Kr	81·8	81·2
Lanthanum	La	138·9	137·9
Lead	Pb	206·9	205·35
Lithium	Li	7·03	6·98
Magnesium	Mg	24·36	24·18
Manganese	Mn	55·0	54·6
Mercury	Hg	200·0	198·5
Molybdenum	Mo	96·0	95·3
Neodymium	Nd	143·6	142·5
Neon	Ne	20	19·9
Nickel	Ni	58·7	58·3
Nitrogen	N	14·04	13·93
Osmium	Os	191	189·6
Oxygen	O	16·00	15·88
Palladium	Pd	106·5	105·7
Phosphorus	P	31·0	30·77
Platinum	Pt	194·8	193·3
Potassium	K	39·15	38·85

Table of Atomic Weights—*continued*

Name	Symbol	O=16	H=1
Praseodymium	Pr	140·5	139·4
Radium	Ra	225	223·3
Rhodium	Rh	103·0	102·2
Rubidium	Rb	85·5	84·9
Ruthenium	Ru	101·7	100·9
Samarium	Sm	150·3	149·2
Scandium	Sc	44·1	43·8
Selenium	Se	79·2	78·6
Silicon	Si	28·4	28·2
Silver	Ag	107·93	107·11
Sodium	Na	23·05	22·88
Strontium	Sr	87·6	86·94
Sulphur	S	32·06	31·82
Tantalum	Ta	183	181·6
Tellurium	Te	127·6	126·6
Terbium	Tb	160	158·8
Thallium	Tl	204·1	202·6
Thorium	Th	232·5	230·8
Thulium	Tm	171	169·7
Tin	Sn	119·0	118·1
Titanium	Ti	48·1	47·7
Tungsten	W	184	182·6
Uranium	U	238·5	236·7
Vanadium	V	51·2	50·8
Xenon	Xe	128	127
Ytterbium	Yb	173·0	171·7
Yttrium	Yt	89·0	88·3
Zinc	Zn	65·4	64·9
Zirconium	Zr	90·6	89·9

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