A system of instruction in quantitative chemical analysis / by C. Remigius Fresenius.

Contributors

Fresenius, C. Remigius, 1818-1897.
Bullock, J. Lloyd

Publication/Creation

London : John Churchill, 1854.

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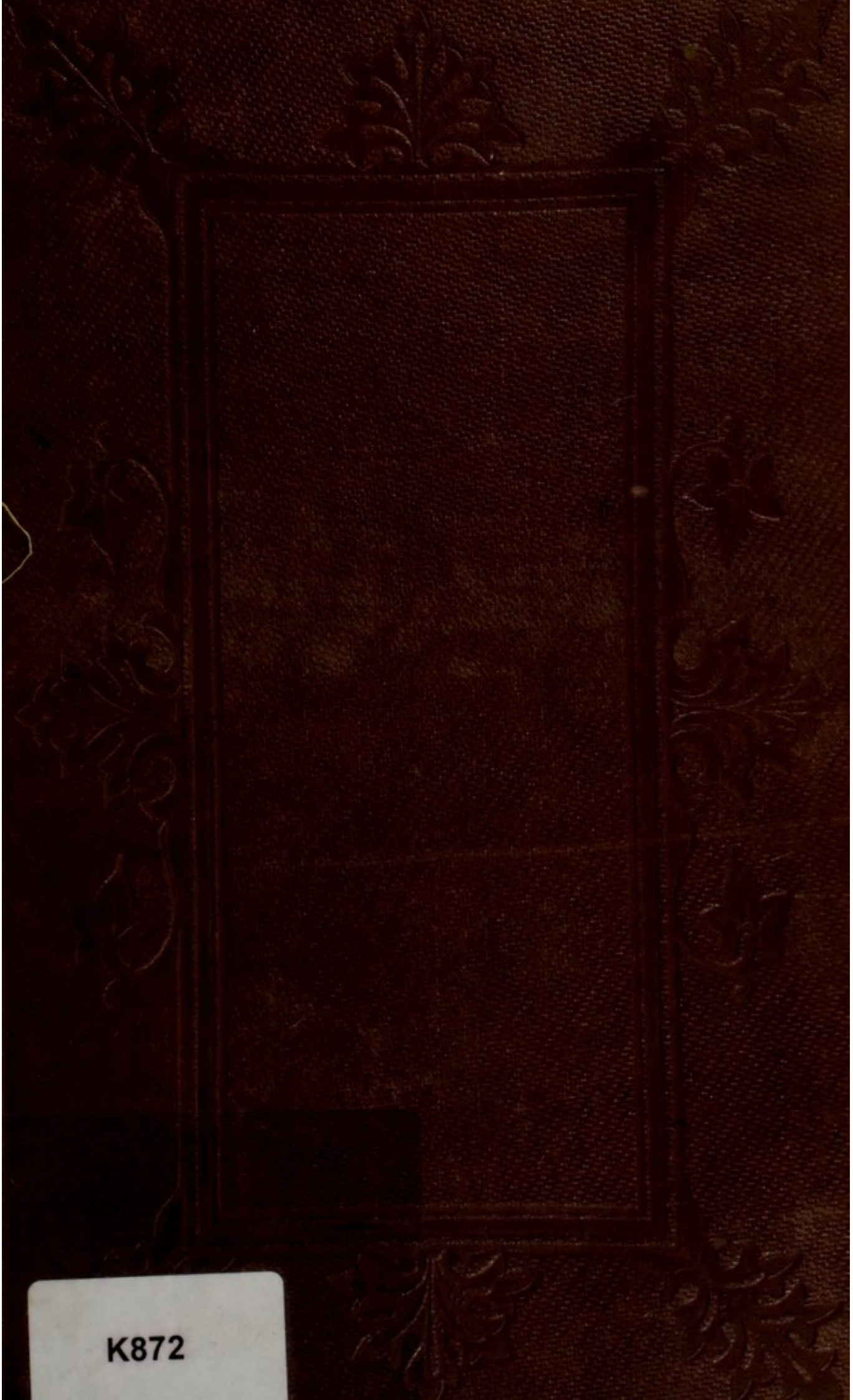
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With kind regards from

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SYSTEM OF INSTRUCTION

IN

QUANTITATIVE CHEMICAL ANALYSIS.

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A

SYSTEM OF INSTRUCTION

IN

QUANTITATIVE CHEMICAL ANALYSIS.

BY

DR. C. REMIGIUS FRESENIUS,

PROFESSOR OF CHEMISTRY AND NATURAL PHILOSOPHY, WIESBADEN.

Second Edition.

EDITED BY

J. LLOYD BULLOCK, F.C.S.



LONDON:
JOHN CHURCHILL, NEW BURLINGTON STREET.
(*Established in Princes Street, Soho,* 1784.)
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LONDON:

G. J. PALMER, SAVOY STREET, STRAND.

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PREFACE.

In introducing a Second Edition of this work of Dr. Fresenius, on

QUANTITATIVE ANALYSIS,

to English Chemists, I congratulate them, and myself, that the work has been duly appreciated.

The Author has spared no pains or labor, not merely to keep it up to the improved state of the science, but to make it the medium of introducing methods of research in advance of all other works. Whatever has been proposed, either in this country or on the Continent, to facilitate the path of analysis, has been tested, and, when found sound and practical, has been introduced in its proper place. Every doubtful point has been rigidly subjected to repeated experiments, errors corrected and faults amended, and many new processes added from the author's ample experience in his own laboratory. Amongst the additions I may mention the introduction of volumetrical methods of determining the constituents of commercial articles, as being particularly valuable for economising time and assisting in every way the practical chemist. To repeat what I had occasion to remark in the preface to the First Edition—this work on

QUANTITATIVE ANALYSIS,

although in itself complete, may be regarded as a sequel to the author's QUALITATIVE ANALYSIS—a work which has been found of the highest

value, nay, almost indispensable, to the student of Chemistry, whatever other books on the subject he may possess.

As a guide to analytical chemistry the merits of the present volume are of the highest order. The arrangement is simple, methodical, and consecutive; the theoretical explanations are appropriate, clear, and intelligible; the language plain, and the directness and honesty of purpose, together with the just appreciation of the labors of others, displayed throughout, must commend it to every one engaged in studying, teaching, or practising Chemistry; and I have great pleasure in being the medium of presenting it to the English Public.

J. LLOYD BULLOCK.

22, *Conduit Street.*

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INTRODUCTION.

In my treatise entitled, "Elementary Instruction in Qualitative Chemical Analysis," I have stated that ANALYTICAL CHEMISTRY comprehends two branches, viz., "*qualitative analysis*" and "*quantitative analysis*," and that the object of the former is to ascertain the individual *kind, and nature*, that of the latter to determine the absolute and relative *quantity, or proportion* of the several component parts of any given compound.

By QUALITATIVE ANALYSIS we convert the *unknown* constituents of a given compound into certain forms or combinations, with the properties of which we are acquainted; and we are thus enabled to draw correct inferences respecting the nature of *every individual constituent* of the compound in question.

QUANTITATIVE ANALYSIS has, as a general rule,* for its object to convert the *known* constituents of a given compound into such forms, or combinations as will admit of the most exact determination of their weight, and of which, moreover, the relative, and combining proportions are accurately known. These new forms, or combinations may be either *educts* from the analysed compound, or mixture, or they may be *products*. In the former case we have simply to weigh the eliminated substance, since its ascertained weight, of course, supplies at once the direct expression of the quantity, or proportion in which it existed in the compound under examination; whilst in the latter case, that is, when we have to deal with *products*, the quantity, or proportion in which the eliminated constituent was originally present in the analysed compound, has to be deduced by calculation from the proportion in which it exists in its new combination.

The following example will serve to illustrate these points:—Suppose we wish to determine the proportional amount of mercury contained in the chloride of that metal; now, we may do this, either by precipitating the metallic mercury from the solution of the chloride, by means of protochloride of tin; or we may attain our object by precipitating the solution of chloride of mercury by sulphuretted hydrogen, and weigh-

* Certain exceptions from the rule, that more especially in indirect estimations, and in estimations by measure, will be treated of afterwards separately.

ing the precipitated sulphide of mercury. 100 parts of chloride of mercury consist of 73·83 of mercury and 26·17 of chlorine; consequently, the precipitation of a solution of chloride of mercury by protochloride of tin will yield 73·83 per cent. of metallic mercury, which may be verified by simply weighing the precipitated metal. The precipitation of the same amount of chloride of mercury, by means of sulphuretted hydrogen, yields 85·638 of sulphide of mercury.

Now, in the former case the number 73·83 expresses *directly* the proportion of mercury contained in the analysed chloride; in the latter case we have to deduce this proportion by calculation, which may be accomplished by means of the following simple equation :—100 parts of sulphide of mercury contain 86·213 parts of mercury; how much mercury do 85·638 parts contain?

$$100 : 86{\cdot}213 : : 85{\cdot}638 : x = 73{\cdot}83.$$

It will be readily understood from the preceding illustration, that all those forms and combinations into which the known constituents of a given compound are to be converted for the purpose of quantitative estimation, must of necessity, in the first place, admit of most accurate weighing (or *measuring*), and that, in the second place, their composition must be correctly known. These two conditions are absolutely indispensable; for it is quite obvious, on the one hand, that accurate quantitative analysis must be altogether impossible if the substance, the quantity of which it is intended to ascertain, does not admit of correct weighing or measuring; and, on the other hand, it is equally evident, that if we do not know the exact composition of a new product, we lack the most indispensable element for our subsequent deductions.

To this brief intimation of the general purport and object of quantitative analysis and the general mode of proceeding in analytical researches, I have to add that certain qualifications are essential to those who would devote themselves successfully to the pursuit of this important branch of the science of chemistry. These qualifications, are, 1, theoretical knowledge; 2, skill in manipulation; and 3, strict conscientiousness.

The preliminary *theoretical knowledge* required, consists in an acquaintance with the qualitative branch of analytical chemistry; together with some practice in simple arithmetic. A previous knowledge of qualitative analysis enables us to understand all the various methods proposed for isolating substances in order to determine their weight; whilst practice in simple arithmetical calculations, enables us to deduce from our analytical results the composition of the substance examined, in equivalents, and to test the correctness of the method we have pursued. To this *knowledge* must be joined the *ability of performing the necessary practical operations*. This is an axiom generally applicable in all practical sciences, but more particularly in quantitative chemical analysis. The most extensive and

solid theoretical acquirements will not enable us, for instance, to determine the amount of common salt present in a solution of that substance, if we are without the requisite dexterity to transfer a fluid from one vessel to another without the smallest loss. The various operations of quantitative analysis demand great aptitude and manual skill, which can be acquired only by practice. But even the possession of the greatest practical skill in manipulation, joined to a thorough theoretical knowledge, will still prove insufficient to insure a successful pursuit of quantitative researches, unless combined also with a sincere love of truth and a firm determination to accept none but thoroughly verified and confirmed results.

No one who has ever been engaged in quantitative analysis can deny that cases will sometimes happen in which doubts may be entertained as to whether the results of the operation are correct, or even where the operator is *positively convinced* that the result of his process *cannot* be correct. Thus, for instance, a small portion of the substance under investigation may be spilled, or some of it lost by decrepitation; or the analyst may have reason to doubt the accuracy of his weighing; or it may happen that two analyses of the same substance do not exactly agree. In all such cases it is indispensable that the operator should be conscientious enough to repeat the whole process over again. He who is not animated with this sincere devotion to science and is afraid of encountering labor and difficulties in the pursuit of truth—he who would be satisfied with mere assumption and suppositions, and guess-work, where the attainment of positive certainty is the object, must be pronounced just as deficient in the necessary qualifications for quantitative analytical researches, as he who is wanting in theoretical knowledge or in practical skill. He, therefore, who cannot firmly and fully rely upon the accuracy of his operations and labors—he who cannot *swear* to the correctness of his results, may indeed occupy himself with quantitative analysis for his own private amusement, but he ought never to *publish* as correct and *positive* the results of his operations and researches, since such a proceeding might be eminently injurious to others, by misleading them, and might, in the end, even prove greatly detrimental to the interests of true science; nor would it be prudent for him to apply such results to any practical purpose of his own, since this would be sure to turn out very little advantageous to himself.

The domain of quantitative analysis may be said to extend over all matter, that is, in other words, anything corporeal may become the object of quantitative investigation. The present work, however, is intended to embrace only the substances used in pharmacy, arts, trades, agriculture, and manufactures.

Quantitative analysis may be subdivided into two branches, viz., analysis of *mixtures*, and analysis of *chemical compounds*. This division may appear at first sight of very small moment, yet it is necessary that we

should establish, and maintain it, if we would form a clear conception of the value and utility of quantitative research. The quantitative analysis of mixtures has not the same aim as that of chemical compounds; and the method applied to secure the correctness of the results in the former case is different from that adopted in the latter. The quantitative analysis of chemical compounds rather subserves the theoretical purposes of science, whilst that of mixtures belongs to the practical purposes of life. If, for instance, I analyse the salt of an acid, the result of the analysis will give me the constitution of that acid, its combining proportion, saturating capacity, &c. &c.; or, in other words, the results obtained will enable me to answer a series of questions, the solution of which is important for the theory of chemical science: but if, on the other hand, I analyse gunpowder, alloys of metals, medicinal mixtures, ashes of plants, &c. &c., I have a very different object in view; I do not want in such cases to apply the results which I may obtain to the solution of any theoretical question in chemistry, but I want to render a practical service either to the arts, trades, or manufactures, or to some other science. If in the analysis of a chemical compound, I wish to control the results obtained, I may do this in most cases by means of calculations based on stœchiometric data, but in the case of a mixture a second analysis is necessary to *confirm* the correctness of the results afforded by the *first*.

The preceding remarks clearly show the immense importance of quantitative analysis. It may, indeed, be averred that chemistry owes to this branch its elevation to the rank of a science, since quantitative researches have led us to discover an determine the laws which govern the combinations and transpositions of the elements. Stœchiometry is entirely based upon the results of quantitative investigations; all rational views respecting the constitution of compounds rest upon them as the only safe and solid basis.

Quantitative analysis, therefore, forms the strongest, and most powerful lever for chemistry as a science, and not less so for chemistry in its applications to the practical purposes of life, to trades, arts, manufactures, and likewise in its application to other sciences. It teaches the mineralogist the true nature of minerals, and suggests to him principles and rules for their recognition and classification. It is an indispensable auxiliary to the physiologist; and no one can deny that agriculture has derived of late, and will continue to derive, incalculable benefit from it. We need not expatiate here upon the advantages which medicine, pharmacy, and every branch of industry derive, either directly, or indirectly, from the practical application of its results. On the other hand, the benefit thus bestowed by quantitative analysis upon the various sciences, arts, &c., has been in some measure reciprocated by some of them. Thus, whilst stœchiometry owes its establishment to quantitative analysis, the stœchiometrical laws

afford us the means of controlling the results of our analyses so accurately as to insure their correctness, and to justify the reliance which we now generally place on them. Again, whilst quantitative analysis has advanced, and continues to advance, the progress of arts, and industry, our manufactures in return supply us with the most perfect platinum, glass, and porcelain-vessels, without which it would be next to impossible to conduct our analytical operations with the minuteness and accuracy to which we have now attained.

Although the aid which quantitative analysis thus derives from stœchiometry, the arts and manufactures greatly facilitate its practice, it must be admitted that the pursuit of this branch of chemistry to any satisfactory purpose, requires notwithstanding considerable expenditure of time. I would therefore advise every one desirous of becoming an analytical chemist, to arm himself with a considerable share of patience, reminding him that it is not at one bound, but gradually, and step by step, that the student may hope to attain to that skill and precision in his operations, that may justify reliance upon the correctness of his results. However mechanical, protracted, and tedious the operations of quantitative analysis may appear to be, the attainment of accuracy will amply compensate for the time and labor bestowed upon them; whilst, on the other hand, nothing can be more disagreeable than to find, after a long and laborious process, that our results are incorrect or uncertain. Let him, therefore, who would render the study of quantitative analysis agreeable to himself, from the very outset endeavour, by strict, nay, scrupulous adherence to the rules and conditions of this science, to attain to correct results, at any sacrifice of time. There cannot be a better, and more immediate reward of labor than that which springs from the attainment of accurate results, and perfectly corresponding analyses. The satisfaction enjoyed at the success of our efforts is surely in itself a sufficient motive for the necessary expenditure of time and labor, even without looking to the practical benefits which we may derive from our operations.

The following are the substances treated of in this work.

I. Metalloids.

Oxygen, Hydrogen, Sulphur, Phosphorus, Chlorine, Iodine, Bromine, Fluorine, Nitrogen, Boron, Silicon, Carbon.

II. Metals.

Potassium, Sodium, Barium, Strontium, Calcium, Magnesium, Aluminium, Manganese, Iron, Nickel, Cobalt, Zinc, Cadmium, Bismuth, Tin, Copper, Lead, Silver, Gold, Platinum, Mercury, Chromium, Antimony, Arsenic.

I have divided my subject into three parts. In the first, I treat of quantitative analysis generally; describing, 1st, the methods of performing analytical operations and processes; and, 2nd, the calculation of the results obtained. In the second, I give a detailed description of several special analytical processes. And in the third, a number of carefully selected examples, which may serve as exercises for the ground work of the study of quantitative analysis.

The following table will afford the reader a clear and definite notion of the contents of the whole work.

I. GENERAL PART.

A—DESCRIPTION OF THE ANALYTICAL METHODS AND PROCESSES.

1. Operations.
2. Reagents.
3. Forms and combinations in which substances are separated from others, or in which their weight is determined.
4. Determination of the weight of substances in simple compounds.
5. Separation of substances.
6. Organic elementary analysis.

B—CALCULATION OF THE RESULTS.

II. SPECIAL PART.

1. Analysis of natural springs, and more especially of mineral waters.
2. Analysis of such minerals, and technical products as are most frequently brought under the notice of the chemist, for the purpose of examination; including assaying, and other processes, to ascertain the commercial value of certain minerals, &c.
3. Analysis of the ashes of plants.
4. Analysis of soils.
5. Analysis of manures.
6. Analysis of the atmospheric air.

III. EXERCISES FOR PRACTICE.

APPENDIX.

1. Analytical notes and experiments.
2. Tables for the calculation of analytical results.

DIVISION I.

GENERAL PART.

SECTION I.

ON THE METHODS OF PERFORMING ANALYTICAL PROCESSES.

CHAPTER I.

OPERATIONS.

§ 1.

Most of the operations performed in quantitative research are the same as in qualitative analysis, and have been accordingly described in my work on that branch of analytical science. With respect to such operations I shall, therefore, confine myself here to pointing out any modifications they may require to adapt them for application in the quantitative branch; but I shall, of course, give a full description of such as are resorted to exclusively in quantitative investigations. Operations forming merely part of certain specific processes will be found described in the proper place, under the head of such processes.

§ 2.

The quantity of solids, and generally also that of fluids, is determined by *weight;* the quantity of gases, and sometimes of fluids by *measure;* upon the care and accuracy with which these operations are performed, depends the value of all our results; I shall therefore dwell minutely upon them.

§ 3.

WEIGHING.

To enable us to determine with precision the correct weight of a substance, it is indispensable that we should possess, 1st, a good BALANCE, and 2nd, perfectly accurate WEIGHTS.

a. THE BALANCE.

There are several points respecting the construction and properties of a good balance, which it is absolutely necessary for every chemist to understand. The usefulness of this indispensable instrument of quantitative chemistry depends upon two points; 1st, its accuracy, and 2nd, its sensibility, or delicacy.

§ 4.

The ACCURACY of a balance depends upon the following conditions:—

α. The fulcrum must be placed above the centre of gravity of the beam.

This is a condition essential to every balance. If the fulcrum were placed *in* the centre of gravity of the beam, it would not oscillate, but remain in any position in which it is placed, assuming the scales to be equally loaded. If the fulcrum be placed below the centre of gravity of the beam, the balance will be overset by the slightest impulse.

When the fulcrum is above the centre of gravity of the beam the balance represents a pendulum, the length of which is equal to that of the line uniting the fulcrum with the centre of gravity, and this line forms right angles with the beam in whatever position the latter may be placed. Now if we impart an impetus to a ball suspended by a thread, the ball, after having terminated its vibrations, will invariably fall back into its original perpendicular position under the point of suspension. It is the same with a properly adjusted balance—impart an impetus to it, and it will oscillate for some time, but it will *invariably* return to its original position; in other words, its centre of gravity will finally fall back into its perpendicular position under the fulcrum, and the beam must consequently reassume the horizontal position.

But to judge correctly of the force with which this is accomplished, and the velocity of the oscillations of a balance, it must be borne in mind that a balance is not a simple pendulum, but a compound one, *i. e.*, a pendulum in which not one, but many material points move round the turning point, or pole. The inert mass to be moved is accordingly equal to the sum of these points, and the moving force is equal to the excess of the material points below, over those above the fulcrum.

β. The suspension points of the scales must be on an exact level with the fulcrum. If the fulcrum be placed below the line adjoining the points

of suspension, increased loading of the scales will continually tend to raise the centre of gravity of the whole system, so as to bring it nearer and nearer the fulcrum; the weight which presses upon the scales, combining in the relatively high-placed points of suspension;—at last, when the scales have been loaded to a certain degree, the centre of gravity will shift altogether to the fulcrum, and the balance will consequently cease to vibrate—any further addition of weight will finally cause the beam to overset by placing the centre of gravity above the fulcrum. If, on the other hand, the fulcrum be placed above the line joining the points of suspension, the centre of gravity will become more and more depressed in proportion as the loading of the scales is increased; the line of the pendulum will consequently be lengthened, and a greater force will be required to produce an equal turn; in other words, the balance will grow the less sensible the greater the load. But when the three edges are placed on a level with each other, increased loading of the scales will, indeed, continually tend to raise the centre of gravity towards the fulcrum, but the former can in this case never *entirely* reach the latter, and consequently the balance will never altogether cease to vibrate upon the further addition of weight, nor will its sensibility be lessened; on the contrary, a greater degree of sensibility is imparted to it. This increase of sensibility is, however, compensated for by other circumstances.

γ. *The beam must be sufficiently strong and inflexible to bear without bending the greatest weight that the construction of the balance admits of;* since the bending of the beam would of course depress the points of suspension so as to place them below the line of the fulcrum, and this would, as we have just seen, tend to diminish the sensibility of the balance in proportion to the increase of the load. It is therefore necessary to avoid this fault by a proper construction of the beam. The form best adapted for beams is that of a rhomb, or of an equilateral obtuse angled triangle.

δ. *The arms of the balance must be of equal length,* i. e., *the points of suspension must be equidistant from the fulcrum or point of support,* for if the arms be unequal, the weights in equipoise will be unequal in the same proportion; *i. e.*, the weights in one scale acting upon the longer arm of the lever, will preponderate over the exact equivalent in the other scale, and this in direct proportion to the greater or lesser excess of length of one arm over the other.

§ 5.

The SENSIBILITY OR DELICACY of a balance depends principally upon the following conditions:—

a. The friction of the edges upon their supports must be as slight as possible. The greater or lesser friction of the edges upon their supports depends upon both the form and material of those parts of the balance.

The edges *must* be made of good steel, or agate, the supporters *may* be made of the same material; it is better, however, that the centre edge should rest upon a perfectly horizontal agate plane. To form a clear conception of how necessary it is that even the lateral edges should have as little friction as possible, we need simply reflect upon what would happen were we to fix the scales in immovable points by means of inflexible rods. Such a contrivance would at once altogether annihilate the sensibility of a balance, for if a weight were placed upon one scale, this certainly would sink, but at the same time, being compelled to form constantly a right angle with the beam, it would incline inwards, whilst the other scale would turn outwards, and thus the weight would be made to act upon the shorter arm of the lever. The more considerable the friction becomes at the end edges of a balance, the more the latter approaches the state just now described, and consequently the more is its sensibility impaired.

β. *The centre of gravity must be as near as possible to the fulcrum.* The nearer the centre of gravity approaches the fulcrum, the shorter becomes the pendulum. If we take two balls, the one suspended from a short, and the other from a long thread, and impart the same impetus to both, the former will naturally, in the extent of its vibrations, swing at a far greater angle from its perpendicular position than the latter. The same must of course happen with a balance; the same weight will cause the scale upon which it is placed to turn the more rapidly, and completely, the shorter the distance between the centre of gravity and the fulcrum. We have seen above, that in a balance where the three edges are on a level with each other, increased loading of the scales will continually tend to raise the centre of gravity towards the fulcrum. A good balance will therefore become more delicate in proportion to the increase of weights placed upon its scales, but, on the other hand, its sensibility will be diminished in about the same proportion by the increment of the mass to be moved, and by the increased friction attendant upon the increase of load; in other words, the delicacy of a good balance will remain the same whatever may be the load placed upon it, ranging from the minimum to the maximum that its construction will enable it to bear.

γ. *The beam must be as light as possible.*—The remarks which we have just now made will likewise show how far the weight of the beam may influence the sensibility of a balance. We have seen that it is necessary that a balance should increase in delicacy in proportion to the increase of load, since the increased friction tends to diminish its delicacy in the same proportion; and further, we have seen that this increase in sensibility is owing to the increased weight continually tending to raise the centre of gravity towards the fulcrum. Now it is evident, that the more considerable the weight of the beam is, the less will an equal load placed upon both scales alter the centre of gravity of the whole system, the more slowly will the centre of gravity approach the fulcrum, the less will the

increased friction be neutralized, and consequently the less sensibility will the balance possess. Another point to be taken into account here is, that the respective moving forces being equal, a lesser mass, or weight is more readily moved than a larger one (compare § 4 *a*).

One of my balances (made by the late M. Hoss, of Giessen) is so arranged, that whilst the beam is lifted up by *one* stop, the scales may be supported from beneath, and thus fixed by *another* independent contrivance, which is worked and regulated from the side. The moveable supports which constitutes one of the principal parts of this contrivance, are provided at the top with crossed silk bands, and move with such perfect steadiness, that the scales do not shake in the least upon the removal of the supports from beneath them (provided, of course, the operation be effected with some degree of delicacy and caution). This arrangement, besides facilitating the loading of the scales, affords this advantage—that it enables the operator to put an immediate stop to all trembling, or shaking of the scales, and the convenience that, in cases where one and the same body, or substance has to be weighed repeatedly, the weights may be left on the scale without risk to the balance.

§ 6.

We will now proceed, first, to give the student a few general rules to guide him in the purchase of a balance intended for the purpose of quantitative analysis; and, secondly, to point out the best method of testing the accuracy, and sensibility of a balance.

1. A balance able to bear 70 to 80 grammes in each scale, suffices for most purposes.

2. The balance must be enclosed in a glass-case to protect it from dust. This case ought to be sufficiently large, and especially its side-walls should not approach too near the scales. It must be constructed in a manner to admit of its being closed with facility when the weights have been placed on the scales, and thus to allow the operation of weighing being effected without any disturbing influence from currents of air. Therefore, either the front part of the case should consist of three parts, viz., a fixed centre piece, and two lateral parts, opening like doors, or if the front part happen to be made of one piece, and arranged as a sliding-door, the two sides of the case must be provided each with a door.

3. The balance must be provided with a proper contrivance to render it immovable whilst the weights are being placed upon the scales. This is most commonly effected by an arrangement which enables the operator to lift up the beam and thus to remove the fulcrum from its support, whilst the scales remain suspended; other contrivances fix the scales, and leave the fulcrum resting on its support.

But whatever contrivance may be had recourse to, at all events it is

highly advisable to have the case of the balance so arranged that the processes of lifting up the beam, fixing the scales, &c., can be conducted while the case remains closed, and consequently from without.

4. It is necessary that the balance should be provided with an index to mark its oscillations; this index is more appropriately placed at the bottom than at the side of the balance.

5. The balance must be provided with a pendulum, or with a spirit level, to enable the operator to place the three edges on an exactly horizontal level; it is best also for this purpose that the case should rest upon three screws.

6. It is very desirable that the beam should be graduated into decimals, so as to enable the operator to weigh the milligramme and its fractions, by suspending a centigramme rider, or hook on, or between the indicated points of a graduated line, instead of placing the weight on the scale. Most modern balances are so constructed that the position of the riders on the beam may be shifted at pleasure, and without opening the glass case, by means of a moveable arm placed in the end of the case.

7. The balance must be provided with a screw to regulate the centre of gravity, and likewise with two screws to regulate the equality of the arms, and finally with screws to restore instantly the equilibrum of the scales, should this have been disturbed.

§ 7.

The following experiments serve to test the accuracy and sensibility of a balance.

1. The balance is, in the first place, accurately adjusted, if necessary, either by the regulating screws, or by means of tinfoil, and a milligramme weight is then placed in one of the scales. A good and practically useful balance must turn distinctly with this weight; a delicate chemical balance should indicate the $\frac{1}{10}$ of a milligramme with perfect distinctness.

2. Both scales are loaded with the maximum weight the construction of the balance will admit of—the balance is then *accurately* adjusted, and a milligramme added to the weight in the one scale. This ought to cause the balance to turn to the same extent as sub. 1. In most balances, however, it shows somewhat less on the index.

3. The balance is accurately adjusted, (should it be necessary to establish a perfect equilibrium between the scales by loading the one with a minute portion of tinfoil, this tinfoil must be left remaining upon the scale during the experiment;) both scales are then equally loaded, say with about fifty grammes each, and, if necessary, the balance is again adjusted (by the addition of small weights, &c.) The load of the two scales is then interchanged, so that the right scale is transferred to the left, and *vice versâ*. A balance, the arms of which are perfectly equal, must maintain

its perfect equilibrium upon this interchange of the weights of the two scales.

4. The balance is accurately adjusted; it is then arrested, and subsequently set again in motion, until it recovers its equilibrium; the same process should be repeated several times. A good balance must invariably re-assume its original equilibrium. A balance, the end edges of which afford too much play to the hook resting upon them, so as to allow the latter slightly to alter its position, will show perceptible differences in different trials. This fault, however, is possible only with balances of defective construction. A balance to be practically useful for the purposes of quantitative analysis, *must* stand the first, second, and last of these tests. A slight inequality of the arms is of no great consequence, since this may be readily and completely remedied by the manner of weighing.

§ 8.

b. THE WEIGHTS.

The French gramme is the best standard for calculation. A set of weights ranging from fifty grammes to one milligramme may be considered sufficient for all practical purposes. With regard to the set of weights, it is generally a matter of perfect indifference in chemical experiments whether the gramme, its multiples and fractions, are really and perfectly equal to the accurately adjusted *normal* weights of the corresponding denominations; but it is *absolutely* and *indispensably necessary* that they should agree *perfectly* among and with each other, *i. e.*, the $\frac{1}{100}$ gramme weight must be exactly the one hundredth part of the gramme weight of the set, &c., &c.

2. The whole of the set of weights should be kept in an appropriate well-closing box; and it is desirable likewise that a distinct compartment be appropriated to every one even of the smaller weights.

3. As to the shape best adapted for weights, I think that of short cylinders, with a handle at the top, the most convenient and judicious form for the large weights; small square pieces of platinum foil, turned up at one corner, are best adapted for the minute and fractional weights. The foil used for this purpose should not be too thin, and the respective compartments adapted for the reception of the several smaller weights in the box, should be large enough to admit of their contents being taken out of them with facility, or else the smaller weights will soon get cracked, bruised and indistinct. Every one of the weights (with the exception of the milligramme),* should be distinctly marked.

* One milligramme = ·0154 grains Troy.
One centigramme = ·1543 " "
One decigramme = 1·5434 " "
One gramme = 15·4346 " "

4. With respect to the material most suitable for the manufacture of weights, I think that, although rock crystal is admirably adapted for normal weights, its high price, and the inconvenient form of the pieces, render it far less so for weights intended to serve in the processes of quantitative analysis. Platinum weights would be sure to be universally adopted, were the metal not too expensive; but as it is, we commonly rest satisfied with having the smaller weights only, from one gramme downwards, made of platinum foil, using brass weights for all the higher denominations. Brass weights must be carefully shielded from the contact of acid or other vapours, or their correctness will be impaired; nor should they ever be touched with the fingers, but always with small pincers. But it is an erroneous notion to suppose that weights slightly tarnished are unfit for use. It is, indeed, hardly possible to prevent weights for any very great length of time from getting slightly tarnished. I have carefully examined many weights of this description, and have found them as exactly corresponding with one another in their relative proportions as they were when first used. The tarnishing coat, or incrustation is in most instances so extremely thin, that even a very delicate balance will generally fail to point out any perceptible difference in the weight. It will, however, be found very advantageous to gild the brass weights (by the electro-galvanic process) previously to adjusting them.

The exact accordance and agreement of the several denominations of weights of the same set, may be fully tested and assayed in the following manner:—

One scale of a very delicate balance is loaded with a one gramme* weight, and the balance is then completely equipoised by placing an exactly equivalent weight in small pieces of brass, and finally tinfoil (not paper, since this absorbs moisture), upon the other scale. The weight is then removed, and replaced successively by the other gramme weights which the operator may happen to possess, and afterwards by the same amount of weight in pieces of lower denominations.

The balance is carefully scrutinised at every fresh assay, and any deviation from the exact equilibrium marked. The several pieces of higher denominations are then tested, and assayed in the same way. In the comparison of the smaller with the larger weights, the former must not show the slightest perceptible difference on a balance turning with $\frac{1}{10}$ of a milligramme; differences, however, of from the $\frac{1}{10}$ to $\frac{2}{10}$ part of a milligramme may be passed over, in the larger weights, since this will not materially impair their usefulness. If you wish them to be more accurate, you must adjust them yourself. In the purchase of weights chemists ought always to bear in mind, that an accurate weight is truly valuable, whilst an inaccurate one is absolutely worthless. Experience has taught

* One gramme = 15·4346 grains Troy.

me that it is invariably the safest way for the analytical chemist to test and assay himself every weight he purchases, no matter how high the reputation of the maker may happen to stand.

§ 9.

c. THE PROCESS OF WEIGHING.

We have two different methods of determining the weight of substances; the one is termed "*direct weighing*," the other is called "*weighing by substitution*."

In *direct weighing*, the substance is placed upon one scale, and the weight upon the other. If we possess a balance, the arms of which are of equal length, and the scales in a perfect state of equilibrium, it is indifferent upon which scale the substance is placed in the several weighings required during an analytical process; *i. e.*, we may weigh upon the right or upon the left side, and change sides at pleasure, without endangering the accuracy of our results. But if, on the contrary, the arms of our balance are not perfectly equal, or if the scales are not in a state of perfect equilibrium, we are compelled to weigh invariably upon the same scale, otherwise the correctness of our results will be more or less materially impaired.

Suppose we want to weigh one gramme of a substance, and to divide this amount subsequently into two equal parts. Let us assume our balance to be in a state of perfect equilibrium, but with unequal arms, the left being 99 millimetres,* the right 100 millimetres long; we place a gramme weight upon the left scale, and against this, on the right scale, as much of the substance to be weighed as will restore the equilibrium of the balance.

According to the axiom, "masses are in equilibrium upon the lever, if the distance of their products from the point of support is equal," we have consequently upon the right scale 0·99 gramme of substance, since 99 : 1·00=100 : 0·99. If we now, for the purpose of weighing one half the quantity, remove the whole weight from the left scale, substituting a 0·5 gramme weight for it, and then take off part of the substance from the right scale, until the balance recovers its equilibrium, there will remain 0·495 gramme; and this is exactly the amount we have removed from the scale: we have consequently accomplished our object with respect to the relative weight; and, as we have already remarked, the absolute weight is not generally of so much importance in chemical experiments. But if we attempted to halve the substance which we have on the right scale, by first removing both the weight and the substance from the scales, and placing subsequently a 0·5 gramme weight upon the *right* scale, and the

* One millimetre = ·03937 inch.
One centimetre = ·3937 inch.
One decimetre = 3·937 inches.
One metre . . = 39·37 inches.

substance upon the *left*, until the balance recovers its equilibrium, we should have 0·505 of substance upon the left scale, since 100 : 0·500 = 99 : 0·505 ; and consequently, instead of exactly halves, we should have one part of the substance amounting to 0·505, the other only to 0·495.

If the scales of our balance are not in a state of absolute equilibrium, we are obliged to weigh our substances in vessels (see § 10, 4), to ensure accurate results (although the arms of the balance be perfectly equal). It is self-evident that the weights in this case must likewise be invariably placed upon one and the same scale, and that the difference between the two scales must not undergo the slightest variation during the whole course of a series of experiments.

From these remarks result the two following rules :

1. It is, under all circumstances, advisable to weigh substances invariably upon one and the same scale.

2. If the operator happens to possess a balance for his own private and *exclusive* use, there is no need that he should adjust it at the commence- of every analysis ; but if the balance be used in common by several persons, it is absolutely necessary to ascertain, before every operation, whether its state of absolute equilibrium may not have been disturbed.

Weighing by substitution yields not only *relatively*, but also *absolutely* accurate results ; no matter whether the arms of the balance be of exactly equal lengths, or not, or whether the scales be in perfect equipoise, or not.

The process is conducted as follows : the substance to be weighed—say a platinum crucible—is placed upon one scale, and the other scale is accurately counterpoised against it. The platinum crucible is then removed, and the equilibrium of the balance restored by substituting weights for the removed crucible. It is perfectly obvious that the substituted weights will invariably express the real weight of the crucible with absolute accuracy. We weigh by substitution whenever we wish to obtain *absolutely* accurate results ; as, for instance, in the determination of atomic weights. The process may be materially shortened by accurately determining, and noting, in the first place, the weight of a certain tare intended to serve as a counterpoise, and which must, of course, be heavier than the substance (or substances) we wish to weigh ; this tare, or counterpoise is then shifted to the opposite scale, and the substance to be weighed placed on the other, together with the smaller weights requisite to restore the equilibrium of the balance. The sum of the weights added is then subtracted from the known amount of the counterpoise : the remainder will at once indicate the exact weight of the substance we are dealing with. Let us suppose, for instance, we have on the left scale a tare requiring on the right a weight of exactly fifty grammes to counterpoise it ; we shift the tare to the right scale, and place on the left, say a platinum crucible. We find that it re-

quires an addition of weight to the extent of 40 grammes to counterpoise the tare on the right scale. Accordingly, the crucible weighs 50 grammes *minus* 40 = 10 grammes.

§ 10.

The following rules will be found useful in performing the process of weighing :—

1. The safest and most expeditious way of ascertaining the exact weight of a substance, is to avoid trying weights at random; instead of this, a strictly systematic course ought to be pursued in counterpoising substances on the balance. Suppose, for instance, we want to weigh a crucible, the weight of which subsequently turns out to be 6·627 grammes; well, we place 10 grammes on the other scale against it, and we find this is too much; we place the weight next in succession, *i. e.*, 5 grammes, and find this too little; next 7, too much; 6, too little; 6·5, too little; 6·7, too much; 6·6 too little; 6·65 too much; 6·62 too little; 6·63 too much; 6·625 too little; 6·627, right.

I have selected here for the sake of illustration a most complicated case; but I can assure the student of quantitative analysis, that this systematic way of trying the counterpoising of substances will in most instances lead to the desired end, in half the time required where weights are tried at random. A few minutes will generally suffice to ascertain the weight of a substance to within the $\frac{1}{10}$ of a milligramme.

2. I have already had occasion to observe, that the placing of small riders, or hooks, weighing one centigramme each, on, or between the points of the decimal divisions of the beam, is a more expeditious way to determine a milligramme, and its decimal divisions, than the use of the corresponding weights upon the scale.

3. Particular attention and care should be bestowed on the writing, or noting down the weights on paper. The best way is to put down the weights first by inference from the blanks, or gaps in the weight box, and to control, and verify the notation subsequently by removing the weights from the scale, and replacing them in their respective compartments in the box.

4. The balance ought to be arrested every time any change is contemplated, such as removing weights, substituting one weight for another, &c., &c., or it will soon get spoiled.

5. Substances must never be placed *directly* upon the scales, but ought to be weighed in appropriate vessels of platinum, silver, glass, porcelain, &c., &c., never in paper or card, since these, being liable to attract moisture, are apt to alter in weight. The most common method is to weigh in the first instance the vessel by itself, and to introduce subsequently the substance into it; to weigh again, and subtract the former weight from the latter. In many instances, and more especially where several portions

of the same substance are to be weighed, the united weight of the vessel and of its contents is first ascertained; a portion of the contents is then taken out, and the vessel weighed again; the difference between the latter and the original weight expresses the amount of the portion taken out of the vessel.

6. Substances liable to attract moisture from the air, must be weighed invariably in closed vessels (in covered crucibles, for instance, or between two watch glasses, or in a stoppered glass tube); fluids are to be weighed in small bottles, closed with glass stoppers.

7. A vessel ought never to be weighed whilst hot, since it will in that case invariably weigh lighter than it really is. This is owing to two circumstances. In the first place, every body condenses upon its surface a certain amount of air and of moisture, the quantity of which depends upon the temperature, and the hygroscopic state of the air, and likewise on its own temperature. Now suppose a crucible has been weighed cold at the commencement of the operation, and is subsequently weighed again whilst hot, together with the substance it contains, and the weight of which we wish to determine. If we subtract for this purpose the weight of the cold crucible, ascertained in the former instance, from the weight found in the latter, we shall subtract too much, and consequently we shall set down less than the real weight for the substance. In the second place, bodies at a high temperature are constantly communicating heat to the air immediately around them; the heated air expands and ascends, and the denser and colder air, flowing towards the space which the former leaves, produces a current which tends to raise the scale, making it thus appear lighter than it really is.

8. If we suspend from the end edges of a correct balance, 10 grammes of platinum and 10 grammes of glass, by wires of equal weight, the balance will assume a state of equilibrium; but if we subsequently immerse the platinum and glass completely in water, this equilibrium will at once cease, owing to the different specific gravity of the two substances; since, as is well known, substances immersed in water lose of their weight a quantity precisely equal to the weight of their own bulk of water. If this be borne in mind, it must be obvious to every one that weighing in the air is likewise defective, inasmuch as the bulk of the substance weighed is not the same with that of the weight. This defect, however is so very insignificant, owing to the trifling specific gravity of the air in proportion to solid substances, that we may generally disregard it altogether in analytical experiments. In cases, however, where *absolutely* accurate results are required, the bulk both of the substance examined, and of the weight, must be taken into account, and the weight of the corresponding volume of air added respectively to that of the substance, and of the weight, making thus the process equivalent to weighing *in vacuo*.

§ 11.

2. MEASURING.

The process of measuring is confined in analytical researches mostly to gases, and fluids. Generally speaking, quantitative determinations by weight may be considered more accurate than those by measure. Yet the method of measuring gases has been lately so greatly improved by Bunsen, and by Regnault and Reiset (as that of measuring fluids has been by Gay-Lussac), that it may almost be said to excel in accuracy the method of weighing. However, such accurate measurement of gases demand an expenditure of time, and care, such as can be bestowed only on the nicest, and most delicate scientific investigations.*

The accuracy of the results obtained by measuring, depends upon the proper construction of the measuring apparatus, and also upon the manner in which the process is conducted.

a. THE MEASURING OF GASES.

We use for the measuring of gases graduated tubes of greater, or less capacity, made of strong glass, and closed by fusion at one end, which should be rounded. The following apparatus will be found sufficient for all the processes of measuring which we shall have occasion to treat of in this work.

1. A bell-glass capable of holding from 150 to 250 cubic centimeters,† and about one and a-half inch in diameter; this bell-glass should be graduated into double cubic centimeters; that is, every divisional line should correspond to two cubic centimeters.

2. From five to six glass tubes, about half an inch in diameter, and capable of holding from 30 to 40 cubic centimeters each, divided into double cubic millimeters, so that every line corresponds to two cubic millimeters. The sides of these tubes should be pretty thick, otherwise they will be liable to break, especially when used to measure over mercury. The sides of the bell-glass should be from 4 to 6, those of the tubes from 2 to 3 millimeters thick.

The most important point, however, is that the tubes be correctly graduated, since upon this of course depends the accuracy of the results.‡

* For a detailed description of Bunsen's method, I refer the student to the article on the "Eudiometer," by H. Kolbe, in Liebig, Poggendorff, and Wöhler's Handwörterbuch der Chemie. Most useful information may be derived from that article by all who wish to occupy themselves with the analysis of gases.

† One cubic centimeter = ·0610 cubic inch.

‡ For the manner of graduating the tubes, the student may consult Berzelius' Manual of Chemistry, 4th edition, vol. x., article Measuring; or Faraday's Chemical Manipulations; or the article on Eudeometry, in Liebeg Wöhler and Poggendorff's Handwörterbuch der Chemie.

The practical usefulness of the measuring tubes depends principally upon the fulfilment of three conditions.

1. The divisions of the tube must exactly correspond with each other.

2. The divisions of every one of the tubes must exactly correspond with those of the other tubes. And,

3. The volumes marked on the graduation line must exactly correspond with the weights used by the analyst.

The following experiments serve to test our gas measuring tubes.

a. The tube which it is intended to examine is placed in a perpendicular position, and filled gradually with accurately measured small quantities of mercury, care being taken to ascertain with the utmost accuracy and precision whether the graduation of the tube is proportionate to the equal volumes of mercury poured in. The measuring of the mercury is effected by means of a small glass tube closed (by fusion) at one end, and ground perfectly even, and smooth at the other. This tube is filled to overflowing by immersion under mercury, care being taken to allow no air-bubbles to remain in it; the excess of mercury is then removed by pressing a small glass plate down on the smooth edge of the tube.

b. Different quantities of mercury are measured off in one of the smaller tubes, and then successively transferred into the other tubes. The tubes may be considered in perfect accordance with one another, if the mercury reaches invariably the same divisional point in every one of them.

Such tubes as are intended simply to determine the relative volume of different gases, need only correspond individually and collectively in the divisions of their graduated scales; but in cases where we want to calculate the *weight* of a gas by inference from its *volume*, it is necessary also to ascertain whether the volumes indicated by the degrees of the graduation scale correspond with the weights in our possession.

c. For this purpose one of the tubes is accurately weighed and then filled with distilled water at a temperature of 39·2° Fahr., to the last mark of the graduated scale; the weight of the water is then accurately determined. If the tubes have been correctly graduated, and the weights properly adjusted, the number of cubic centimeters of this scale will be equal to that of the gramme weights placed against the water. In this case, the weight of gases may be calculated at once from their measured volumes. But should it happen that the accordance between the divisions of the tubes and the weights of the balance be not so perfect, no matter whether the error lie in the graduation of the tube or in the adjustment of the weights, we cannot proceed at once to calculate the weight of a gas from its ascertained volume, but have, in the first place, to reduce the latter in proportion to the difference existing between the divisions of our graduated scales and our weights. Let us suppose, for instance, that upon examin-

ing our gas tubes, we find 99 cubic centimeters of water, as indicated by the graduated scale of the tubes to weigh 100 grammes, and to correspond consequently to 100 grammes, according to our weights; to convert in this case the measured volume of a gas into weight, we must, in the first place, multiply by $\frac{100}{99}=1{\cdot}0101$, the number of cubic centimeters found.

If, therefore, we wish to employ such tubes we must have a table, reducing the measures to their corresponding weights for every tube we employ.

Bunsen's measuring tubes are all graduated simply into millimetrical divisions, by means of a very ingeniously constructed divider. To what volumes the respective divisional lines correspond, is subsequently determined by measuring into the tube equal volumes of mercury. The corresponding volumes are noted down in a table. This mode of graduating and adjusting measuring tubes, is unquestionably the best.

In the measuring of gases we must have regard to the following points.

1. We must endeavour to determine as accurately as possible the exact height at which the water, or mercury stands. 2. We must take into consideration the temperature of the gas. 3. The degree of pressure operating upon it. And 4. The circumstance whether it is dry, or moist. The three latter points will be readily understood, if it be borne in mind that any alteration in the temperature of gases, or in the pressure acting upon them, or in the tension of the admixed aqueous vapour, involves likewise a considerable alteration in their respective volumes.

With regard to the first point, it is somewhat difficult to decide with absolute accuracy the exact degree of the scale at which the mercury, or water may happen to stand in the gasometer, since mercury in a jar, or cylinder (more especially in a narrow one), has a convex surface owing to its own cohesion; whilst water, on the other hand, under the same circumstances has a concave surface, owing to the attraction which the walls of the tube exercise upon it. To ascertain the exact position of the mercury, or water, the jar, or cylinder should invariably be placed in a perfectly perpendicular position, and the eye directed on a level with the surface of the fluid. The perpendicular position of the cylinder may be readily adjusted by means of two plummets suspended at a short distance from the cylinder, in such a manner that their respective directions intersect each other in the vertical line of the latter. To place the eye on an exact level with the surface of the fluid in the cylinder, a small mirror is pressed firmly against the tube, on the opposite side, and the centre of the eye fixed on the mirror right across the surface of the fluid. When the eye is thus placed in the right position, the mirror is removed, and the exact heighth of the fluid read off. If water be used as the confining fluid, the middle of the dark zone formed by the water around the inner

walls of the tube, in obedience to the attraction exercised upon it by these walls, is assumed to be the real surface; whilst when operating with mercury, we have to place the real surface in a line drawn exactly in the centre between the highest point of the surface of the mercury, and the points at which the latter is in actual contact with the walls of the tube. However, the results obtained in this way, are only approximate. Absolutely accurate results cannot be arrived at, in measuring over water, or any other fluid that adheres to glass. But over mercury they may be arrived at. To this end, it is simply requisite to determine the error of the meniscus. This is done for each respective tube, once for all, in the following manner: a certain amount of mercury is poured into the tube, and its height read off right on a level with the top of the convex surface exhibited by it; a few drops of solution of chloride of mercury are then poured on the top of the metal; this causes the convexity to disappear; the height of the mercury in the tube is now read off again: the difference between the two readings is the error of the meniscus. In the process of graduation, the tube stands upright, in that of measuring gases, it is placed upside down; the error of the meniscus must accordingly be doubled, and the sum added to each volume of gas read off over the top of the convex surface of the mercury. (*Kolbe.*)

The mercury intended to serve in the measuring of gases should be pure; it must, more particularly, be free from lead, and tin, since an admixture of either of these metals imparts to mercury the property of adhering to glass. Should lead, or tin happen to be present, it may be removed by keeping the mercury in contact for a day with dilute nitric acid in a shallow basin, taking care to stir frequently. From dust, &c., mercury may be freed by filtration through a cloth.

With regard to the second point, the temperature of the gas is made to correspond with that of the confining fluid, which latter may be readily ascertained.

If the construction of the pneumatic apparatus is such as to permit the total immersion of the cylinder into the confining fluid, a corresponding temperature between the latter and the gas, which it is intended to measure, is most readily induced; but if the construction of the apparatus will not allow this total immersion of the cylinder, it is necessary that the surrounding air should have the same temperature with the fluid, and we are consequently obliged in such cases to keep the cylinder for a considerable time exposed to the influence of both, before we can proceed to determine the exact degree of the scale at which the mercury or water stands. The operator should take care also to perform his experiment at an effectual distance from the heat of a stove, or the direct rays of the sun, &c.; and, moreover, he should not grasp the cylinder with his hand, but simply press it down with the finger, or, better still, with small wooden pincers,

or a clothes peg. Since if either of these rules be neglected, the gas will expand again, and of course inaccurate results will be the consequence.

With regard to the third point, the gas is under the actual pressure of the atmosphere, if the confining fluid stands on an exact level both in, and outside the cylinder; the degree of pressure exerted upon it may therefore at once be ascertained by consulting the barometer. But if the confining fluid stands *higher* in the cylinder than outside, the gas is under *less* pressure,—if *lower*, it is under *greater* pressure than that of the atmosphere; in the latter case, the perfect level of the fluid inside, and outside the cylinder may readily be restored by raising the tube; if the fluid stands higher in the cylinder than outside, the level may be restored by depressing the tube; this however can only be done in cases where we have a trough of sufficient depth. When operating over water, the level may in most cases be readily effected; when operating over mercury, it is frequently impossible to bring the fluid to a perfect level inside and outside the cylinder.

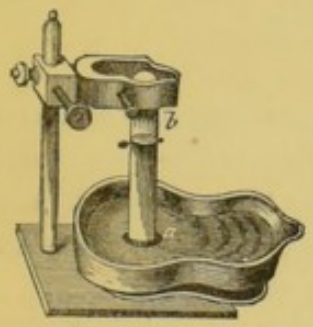


Fig. 1.

In the case illustrated in Fig. 1, we have the gas under the pressure of the atmosphere, *minus* the pressure of a column of mercury equal in length to the line *a b*. This pressure may be determined, therefore, by measuring the length of *a b*, with the greatest possible accuracy, and subtracting it from the actual state of the barometer. Suppose, for instance, the barometer stands at 29 inches, and length of *a b* is=3 inches, the actual pressure upon the gas will be 29—3=26 inches.

If we have water, or some other fluid (solution of potassa, for instance) over the mercury, we proceed generally as if this were not the case; *i.e.*, we either place the mercury on a level inside and outside the cylinder, or measure the difference between the surface of mercury in the cylinder, and that in the trough. The pressure of the column of water, &c., &c., floating over the mercury, is mostly so trifling that it may safely be disregarded altogether. The more correct way, of course, would be to measure the height of the column of water, &c., to reduce this upon mercury, and to subtract the resulting figure from the actual state of the barometer. But this correction may be omitted as immaterial, as already stated above. Absolutely correct results cannot be arrived at under such circumstances.

In the measuring of gases saturated with aqueous vapour, it must be taken into account that the vapour, by virtue of its tension, exerts a pressure upon the confining fluid; the result must, therefore, be corrected accordingly. This is an easy task, however, since we know the respective tension of aqueous vapour for the various degrees of temperature. To this end it is, of course, necessary that the gas should be actually saturated

with the vapour. It is, therefore, indispensable in the measuring of gases, to take care either to have the gas absolutely dry, or thoroughly saturated with aqueous vapour.

It is quite obvious from the preceding remarks, that volumes of different gases can be compared only if measured at the same temperature, under the same pressure, and in the same hygroscopic state. The temperature is generally reduced to 32° Fahr., the hygroscopic state of the gases to 0, and the pressure is maintained at 29·8 of the barometer. How this is effected, as well as the manner in which we deduce the weight of gases from their bulk, will be found in the chapter on the calculation of analytical results.

§ 12.

b. THE MEASURING OF FLUIDS.

As the operation of measuring fluids is more expeditious than that of weighing them, it is frequently resorted to, more particularly in analytico-technical investigations.

The following vessels are used for measuring fluids :—

1. *The Graduated Pipette.*

We use two sorts of pipettes ; the one made to measure off only *one* certain definite quantity of fluid, say 10, 20, 50, cubic centimeters, and, accordingly marked with a single line only ; the other to measure off any given quantity of fluid, within the limit of the capacity of the glass, of course. The latter is illustrated by Fig. 2.



Fig. 2.

The lower aperture has a diameter of 1·5 m. m. (millimeters), the upper of 3·4 m. m. The glass holds, up to the 0 mark, 50 c. c. (cubic centimeters), every degree corresponds accordingly to 0·5 c. c.

This instrument serves only to measure off definite quantities of fluid. For this purpose the end *a* is dipped into the fluid, and suction applied to *b*, until a somewhat larger quantity of the fluid than required has ascended into the tube ; *b* is then closed with the finger, which is a little moistened for the purpose, and the eye being placed on an exact level with the surface of the fluid, the excess over the quantity required is allowed to drop out from *a*.

From its peculiar shape and construction, this instrument enables the operator to transfer without loss to any other vessel the fluid measured off.

In measuring with the graduated pipette, the dark zone formed by the adhesion of the fluid to the inner walls of the tube, must be taken into account ; as it is by no means a matter of indifference whether the mark line coincides with the lower border, or with the centre, or with the upper

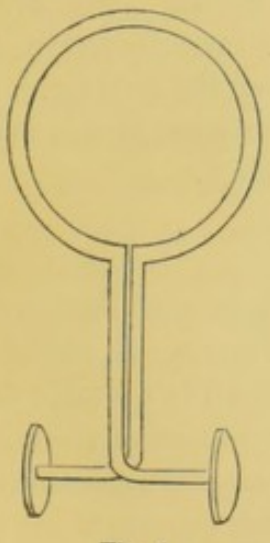
border of the zone. The measuring will be found most accurate when the mark line is made to coincide with the lower straight border of the dark zone (see *a*, Fig. 3); which may be accomplished with great exactness in a good light, more particularly by holding the glass up before the sun, or before a strong gas light. The circumstance whether the glass is so graduated that the last drop of the fluid which gathers sometimes at the lower aperture of the glass, and may be got out by blowing in at the upper mouth, is to be counted in, or not, must not be overlooked.



Fig. 3.

If it is intended to use the pipette for the purpose of mixing one fluid with another up to a certain point, *e. g.*, the point of neutralisation, and of ascertaining subsequently the exact quantity of fluid so added to another, the lower tube of the instrument is provided either with a small glass-cock, or with a *compression stop-cock,* as recommended by *Mohr.*—(Transactions of the 29th Meeting of German Natural Philosophers.)

This simple and most practical contrivance consists of a short piece of tube of vulcanized india-rubber, which is kept compressed, and completely closed by means of a wire clasp, but may be opened at pleasure to a greater, or less extent, by a stronger or less pressure. Fig. 4 shows the form of the wire clasp.


Fig. 4.

One end of the little india-rubber tube is inverted over the point of the pipette, and securely tied to it; at the other end is fastened a short piece of a small strong glass tube drawn out to a moderately fine point.

The pipette thus arranged is fixed vertically in a clasp, or other appropriate instrument, and placed so that the analyst standing, or sitting before it has his eye on an exact level with the 0 point of the pipette. This contrivance enables the analyst not only to read off the height of the fluid, accurately, and deliberately, both before, and after the experiment, but also to control the flowing off of the fluid from the glass, and even to restrain it, with positive certainty, to single drops.

2. *The Graduated Burette, or Dropping-glass.*

This instrument, illustrated by Fig. 5, serves for the same purpose as the pipette provided with a stop-cock. The dropping aperture is about 1·5



Fig. 5. Fig. 5.*a*.

m. m. in diameter, and must be placed so much lower than the mouth of the wide tube, that the operation of pouring out, or rather dropping out, the fluid may be effected, without the slightest risk of the fluid running over the mouth of the wide tube.

It is advisable to have the burette fixed in a solid wooden stand.

Burettes hold generally about 50 or 100 c. c.; in the former case they are graduated into 100°, in the latter into 200°, each degree corresponding accordingly to 0·5 c. c.

Some prefer the burette illustrated by Fig. 5 *a*.

As a burette is graduated, not like a pipette, from below upwards, but from the top downwards, we must, when we want to use it, fill it up in the first place to the 0 point, then let the fluid run out, or drop out to the extent required, and afterwards read off the remainder.

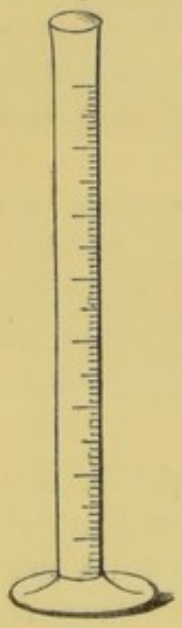


Fig. 6.

3. *The Graduated Cylinder.*

The graduated cylinder, illustrated by Fig. 6, serves to prepare fluid mixtures that are to hold in solution a known amount of substance in a definite volume of the mixture. To this end the fluid which is to be diluted (solution of common salt for instance), is poured into the cylinder, and the other fluid with which it is to be mixed, is added until the mixture reaches the desired divisional line. A perfectly even and smooth glass plate is then laid on the ground edge of the mouth of the cylinder, and firmly held down on it; the fluids are then carefully intermixed by shaking, and occasional inversion of the cylinder. Instead of the graduated cylinder we may use also in many cases the measuring flask, described sub. 4.

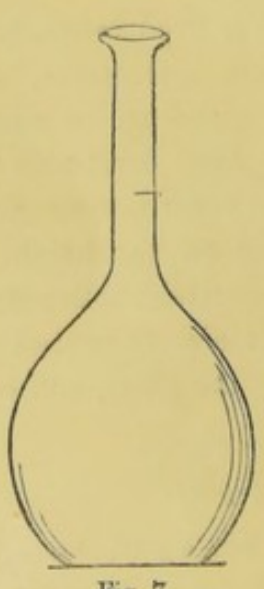


Fig. 7.

4. *The Measuring Flask.*

It occurs not unfrequently in analytical investigation that we dissolve a compound substance in a fluid, dilute the solution up to a certain definite volume, and proceed then to make the quantitative estimations of the respective constituents in several carefully measured quantities of the solution. The most appropriate instrument for this purpose, is a flask, with a line cut in with a file, at some part of the neck. (See Fig. 7.)

To prepare a vessel of this kind for use, select a small, somewhat long-necked flask, holding, as is ascertained by a preliminary experi-

ment, 100 c. c. of water up to a convenient part of the neck. Let the water run out to the last drop, but without wiping the inner side of the flask dry. Weigh into the flask accurately 100 grammes of water of 39·2° Fahr., put the flask on a solid, perfectly horizontal base, place your eye on an exact level with the surface of the fluid in the flask, and mark both the upper and lower border of the dark zone formed by the fluid around the inner walls, by little dots made on the glass with a point dipped into asphaltum varnish, or some other substance of the kind. Now let the water run off, place the flask in a convenient position before you, and replace the dots by fine distinct lines cut with a diamond into the glass.

In the same way you may prepare flasks, holding respectively 200, 300 400, &c., grammes of water of 39·2° Fahr. Mark the whole of these flasks, besides with the number of cubic centimeters, which they respectively hold up to the mark, with *a* to indicate that they, when filled up exactly to the mark, *give*, on being emptied, and drained to the last drop, the number of cubic centimeters marked on them.

Besides these, we use flasks prepared on a different plan, and which we will mark *e*. The flasks when filled up to the line-marks cut into them, *hold* actually the number of cubic centimeters inscribed on them. They are prepared by weighing into flasks *perfectly dry inside*, respectively 200, 300, 400, 1000, &c., grammes of water, of 39·2° Fahr., and marking the height of the water in the respective flasks, by lines cut into the glass, in the way just now described.

I will give here an illustration of the method in which the flasks belonging respectively to these two systems are used. Suppose we have ten grammes of a mixture of chloride of sodium, and of sulphate of magnesia dissolved in water, and we wish to determine in separate portions of the solution, the chlorine, the sulphuric acid, the soda, and the magnesia; to this end, we pour the solution into the flask of the system *e*, holding 500 c. c., and fill up with water to the line-marks; we then carefully intermix the fluid in the flask, by shaking and occasional inversion (closing the mouth of the flask with the palm of the hand, or, better still, if it has ground edges, with a smooth, and perfectly even glass plate). We now fill out of this flask, a flask of the system *a*—holding 100 c. c., up to the line-marks; we empty this flask then into another vessel for the estimation of the sulphuric acid; we fill it again and empty it again in the same way into another separate vessel, for the estimation of the chlorine, &c.

To understand how necessary (or, at all events, advantageous) it is that there should be flasks belonging respectively to the two systems, we need simply consider what additional and troublesome operations would be required if the flask of the capacity of 100 c. c. belonged to the system *e*, instead of to *a*. We should, in that case, have to rinse the flask after the first emptying, and to add the rinsings to the fluid; we should then

have to wipe the flask perfectly dry inside, or to rinse it carefully with the fluid under examination, before we could proceed to a second measuring, and at each successive measuring we should have to go through the same tedious process again.

That this method of measuring has hitherto often yielded much less accurate results than may be obtained by it, is to be attributed to the circumstance that analysts have but rarely distinguished properly between the flasks of the two systems.

In examining the graduated pipette, burette, and cylinder, it is to be observed that the two former must belong to system *a*, the latter to system *e*.

To point out the difference between flasks marked to contain the same volume of fluid, but belonging respectively to the two different systems, I will mention here that my flask of system *a*, marked to contain 100 c. c., contains *actually* 100·2 c. c.

If it is required simply to measure off repeatedly the same volume of a fluid, a flask furnished with a glass stopper, rounded at the bottom, will answer the purpose.

CHAPTER II.

PRELIMINARY OPERATIONS.—PREPARATION OF SUBSTANCES FOR THE PROCESSES OF QUANTITATIVE ANALYSIS.

§ 13.

1. THE SELECTION OF THE SAMPLE.

BEFORE the analyst proceeds to make the quantitative analysis of a body, he cannot consider too carefully whether the desired result is indeed attained if he knows the respective quantity of every individual constituent of that body. This primary point is but too frequently disregarded, and thus false impressions are made, and wrong notions created, even by the most careful analysis. This remark applies both to scientific, and to technical investigations.

Therefore, if you have to determine the composition and constitution of a mineral, take the greatest possible care to remove, in the first place, every particle of adhering impurities ; then wrap the ore up in a sheet of thick paper, and crush it to pieces on a steel anvil ; select and pick out with a pair of small pincers the cleanest pieces. Crystalline substances, that may be

prepared artificially, ought to be purified by re-crystallization ; precipitates by thorough washing, &c. &c.

In technical investigations—when called upon, for instance, to determine the amount of peroxide present in a manganese ore, or the amount of iron present in an iron stone, &c.—the first point for consideration ought to be whether the samples selected correspond as much as possible to the average quality of the ore. What would it serve, indeed, to the purchaser of a manganese mine to know the amount of peroxide present in a select, and probably particularly rich, sample.

These few observations will suffice to show that no universally applicable and valid rules to guide the analyst in the selection of the sample can be laid down ; he must in every individual case, on the one hand, examine the substance carefully, and more particularly also under the microscope, or through a magnifying lens ; and, on the other hand, keep clearly in view the *object* of the investigation, and then take his measures accordingly.

§ 14.

2. MECHANICAL DIVISION.

In order to prepare any substance for analysis, *i. e.*, to render it accessible to the action of solvents, or fluxes, it is generally indispensable, in the first place, to divide it into minute parts, since this will create abundant points of contact for the solvent, and counteract, and remove as much as possible, the adverse influence of the power of cohesion, thus fulfilling the principal conditions necessary to effect a complete, and speedy solution.

The means employed to attain this object, vary according to the nature of the different bodies we have to operate upon. In many cases, crushing, or pounding is sufficient ; in other cases it is necessary to reduce the powder to the very highest degree of fineness, by sifting, or by elutriation.

The operations of pounding, and levigating are conducted in mortars, or levigating slabs ; the first and most indispensable condition is, that the material of the mortar, or slab be considerably harder than the substance to be pulverised, so as to prevent, as much as possible, the latter from being contaminated with any particles of the former. Thus, for pounding salts, and generally of substances possessing no very considerable degree of hardness, porcelain mortars may be used, whilst the pounding of harder substances (of most minerals, for instance), requires vessels of agate, chalcedony, or flint. In such cases the larger pieces are first broken into a coarse powder ; this is best effected by wrapping the pieces up in several sheets of paper, and beating them with a hammer upon a steel, or iron anvil, or plate ; the coarser powder thus obtained is subsequently triturated in small portions in an agate mortar, until it is completely reduced to the

state of an impalpable powder. If we have but a small portion of a mineral to operate upon, and, in fact, in all cases where we are desirous of avoiding loss, it is advisable to use a steel mortar for the preparatory reduction of the mineral into coarse powder. Fig. 8 represents a mortar adapted for this purpose.

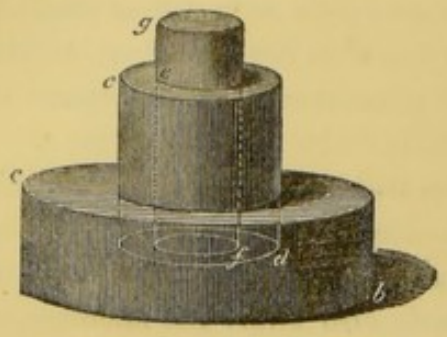


Fig. 8.

a b and *c d* represent the two component parts of the mortar; these may be readily taken asunder. The substance to be pounded is introduced (previously broken into small pieces, if possible), into the cylindrical cavity *e f;* the steel cylinder *f g*, which fits somewhat loosely into this cavity, serves as a pestle. The mortar is placed upon a solid support, and perpendicular blows are struck upon the pestle repeatedly, until the object in view is attained.

Minerals which are very difficult to pulverise should be ignited, and whilst red hot plunged suddenly into cold water, and subsequently again ignited, if necessary. This process is, of course, applicable only to minerals which lose no essential constituent at a red heat, and which are perfectly insoluble in water.

In the purchase of agate mortars, especial care ought to be taken that they have no palpable fissures, or indentations; very slight fissures, however, do not render the mortar useless, although they impair its durability.

Minerals insoluble in acids, and which consequently require fluxing, must be divided as finely as possible, otherwise we cannot calculate upon complete decomposition. This object may be obtained by triturating the pounded mineral with water, by sifting, or by elutriation; the two latter processes, however, ought to be resorted to only in the case of thoroughly uniform substances.

Trituration with Water.—Add a little water to the pounded mineral in the mortar, and triturate the paste until all crepitation ceases, or, which is a more expeditious process, transfer the mineral paste from the mortar to an agate, flint, or porphyry slab, and triturate it thereon with a muller until it is perfectly smooth. Wash the paste off, with the washing bottle, into a smooth porcelain basin of hemispheric form, evaporate the water in the waterbath, and mix the residue most carefully with the pestle. (The paste may be dried also in the agate mortar, but at a very gentle heat, since otherwise the mortar might crack.)

To perform the process of *elutriation*, the pasty mass, having been previously very finely triturated with water, is washed off into a beaker-glass, and mixed with distilled water; the mixture is left at rest a minute or so, after which the supernatant turbid fluid is poured off into another beaker-

glass. The sediment which contains the coarser parts is then again subjected to the processes of trituration, and elutriation, &c., and the same operation is repeated until the end in view is attained. The turbid fluid collected from the successive decantations is left to stand at rest until the minute particles of the substance held in suspension have subsided, which generally takes many hours. The clear supernatant fluid is then finally decanted, and the residuary powder dried in the beaker-glass.

The process of *sifting* is had recourse to, instead of elutriation, in the case of substances partially soluble in water. The substance is, in the first place, most finely pounded, or triturated; the powder is then sifted through fine muslin. The portion remaining is again subjected to trituration, and subsequently sifted; and the same process is continued until the end in view is attained.

When operating on compound, and mixed minerals, it would be a grave error indeed to use for analysis the powder resulting from the first process of elutriation, or sifting, since this will contain the more readily pulverizable parts in a greater proportion to the more resisting parts, than is the case with the original substance.

As it is difficult to avoid a loss of substance in the processes of elutriation and sifting, and as this loss is likely to be distributed unequally among the several component parts which happen to be of different degrees of fineness, I prefer, for my own part, to reduce compound and mixed minerals to the requisite degree of fineness, by the simple, though of course, somewhat tedious process of trituration, either dry, or with water.

In cases where it is intended to ascertain the average composition of a mixed substance, of an iron ore for instance, a large average sample is selected, and reduced to a coarse powder; the latter is thoroughly intermixed, and a portion of it is then brought to the requisite degree of fineness. The most convenient and best adapted instrument for the crushing and coarse pounding of large samples of ore, is a steel anvil and hammer. The anvil in my own laboratory consists of a wood pillar 85 centimeters high, and 26 centimeters in diameter, into which a steel plate 3 centimeters thick and 20 centimeters in diameter is let to the depth of one-half of its thickness. A brass ring, 8 centimetres high, is put round the upper projecting part of the steel plate. The hammer, which is well steeled, has a striking surface of 5 centimetres diameter. An anvil and hammer of this kind present, among others, this advantage, that their steel surfaces admit most readily of cleaning.

§ 15.

3. DESICCATION OR DRYING.

Substances which it is intended to analyse, must be submitted to the

requisite operations, and processes in a clearly, and distinctly characterised and definite state, or form.

In our introductory remarks we have laid it down, as an indispensable condition of quantitative analysis, that the *kind*, and *nature of every individual constituent* of the compounds under examination must be *exactly* and *accurately* known before we can proceed to their quantitative estimation. Now, the essential constituents of a substance are usually accompanied by an accidental admixture, viz., a greater, or less amount of water, inclosed either within its lamellæ, or adhering to it from the mode of its preparation, or absorbed by it from the atmosphere. It is perfectly obvious that to estimate correctly the quantity of a substance, we must, in the first place, remove the water which it may happen to hold in admixture. *Most solid bodies*, therefore, *require to be dried before they can be quantitatively analysed.*

The operation of drying is of the very highest importance for the correctness of the results; indeed it may safely be averred that many of the differences observed in analytical researches, proceed entirely from the fact that substances are analysed in different states of moisture.

It must be borne in mind, of course, that many substances contain water among their *essential* constituents (constitutional water, or water of crystallization). With this water we must not interfere; the operation of drying, which we have here in view, is intended only to remove the water accidentally admixed, or mechanically adhering to the substance, and which we will term here "*moisture*," the better to distinguish it from the water essentially inherent in a substance. Accordingly, in the drying of substances for quantitative analysis, our only object is to remove all *moisture* from them, without interfering, in the slightest degree, with their *constitutional* water, or any other *essential* constituent. To accomplish this object, it is absolutely requisite that we should know the properties which the substance under examination manifests in the *dry* state, and whether it loses water, or other constituents at a red heat, or at 212° Fahr., or in dried air, or even simply in contact with the atmosphere. These data will serve to guide us in the selection of the process of desiccation best suited to the substance under examination.

The following classification may accordingly be adopted:—

a. Substances which yield water even in simple contact with the atmosphere; such as sulphate of soda, carbonate of soda, &c. Substances of this kind turn dull and opaque when exposed to the air, and finally crumble wholly, or partially into a white powder. They are more difficult to dry than many other bodies. The process best adapted for the purpose, is to press the pulverized salts with some degree of force between thick layers of fine white blotting-paper, until the last sheets remain *absolutely dry*.

It is generally advisable to subject the pulverized salts, in the course of this operation, once more to the process of trituration.

b. Substances which do not yield water to the atmosphere (unless perfectly dry), but which effloresce in artificially dried air; such as sulphate of magnesia, tartrate of soda and potassa (Rochelle salt), &c. Salts of this kind are reduced to a fine powder, which, if it be very moist, is pressed between sheets of blotting-paper, as sub *a;* after this operation, it must be allowed to remain for some time spread in a thin layer upon a sheet of blotting-paper, effectually protected against dust, and shielded from the direct rays of the sun.

c. Substances which undergo no alteration in dried air, but lose water at 212°; tartrate of lime, for instance. These are finely pulverized; the powder is put in a thin layer upon a watch-glass, or into a small dish, and the latter placed inside a bell-glass, in which the air is kept dry by means of sulphuric acid. This process may be conducted either in the apparatus illustrated by Fig. 9, or in that illustrated by Fig. 10.

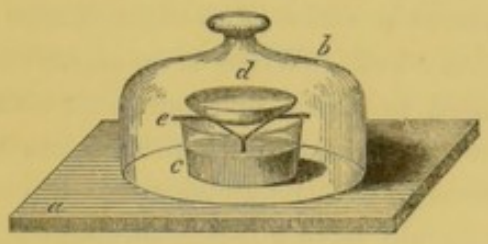


Fig. 9.

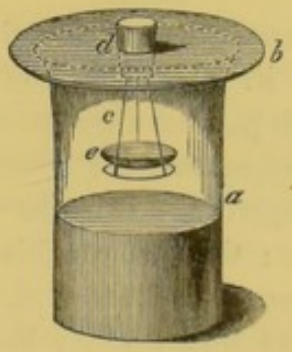


Fig. 10.

Fig. 9, *a* represents a glass plate (ground glass plates answer the purpose far better than polished ones), *b* a bell-shaped glass cover, with ground rim, which is greased with tallow; *c* is a glass basin with sulphuric acid; *d* a watch-glass containing the substance which is to be dried, and resting upon a triangle made of wire (*e*).

Fig. 10, *a* represents a beaker-glass, with a ground rim, greased with tallow, and filled to *one-fourth* or *one-third* with concentrated sulphuric acid; *b* is a ground glass plate, with an aperture in the centre; this aperture is closed by means of a cork, *d*. *c* is a small wire support attached to the cork, and upon which rests, *e* a watch-glass, containing the substance under examination.

The body which it is intended to dry, is kept exposed to the action of the dry air in the glass, until it shows no further diminution of weight. Substances upon which the oxygen of the air exercises a modifying influence, are dried in a similar manner under the exhausted receiver of an air-pump. Substances which, though losing no water in dry air, yet give

off ammonia, are dried over lime, mixed with some chloride of ammonium in powder, and consequently in an anhydrous ammoniacal atmosphere.

d. Substances which undergo no alteration at 212°, *but are decomposed at a red heat,* such as bitartrate of potassa, sugar, &c., are dried in the water-bath; in the case of slowly drying substances, with the aid of a current of dry air. There are many bodies, also, that do not completely lose their moisture at 212°, or the drying of which would, at all events, require a very protracted exposure in the water-bath; the desiccation of substances of this kind is effected in the air, or oil-bath.

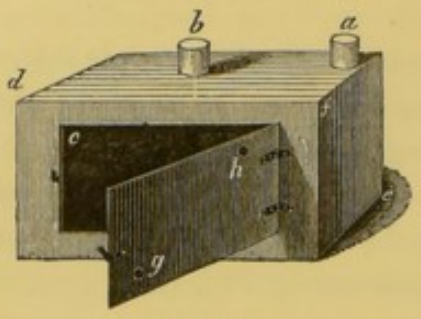


Fig. 11.

Fig. 11 represents the water-bath most commonly used. It is made either of sheet tin, or, better, of sheet copper, and is soldered with brass, to adapt it for use also as an oil-bath (in which case a thermometer is fixed into *a* by a cork). The engraving renders a detailed explanation unnecessary. The inner space, *c*, is surrounded on five sides by the outer case *d e*, without communicating with it. The object of the apertures *g* and *h* is to effect change of air, which purpose they answer sufficiently well. When it is intended to use the apparatus, the outer case is filled to about one-half with water, and the aperture *a* is closed with a perforated cork, into which a glass tube is fitted; the aperture *b* is entirely closed. If the apparatus is intended to be heated over charcoal, or gas, it should have a length of about 22 centimeters from *d* to *f*; but if over a spirit-lamp, or an oil-lamp, it should be only about 13 centimeters long. The substances to be dried are put on double watch-glasses, laid one within the other, and which are then placed in the inner space, *c*. In the subsequent process of weighing, the upper glass, which contains the substance, is covered with the lower one. The glasses must be quite cold before they are placed on the scale. In cases where we have to deal with hygroscopic substances, the re-absorption of water upon cooling is prevented by the selection of close fitting glasses, which are held tight together by a clasp, and allowed to cool with their contents under a bell-glass over sulphuric acid (see Fig. 9). These latter instructions apply equally to the process of drying, conducted in other apparatus.

The clasps used for keeping the watch-glasses pressed together—and which in all cases where it is intended to ascertain the loss of weight which a substance suffers on desiccation, are to be looked upon as part and parcel of the glasses, and must accordingly be weighed with them—are constructed of two strips of thin brass plate, about ten centimeters long, and one centimeter wide, which are laid the one over the other, and soldered together at the ends, to the extent of 5 to 6 millimeters. The following apparatus serve for drying substances in a current of air.

In Fig. 12 the current is caused by heating the air, which renders this apparatus very convenient for use.

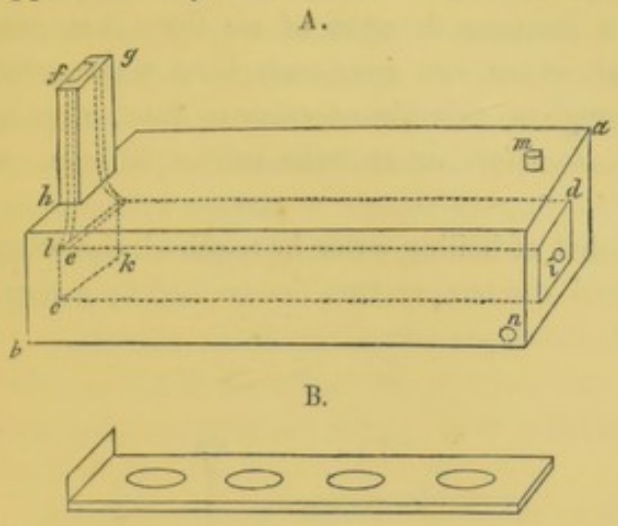


Fig. 12.

a b is a case of sheet copper, or sheet tin, into which the canal *c d* is soldered; the latter communicates with the chimney *e f;* this is surrounded on three sides by the cover *g h*, which again communicates with *a b*. The cover has no opening at the top. At *i* we have a round aperture, leading into the canal, and which may be closed with a cork; *l k* is provided with a well-fitting sliding lid running in grooves.

The operation is commenced by filling the case *a b* to one half with water, through the aperture *m*—the aperture *n*, which serves to let off the water, being closed with a cork—and heat is then applied to raise the temperature of the water to the boiling-point. The watch-glasses with the substances to be dried are placed into the hollows of the sliding shelf, B, and the latter is introduced into the canal *c d* at *l k*, which is then closed by the sliding lid.

The air in the canal, becoming heated by the surrounding steam, ascends, and the cold atmospheric air passing in, through the aperture *i*, over the drying substances, carries away with it the evaporating moisture. There is a slight disadvantage attending this mode of proceeding, viz., the cold air which passes through *i* keeps the drying substances always a little below 212°; this may be easily remedied, however, by conducting the air, in the first place, through a long tube running along under the bottom of the canal down to *l k*, and returning thence to the other extremity, where it is finally fitted into *i*; this tube must be soldered in its whole length to the outer lower surface of the canal. The air conveyed through this tube is thus heated to 212° before coming into contact with the drying substance. This tube has been omitted from the engraving, to avoid confusion.

To render the apparatus still more useful, round holes of different sizes may be cut in the top of the case; these holes, for which proper covers must be provided, serve for the reception of small evaporating dishes. The aperture *m* may, in that case, be omitted, as the water may be poured in through one of the holes. This apparatus may be from 20 to 30 cen-

timeters long, and about 10 centimeters deep. The canal should be 5 centimeters wide, and 2·5 centimeters deep.

If it be desirable to create a stronger draught of air than that produced by the little chimney, air which has previously been transmitted through sulphuric acid, or through a chloride of calcium tube, may be blown into *i* by means of a gasometer, or an india-rubber balloon, or some other contrivance.

If a higher temperature than that of boiling water be required, the outer (copper) case is filled with oil, and the temperature determined by a thermometer, fixed into *m* by a cork.

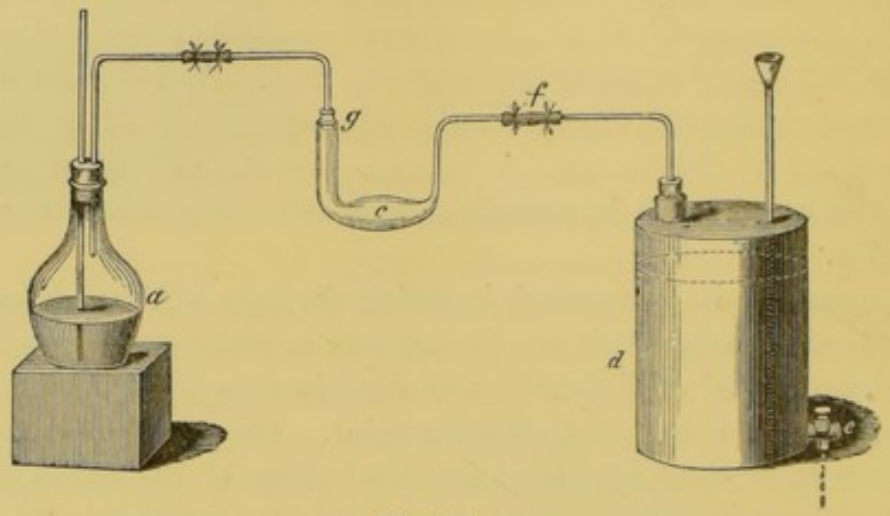


Fig. 13.

In the apparatus represented in Fig. 13, the current of air is produced by an aspirator.

a represents a flask filled to one-third with concentrated sulphuric acid; *c* a glass vessel, commonly called a Liebig's drying tube; and *d* a tin vessel, provided with a stop-cock at *e*, and arranged in other respects as the engraving shows.



Fig. 14.

Fig. 14 represents a small tin vessel, containing water, and covered with a lid; two apertures, *a* and *b*, are cut into the border of the latter, to receive the ascending limbs of *c*.

The substance intended for drying is accurately weighed, and placed in the tube *c*, the exact weight of which has been previously ascertained; *c* is then suspended in the vessel represented in Fig. 14, and the water contained in the latter is heated to boiling, by means of a spirit-lamp, or gas; the tin vessel *d* is then filled with water, and *c* connected with the flask *a* by the perforated cork *g*, and with *d* by means of a caoutchouc tube *f*. If the stop-cock *e* be now opened so as to cause the water to flow from *d*, the air will pass through the tube *b* into *a*;

its moisture will be retained by the sulphuric acid, and the dry air will then pass over the substance in *c*. After the operation has been continued for some time, it is interrupted for the purpose of weighing the tube *c* and its contents, and then resumed again, and continued until the weight of *c* (and its contents) remains stationary. The current of cold air, exercising its constant cooling action upon the drying substance, the latter never really reaches a temperature of 212°. It is, therefore, sometimes advisable to substitute for the water in Fig. 14 a saturated solution of common salt.

With this substitution, the apparatus represented in Figs. 13 and 14 will be found to effect its purpose the most expeditiously. It is not adapted, however, for drying such substances as have a tendency to fuse at 212°.

It has been stated above that many substances do not lose their moisture completely at 212°, but require for their perfect desiccation from 230° to 250°, and still higher temperatures. The drying of such substances is effected in the oil-bath, or in the air-bath.

Figs. 15 and 16 represent two air-baths of the simplest construction; the former (Fig. 15) adapted for the simultaneous drying of several substances, the latter more particularly suited for the desiccation of a single substance.

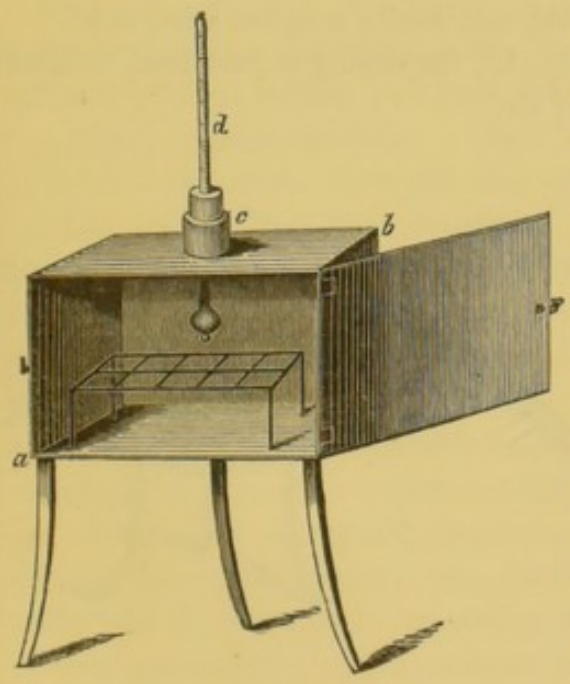


Fig. 15.

a b is a case of strong sheet copper, soldered with brass, of a width and depth of 15 to 20 centimeters, and of a height corresponding. The aperture *c* is intended to receive a perforated cork, into which is fixed a thermometer *d*, which reaches into the interior of the case; *e* is a wire stand, on which are placed the watch-glasses with the substances to be dried. The case is heated by means of a spirit or oil-lamp, or by gas. When the temperature has once reached the intended point, it is easy to maintain it pretty constant, by regulating the flame. In order to lessen as much as possible the chance of cooling from without, it is advisable to put over the whole apparatus a pasteboard cover with a moveable front.

By having round holes, about two centimeters in diameter, cut into the

side walls of the case, the apparatus may be made useful also for the drying of substances in bulbs. The ends of the tubes are fitted into the apertures by corks; the requisite change of air is brought about by an aspirator. (Compare Fig. 13.)

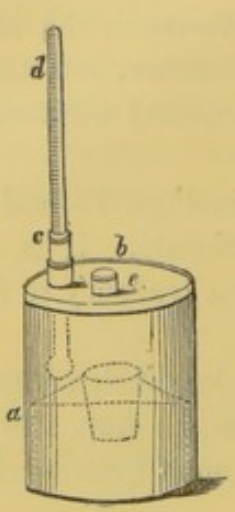


Fig. 16.

a is a box of strong sheet copper, about 11 centimeters high, and 9 centimeters in diameter. The box is closed with the loose-fitting cover *b*, which is provided with a narrow rim, and has two apertures, *c* and *e*. *c* is intended to receive the thermometer *d*, which is fitted into it by a perforated cork. *e* affords an exit to the aqueous vapors, and is, according to circumstances, either left open, or loosely closed. In the interior of the box, about half way up, are fixed three pegs, supporting a triangle of moderately stout wire, upon which the crucible with the substance is placed uncovered. The ball of the thermometer approaches the crucible as close as possible, but without touching the triangle. The heating is effected by means of a gas, or spirit-lamp. When the apparatus has cooled sufficiently to allow its being laid hold of without inconvenience, the lid is removed, the crucible, which is still warm, taken out, covered, and put under a bell-glass, over sulphuric acid, and finally weighed when cold.

In the air-bath illustrated by Fig. 17, the drying is promoted by alternate exhaustion and re-admission of air.

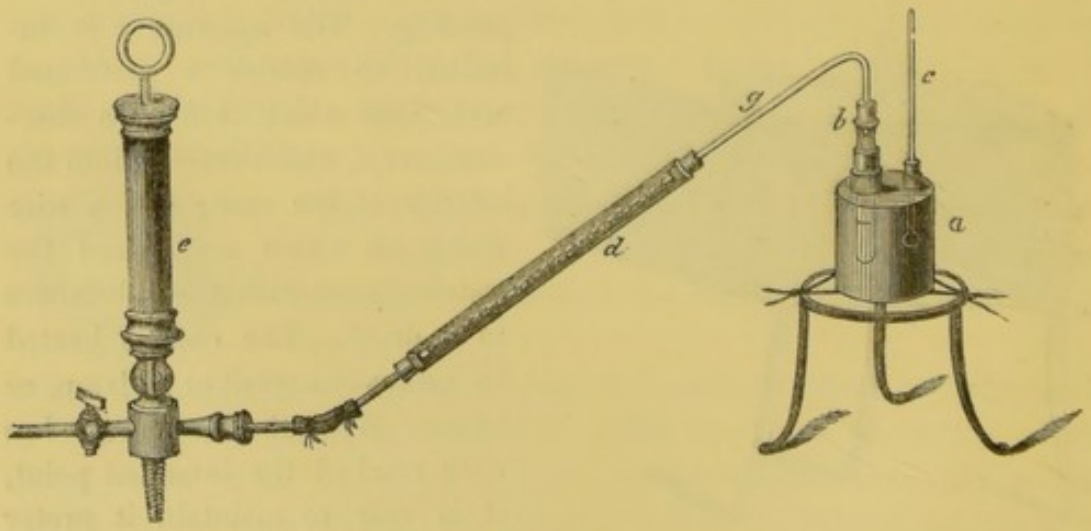


Fig. 17.

a represents a vessel of strong sheet copper, soldered with brass, and provided with two apertures at the top; *b* is a small glass tube, containing the substance intended for desiccation; *c* a thermometer; *d* a tube with chloride of calcium; *e* an exhausting syringe.

The operation is commenced by heating *a* to the desired degree; *b* and *d* are then exhausted by working the syringe. After the lapse of a few minutes, fresh air is re-admitted through the stop-cock *f*, and which, passing over the chloride of calcium in *d*, is completely freed from moisture. The same process of alternate exhaustion, and re-admission of air is repeated over and over again, until the interior of the tube *g* ceases to exhibit even the faintest trace of moisture, when cooled by the application of cotton saturated with ether.

This apparatus may also be used as an oil-bath; however, the apparatus represented in Fig. 11 is more commonly employed for that purpose. Vegetable lamp-oil should be used for the oil-bath.

e. Substances which suffer no alteration at a red heat, such as sulphate of baryta, chloride of sodium, &c., are very readily freed from moisture. They need simply be heated in a platinum, or porcelain crucible over a spirit-lamp until the desired end is attained. The crucible, having first been allowed to cool a little, is put, still hot, under a bell-glass, over sulphuric acid, and finally weighed when cold.

III. GENERAL PROCESS IN QUANTITATIVE ANALYSES.

§ 16.

It is important, in the first place, to observe, that we embrace in the following general analytical method only the analysis and quantitative estimation of the metals, and their combinations with the metalloids, and the inorganic acids and salts. With respect to the quantitative analysis of other compounds, it is not easy to lay down a universally applicable method, except that their respective constitutents usually require to be converted first into acids, or bases, before their separation and quantitative estimation can be attempted; this is the case, for instance, with sulphide of phosphorus, chloride of sulphur, chloride of iodine, sulphide of nitrogen, &c.

As has already been observed before, the quantitative analysis of a substance presupposes an accurate knowledge of the nature and properties of the same, and of its several constitutents; as this will enable the operator at once to decide whether the direct quantitative estimation of each individual constitutent be necessary, or not; and, consequently, whether he need operate only on one sample of the substance, or whether he has to determine in several different portions respectively, the relative amount of each individual constitutent. Let us suppose, for instance, we have a mixture of chloride of sodium and anhydrous sulphate of soda, and wish to ascertain the exact proportion in which each of these two substances is contained in the mixture. Here it would be superfluous to determine

directly the proportional amount of every individual constituent, since the determination either of the quantity of the chlorine, or of the sulphuric acid, is quite sufficient to answer the purpose; still the double estimation of both the chlorine, and the sulphuric acid, will afford us an infallible control for the correctness of our analysis; since the united weights of these two substances, added to the known proportion of their respective equivalents of sodium, and soda, must be equal to the weight of the analysed portion of the mixture.

This double estimation may be made, in this instance, either in one and the same sample of the mixture, by first precipitating the sulphuric acid with nitrate of baryta, and subsequently the hydrochloric acid from the filtrate, with solution of nitrate of silver; or a separate portion of the mixture may be appropriated to each of these two operations. The latter method, whenever it is at all applicable, is preferable to the former, in cases where we have to deal with perfectly homogeneous substances; and where we have a sufficient quantity of substance to act upon. It is more convenient than the former method, and leads to more accurate results, since when operating upon one and the same sample of a substance, the unavoidable washing of the first precipitate swells the amount of liquid so considerably, that the analysis is thereby protracted, and, moreover, loss of substance less easily guarded against.

We will now proceed to describe the various operations constituting the actual process of quantitative analysis.

§ 17.

1. WEIGHING OF THE SUBSTANCE.

The amount of matter required for the quantitative analysis of a substance depends upon the nature of its constitutents; it is, therefore, impossible to lay down rules for guidance on this point. One half gramme of chloride of sodium, and even less, is sufficient to effect the estimation of the chlorine in it. For the quantitative analysis of a mixture of common salt, and sulphate of soda, one gramme will suffice; whereas, in the case of ashes of plants, complex minerals, &c., three, or four grammes, and even more, are required. The average quantity of substance required for the purposes of quantitative analysis may, accordingly, be said to range, in most cases, between one, and four grammes.

The greater the amount of substance operated upon, the more accurate will be the results of the analysis; the less the amount, the less time will be required for the performance of the operation. We would advise the student to endeavour to combine accuracy, with economy of time. The less substance he takes to operate upon, the more carefully he ought to weigh;

the larger the amount of substance, the less harm can result from slight inaccuracies in weighing. For largish quantities of substance, the accuracy of weighing may be safely limited to within about one milligramme; for minute quantities, to about $\frac{1}{10}$ of a milligramme.

If several different quantities of a substance are to be operated upon, the best way is to weigh off the several portions successively; which may be accomplished most readily by weighing in a glass tube, or other appropriate vessel of known weight, the whole amount of substance intended to be devoted to the analytical process. Out of this tube the portions required for the several operations are taken, and the weight is ascertained each time from the diminution in the weight of the tube (compare § 10, 5).

§ 18.

2. ESTIMATION OF THE AMOUNT OF WATER CONTAINED IN A SUBSTANCE.

If the substance to be examined contains water, it is usual, in the great majority of cases, to begin by determining the amount of this water. This operation is generally simple; in some instances, however, it has its difficulties. This depends upon various circumstances, viz., whether the compounds intended for analysis yield their water readily or not; whether they can bear a red heat without suffering decomposition, or whether, on the contrary, they give off other volatile substances, besides water, even at a lower temperature.

The correct knowledge of the constitution of a substance depends frequently upon the accurate estimation of the quantity of water contained in it; in many cases—for instance, in the analysis of the salts of known acids—the estimation of the amount of water contained in the analysed compound suffices to enable us to deduce the formula. The estimation of the amount of water contained in a substance, is, therefore, one of the most important, as well as most frequently occurring operations of quantitative analysis. The proportion of water contained in a substance may be determined in two ways, viz., 1, from the diminution of weight consequent upon the expulsion of the water; 2, by weighing the amount of water expelled.

A. ESTIMATION OF THE WATER FROM THE LOSS OF WEIGHT CONSEQUENT UPON ITS EXPULSION.

This method, on account of its simplicity, is almost invariably resorted to in quantitative analysis, except in cases where it is inapplicable, from

the nature of the substance examined. The *modus operandi* depends upon the nature of the substance under examination.

α. The substance bears a red heat, without losing any other constituent, than water, and without absorbing oxygen.

The substance is weighed in a platinum, or porcelain crucible, which is then heated over the flame of a gas, or spirit-lamp, very gently at first, but increasing gradually to the desired point. When the crucible has been maintained some time at a red heat, it is removed from the flame, let cool a little, put still warm under the bell-glass, and finally weighed when cold. The same operation is then repeated, and the weight again ascertained. If no further diminution of weight has taken place, the process is at an end, the desired object being fully attained. But if the weight is less than after the first heating, the operation must be repeated until the weight remains perfectly stationary.

In the case of silicates, the heat must be raised to a very high degree, since many of them (*e. g.* talc, steatite, nephrite), begin only at a red heat to give off water, and require a yellow heat for the complete expulsion of that constituent. (*Scheerer*, in Liebig and Kopp's Annual Report for 1851).

In the case of substances that have a tendency to puff up, or to spirt, a small glass flask may sometimes be advantageously substituted for the crucible. Care must be taken to remove the least traces of aqueous vapor from the vessel, by suction through a glass tube.

Decrepitating salts (chloride of sodium, for instance) are put—finely pulverized if possible—in a small covered platinum crucible, which is then placed in a large covered crucible, and a gentle heat applied, which is gradually increased to the requisite degree.

β. The substance does not yield other constituents besides water, upon the application of a red heat; but it has a tendency to absorb oxygen (as many proto-salts of iron, for instance).

The substance is put into the bulb of a bulb-tube, made of difficultly fusible glass, and gradually heated to redness, whilst a slow current of carbonic acid gas, dried previously by transmission through sulphuric acid, is kept passing through the tube; the substance is maintained at a red heat, until the complete expulsion of the water is accomplished; it is then allowed to cool in the bulb, the transmission of the carbonic acid gas being continued all the while; when cold, the substance is weighed. The water expelled may readily be collected in a chloride of calcium tube provided with an empty bulb at the fore-part, which will afford a means of controlling the result obtained. (Compare § 19.)

γ. *The substance loses other constituents besides water, upon the application of a red heat* (*carbonic acid, sulphuric acid, fluoride of silicon, &c.*)

Here the analyst has to consider, in the first place, whether the water may not be expelled at a lower degree of heat, which does not involve the loss of other constituents. If this may be done, the substance is heated either in the water-bath, or where a higher temperature than 212° is required, in the air-bath, or oil-bath, the temperature being regulated by the thermometer. The expulsion of the water may be promoted, if necessary, or desirable, by the co-operation of a current of air; or by the addition of pure dry sand to the substance, to keep it more porous (Ann. der Chemie und Pharm. 53, 233). The process must be continued under these circumstances also, until the weight remains perfectly stationary.

In cases where, for some reason or other, a degree of heat below redness is insufficient to effect the purpose in view, the analyst has to consider whether the desired end may not be attained, at a red heat, by adding some substance that will retain the volatile constituent, whose loss is apprehended. Thus, for instance, the crystallized sulphate of alumina loses at a red heat, besides water, also sulphuric acid; now, the loss of the latter constituent may be guarded against, by adding to the sulphate an excess (about six times the quantity) of finely pulverized, recently heated, pure oxide of lead. But the addition of this substance will not prevent the escape of fluoride of silicon from silicates, when exposed to a red heat (*List.* Ann. d. Chemie und Pharm. 81, 189).

The amount of water in iodine of commerce may be determined by mixing the iodine with eight times the quantity of mercury, and drying the mixture at 212° (*Bolley.* Dingler's Polytechnic Journal, 126, 39).

δ. *The substance contains several distinct proportions of water, requiring different degrees of temperature for their expulsion.*

Substances of this nature are heated first in the water-bath, until their weight remains stationary; they are then exposed in the oil, or air-bath to temperatures of 302°, 392°, or 482°, &c., successively; and finally heated to redness over the flame of a spirit-lamp, or over gas.

In this manner differently combined equivalents of water may be distinguished, and their respective quantities correctly estimated. Thus, for instance, the common perphosphate of iron, dried over sulphuric acid, contains 13 equivalents of water, 6 of which volatize at 212°, 4 at between 392° and 572°, and 3, finally, at a red heat.

§ 19.

B. ESTIMATION OF THE WATER BY COLLECTING THE SAME UPON ITS EXPULSION, AND ASCERTAINING ITS WEIGHT.

This method is resorted to in the case of substances that lose some other constituent, at a red heat, besides their water, and which cannot be retained even by the addition of some other substance (*e. g.* carbonic acid, oxygen); and sometimes also to control and verify the results obtained by one of the methods described sub A. The principle of the method is to expel the water by the application of a red heat, so as to admit of the condensation of the aqueous vapor, and the collection of the condensed water in an appropriate apparatus, or the passing of the same over some hygroscopic substance of accurately known weight. The increase in the weight of this apparatus represents the quantity of the water expelled.

The operation may be conducted in various ways; the following, however, is one of the most appropriate:—

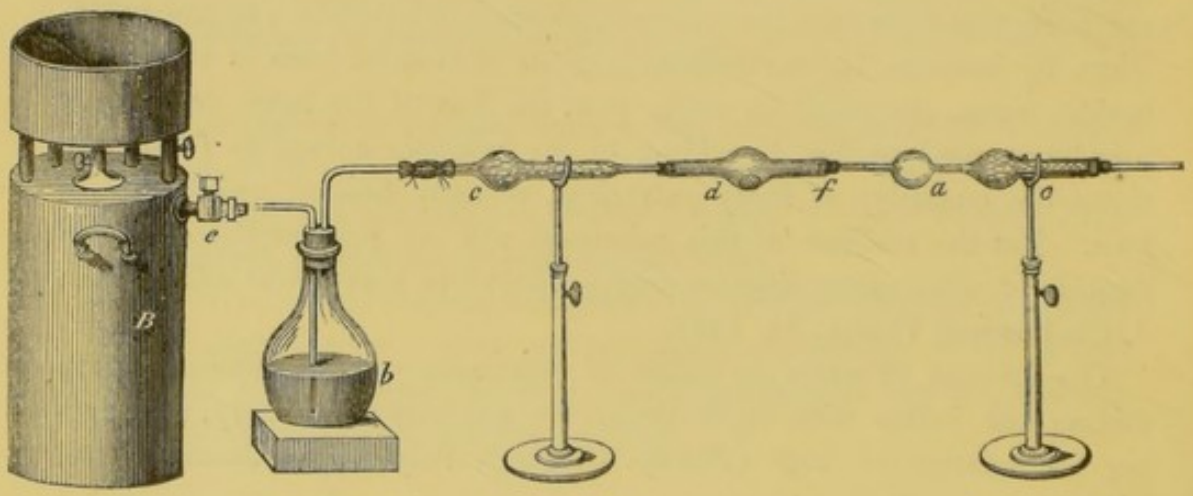


Fig. 18.

B represents a gasometer filled with air; *b* a flask half filled with concentrated sulphuric acid; *c* and *a o* are chloride of calcium tubes; *d* is a glass tube expanded in the middle into a bulb.

The substance intended for examination is accurately weighed in the perfectly dry tube *d*, which is then connected with *c* and the accurately weighed chloride of calcium tube *a o*, by means of sound, and well-dried perforated corks.

The operation is now commenced by opening the stop-cock *e* a little, to allow the air, which loses all its moisture in its passage through *b* and *c*, to pass slowly through *d*; the tube *d* is then heated to beyond the boiling-point of water, by the application of the flame of a spirit-lamp at the point *f*, taking care, always, not to burn, or singe the cork; and finally,

the bulb of *d*, which contains the substance, is exposed to a slight red heat, the temperature at *f* being maintained meanwhile at the point indicated. When the expulsion of the water has been accomplished, the air is allowed to pass a few instants longer through the apparatus, which is then taken asunder, and the chloride of calcium tube *a o* accurately weighed when cold. The increase in the weight of this tube represents the quantity of water originally present in the substance examined.

The empty bulb *a*, in which the greater portion of the water collects, has not only for its object to prevent the liquefaction of the chloride of calcium, but enables the analyst also to test the condensed water as to its reaction, and purity.

The expulsion of the aqueous vapour from the tube containing the substance under examination, into the chloride of calcium tube, may be effected also by other means than a current of air supplied by a gasometer; viz., the substance, the amount of water of which it is wished to determine, may be heated to redness in a perfectly dry tube, together with carbonate of lead, since the carbonic acid of the latter, escaping at a red heat, serves here the same purpose as a stream of air. This method is principally applied in cases where it is desirable to retain an acid which otherwise would volatilize together with the water; thus, it is applied, for instance, for the direct estimation of the water contained in the bisulphate of potassa, &c.



Fig. 19.

Fig. 19, represents the apparatus used for the application of this method.

a b is a common combustion furnace; *c f'* a tube filled from *c* to *d* with carbonate of lead, which has been heated to incipient decomposition, and cooled subsequently, in a close tube; from *d* to *e* is placed the substance to be analysed, intimately mixed with carbonate of lead; and from *e* to *f* again pure carbonate of lead. The chloride of calcium tube *g*, being accurately weighed, is connected with the tube *c f'*, by means of a well-dried perforated cork *f'*.

The operation is commenced by surrounding the tube *c f'* with ignited charcoal, advancing from *f* towards *c*; the fore part of the tube which protrudes from the furnace, should be maintained at a degree of heat which barely permits the operator to lay hold of it with his fingers. All further particulars of this operation will be found below in the chapter on organic elementary analysis. The mixing of the carbonate of lead with the substance to be analysed is performed best with a piece of wire. The tube *c f'* may be short and narrow.

These methods of the direct estimation of water, do not, however, yet

suffice for all cases in which those described in § 18, are inapplicable; namely, they can be employed with success only if the substances evolved simultaneously with the water, are such as will not condense wholly or partly in the chloride of calcium tube, or in a potassa tube, which might be substituted for the latter. Thus they are perfectly well adapted for determining the amount of water in the basic carbonate of zinc, but they cannot be applied to determine the amount of water in sulphate of soda and ammonia. With substances like the latter, we must either have recourse to the processes of organic elementary analysis, or we must rest satisfied with the indirect estimation of the water.

§ 20.

3. SOLUTION OF SUBSTANCES.

Before pursuing the analytical process further, it is in most cases necessary to dissolve the substance under examination. This operation is simple where the substance to be analysed may be dissolved by the direct action of water, or acids, or alkalies, &c., upon it; but it is more complicated in cases where we have to operate upon substances requiring fluxing as an indispensable preliminary to their solution.

When we have mixed substances to operate upon, the several component parts of which respectively comport themselves differently with solvents, it is not by any means necessary to dissolve the whole substance in mass; on the contrary, the separation may, in such cases, be effected in the most simple, and expeditious manner by the successive application of the different solvents required. Thus, for instance, a mixture of nitrate of potassa, carbonate of lime, and sulphate of baryta, may be readily and accurately separated into these three salts by dissolving out, in the first place, the nitrate of potassa with water, and subsequently the carbonate of lime by hydrochloric acid, leaving the insoluble sulphate of baryta behind.

§ 21.

a. DIRECT SOLUTION.

The direct solution of substances is effected, according to circumstances, either in beaker-glasses, or in flasks, or dishes, and may, if necessary, be promoted by the application of heat; for which purpose the water-bath will be found to answer best. In cases where an open fire, or the sand-bath is resorted to, the analyst must take care to guard against actual ebullition of the fluid, since this would render it next to impossible to avoid loss of substance from spirting of the liquid. Fluids containing a sediment, either insoluble, or, at least, undissolved, will often spirt even at temperatures falling far short of the boiling-point.

In cases where the solution of a substance is attended with evolution of gas, the process is effected in a flask, placed in a sloping position,

that the spirting drops may be thrown against the walls of the vessel, and thus secured from being carried off with the stream of the evolved gas; or it may be effected in a beaker-glass, covered over with a large sized watch-glass, or porcelain dish, which, after the solution is effected, and the gas expelled by heating in the water-bath, must be thoroughly rinsed with the wash bottle.

§ 22.

b. DECOMPOSITION BY FLUXING.

According to the nature and constituents of the substance which it is wished to render soluble, we use as a flux carbonate of soda, or carbonate of soda and potassa, carbonate of baryta, or hydrated baryta, bisulphate of potassa, or some other body. As a general rule, carbonate of soda and carbonate of soda and potassa, serve as fluxes for heavy spar, celestine, gypsum, and also for siliceous minerals, either free from alkali, or in which we do not want to determine the alkali they may contain. Carbonate of baryta and hydrated baryta serve to decompose, in the dry way, siliceous compounds containing one, or several alkalies, in cases where the estimation of the latter is the object which we have in view; the bisulphate of potassa is particularly well adapted for the fluxing of certain alumina compounds insoluble in hydrochloric acid.

In almost every case of decomposition by fluxing, it is indispensable to reduce the substance to be operated upon to the very highest degree of comminution, by levigation, and elutriation; if this preliminary operation be imperfectly performed, complete decomposition can never be reasonably expected.

a. FLUXING WITH CARBONATE OF SODA.

The pulverized substance to be fluxed is mixed in a platinum crucible with from three to four times its amount of effloresced, and perfectly anhydrous carbonate of soda; the mixing is performed with a glass rod, rounded at the lower end; the minute particles adhering to the rod are subsequently wiped off against a small quantity of carbonate of soda on a card, which is then likewise put into the crucible. The crucible is well covered—and, according to its size, either exposed to the flame of a gas or spirit-lamp with a double draught, or inserted into a Hessian crucible compactly filled with calcined magnesia, and in this state exposed to a charcoal fire. The heat applied should be gentle at first, but increased *gradually* to the most intense red heat, and the operation continued for from half an hour to an hour, when the mixture will be found in a state of fusion, or at least of semi-fusion.

In the fluxing of siliceous minerals, the application of a moderate heat is continued for some time, in order to get the mineral simply into a state

of semi-fusion at first, in which state the carbonic acid escapes readily from the porous mass, its evolution being unattended with spirting. After a time, a stronger heat is applied, which is finally raised to a very high degree of intensity; and the operation is continued until the mass is in a state of calm fusion, and throws up no more bubbles.

The platinum crucible, in which the operation is effected, must not be too small; the best way is to select it always of a size sufficient to hold double the quantity of substance which it is intended to fuse. The larger the crucible, the less is the risk of loss of substance. The cover must be easily removable, that the analyst may properly watch the progress of the operation; the concave lids which are simply laid on the crucible are, therefore, preferable by far to covers with rims fitting over the crucible.

For fluxing over a spirit-lamp or over gas, a mixture of carbonate of soda and potassa is preferable to the simple carbonate of soda, on account of its readier fusibility. The ring on which the crucible is supported, is made of iron wire about two or three millimeters thick; it should be eight centimeters in diameter. Upon this ring is laid a triangle of platinum wire, of the thickness of stout hair-pin wire. The opening of the triangle must be of a size to let the crucible drop into it to fully one-third, but yet to retain it firmly, even with the wire at an intense red heat.

Where it is wished to apply a most intense heat, the crucible is placed in such a manner as to make the bottom lie somewhat higher than the upper border of the chimney (which on no account should be too narrow); and a second conical chimney of thin iron plate is put over the crucible. This chimney is of the same width at the lower end as the ring, and rests on the latter, or rather on the three ends of the triangle; its height ranges from twelve to fourteen centimeters; the upper opening may have a diameter of about four centimeters. With the aid of this simple contrivance, we may produce such high degrees of heat as to supersede, in most cases, the necessity of a recurrence to a charcoal fire.

The contents of the crucibles are treated, when cold, with water, in the case of the sulphates of the alkaline earths, or with dilute hydrochloric acid, or nitric acid, in the case of silicates.

A gentle blow, or pressure on the crucible will mostly suffice to effect the liberation of the fused cake from the bottom and sides. When we have to operate upon silicates, the fused mass, or even the crucible together with its contents, is put into a beaker-glass, and covered with from ten to fifteen times its bulk of water; hydrochloric acid is then gradually added, taking care to cover the vessel with a glass plate, or, better still, with a large watch-glass, or a perfectly clean porcelain dish; the cover serves here to prevent the loss of the minute drops of fluid which the escaping carbonic acid gas is apt to carry along with it.

The solution is promoted by the aid of a gentle heat, which is continued

even for some time after a complete solution has been effected. The object of this latter proceeding is to expel the carbonic acid thoroughly, and thus to guard against possible loss by spirting, upon the subsequent evaporation of the solution. Should the fluid, upon the addition of the hydrochloric acid, deposit a powder (chloride of sodium, or chloride of potassium), this is a sign that the quantity of water used was insufficient, and that more of that menstruum must be added.

At the completion of the process, the minute drops of liquid adhering to the glass plate, watch-glass, or porcelain dish, that has been used to cover the beaker-glass, are washed off into the solution; and the crucible, also, is rinsed with dilute hydrochloric acid, the rinsing being likewise added to the solution.

If the object of the process has been fully attained, the solution effected by the hydrochloric acid will be quite clear, or light flakes of silica will appear floating in it. But if a heavy, gritty powder subsides to the bottom of the glass, this may be looked upon as undecomposed mineral, the non-decomposition of which is owing mostly to insufficient comminution. The sediment may, in such cases, be fluxed once more with carbonated alkali; it is better, however, to recommence the whole operation with a fresh portion of most *thoroughly levigated* and *elutriated* mineral.

β FLUXING WITH HYDRATE OF BARYTA, OR CARBONATE OF BARYTA.

Fluxing with carbonate of baryta requires an extremely high temperature, to be attained only by a Sefström furnace, since this flux remains refractory in the very strongest heat obtainable by a common wind furnace; and it is only in a state of fusion that it effects complete decomposition. But, once in fusion, the power of carbonate of baryta is so energetic, that even the most difficultly decomposable minerals are readily and completely decomposed by its action. From four to six parts of carbonate of baryta are used to one part of the mineral to be analysed. The fusion is effected in a platinum crucible inserted in an infusible clay crucible filled with magnesia. The crucible is left exposed a quarter of an hour to the action of the fire.

In the case of more readily decomposable minerals, the object in view may be attained more easily with hydrate of baryta freed from its water of crystallization. From four to five parts of the hydrate are intimately mixed with one part of the mineral; the mixture may, in addition, be covered with a layer of carbonate of baryta. The fusion is effected best over a gas, or spirit-lamp; silver crucibles are preferable here to platinum crucibles, as the latter are slightly affected by the operation. The mixture fuses thoroughly, or, at any rate, its particles agglutinate completely into a state of semi-fusion.

When the operation is completed (no matter whether with carbonate or

hydrate of baryta), the crucible is allowed to cool, carefully washed outside, and put with its contents into a beaker-glass, when it is covered with from ten to fifteen parts of water; hydrochloric or nitric acid is then added, and the rest of the operation conducted as *sub a* (fluxing with carbonate of soda). Care must be taken, however, not to add too much hydrochloric acid at once, as the chloride of barium, which forms, is insoluble in that acid, and might, consequently, impede further solution by forming a species of insoluble protecting crust round the still undissolved portion of the mixture.

γ. FLUXING WITH BISULPHATE OF POTASSA.

One part of finely pulverised and elutriated mineral is mixed with from five to six parts of pounded bisulphate of potassa, put into a platinum crucible, which is then covered with the lid, in order to avoid the too rapid evaporation of the excess of acid, and exposed to the flame of a gas or spirit-lamp until the contents of the crucible begin to fuse; the temperature is then maintained at the same point until the whole mixture is fused into a transparent mass. This mass, after cooling, is mixed with water, and heated to boiling; when, according to the nature of the mineral operated upon, either the whole mass will dissolve, or only a portion of it, leaving an undissolved residue.

The bisulphate of potassa is not well adapted as a flux for silicates, since it fails to effect their decomposition with the same facility and completeness as the carbonated alkali, and with it, moreover, it is difficult to obtain the silica in a state of purity.

Other methods of fluxing—for instance, that of silicates with hydrofluoric acid or fluorine compounds, that of chromium ores with oxidising agents, &c., will be treated of hereafter.

§ 23.

4. CONVERSION OF THE DISSOLVED SUBSTANCES INTO A FORM ADAPTED FOR WEIGHING.

The conversion of a substance in a state of solution into a form adapted for weighing, may be effected either by evaporation, or by precipitation. The former of these operations is applicable only in cases where the substance, the weight of which we are desirous to ascertain, either exists already in the solution in the form suitable for the determination of its weight, or may be converted into such form by evaporation in conjunction with some re-agent. The solution must, moreover, contain the substance unmixed, or, at least, mixed only with such bodies as are expelled by evaporation, or at a red-heat. Thus, for instance, the amount of sulphate of soda present in an aqueous solution of that substance may be ascertained by simple evaporation; whilst the carbonate of potassa contained in a

solution had always better be converted into chloride of potassium, by mixing the fluid with solution of chloride of ammonium, and evaporating the mixture.

Precipitation may always be resorted to whenever the substance in solution admits of being converted into a state, or combination in which it is insoluble in the menstruum.

§ 24.

a. EVAPORATION.

In the processes of evaporation for pharmaceutical or technico-chemical purposes, the principal object to be considered is saving of time, and fuel; but in evaporating processes in quantitative analytical researches this is merely a subordinate point, and the analyst has to direct his principal care and attention to the means of guarding against loss, or contamination of the substance operated upon.

The simplest case of evaporation is when we have to *concentrate a clear fluid, without carrying the process to dryness.* To effect this object, the fluid is poured into a basin of sufficient size to hold at least one-third more than the quantity of fluid to be operated on. Heat is then applied by placing the basin either in the water-bath, or sand-bath, or on a common-stove, or over the flame of a gas, or spirit-lamp, care being taken always to guard against actual ebullition, as this invariably and unavoidably leads to loss in the shape of small drops of fluid bubbling and spirting out. The heating over a gas, or spirit-lamp when conducted with proper care and caution, is an expeditious and very cleanly way.

If the evaporation is to be effected in the water-bath, and the operator happens to possess a Beindorf's, or other similarly constructed steam apparatus, the evaporating-dish may be placed simply into one of the apertures corresponding to its size. Otherwise recourse must be had to the water-bath illustrated by Fig. 20.



Fig. 20.

The engraving represents a basin made of strong sheet copper. This basin is half filled with water, which is kept boiling over the flame of a gas, spirit, or oil-lamp. Rings adapted to the different sizes of the evaporating-dishes serve to receive the latter. The diameter of the vessel from *a* to *b* should be from four to six inches.

If the operator can conduct his processes of evaporation in a private room, where he may easily guard against any occurrence tending to suspend minute particles of dust, or ashes in the air, he will find it no very difficult task to keep the evaporating fluids clean; and he may, therefore, safely leave the dishes uncovered, which, in that case, is the best mode of pro-

ceeding. But in a large laboratory, frequented by many people, or in a room exposed to draughts of air, or in which coal fires are burning, the greatest caution is required to shield the evaporating fluid from contamination by dust, dirt, or ashes.*

For this purpose the evaporating dish is either covered with a sheet of filtering-paper, turned down over the edges, or a glass rod twisted into a triangular shape (Fig. 21) is laid upon it, and a sheet of filtering-paper spread over it, which is kept in position by a glass rod laid across, the latter again being kept from rolling down by the slightly turned up ends, *a* and *b*, of the triangle.

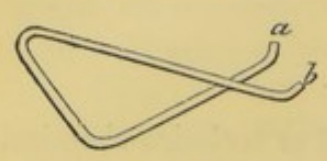


Fig. 21.

The best way, however, is the following :—Take two small thin wooden hoops (Fig. 22), one of which fits loosely in the other; spread a sheet of blotting-paper over the smaller of the two, and push the larger one over it. This forms a cover admirably adapted to the purpose; it protects the evaporating fluid from particles of dust floating in the air, it may be readily taken off, the paper cannot dip into the fluid; the cover is durable, and may, moreover, at any time be easily renewed.


Fig. 22.

It must be borne in mind, however, that the common filtering paper contains always certain substances soluble in acids, such as lime, sesquioxide of iron, &c., which, were covers of the kind just described used over evaporating dishes, containing a fluid evolving acid vapor, would infallibly dissolve in these vapors, and the solution dripping down into the the evaporating fluid, would speedily contaminate it. Care must be taken, therefore, to use only such filtering paper as has been freed by washing from the presence of substances soluble in acids.

Evaporation for the purpose of concentration may be effected also in glass flasks; these are only half filled, and placed obliquely. The process may be conducted in the sand-bath, or over the flame of a gas, or spirit-lamp, or even, and with equal propriety, over a charcoal fire. Gentle ebullition of the fluid can do no harm here, since the oblique position of the flask guards effectively against risk of loss from the bubbling and spirting of the liquid.

The evaporation of fluids containing an insoluble sediment had always

* In my own laboratory we have separate evaporating cases made entirely of unpainted wood, and provided in front with glass windows, which open either on a slide or with hinges; it is in these cases that we conduct the processes of evaporating in quantitative researches. The wooden roof, sloping obliquely from three sides, terminates in a wooden channel which leads to the chimney. About half a foot below the lower orifice of this channel there is a wooden support, on which is placed a dish intended to catch any fluid that may condense in the canal, and which might, but for this precaution, drop or trickle down.

better be conducted in the water-bath; since in the sand-bath, or over the flame of a lamp, it is next to impossible to guard against loss from spirting, occasioned by slight explosions of steam bubbles arising from the sediment impeding the equal diffusion of the heat. Still there remains another, though less safe way, viz., to conduct the evaporating in a crucible placed obliquely over the flame, as illustrated in Fig. 23. In this process, the flame is guided in a manner to play upon the crucible above the level of the fluid.

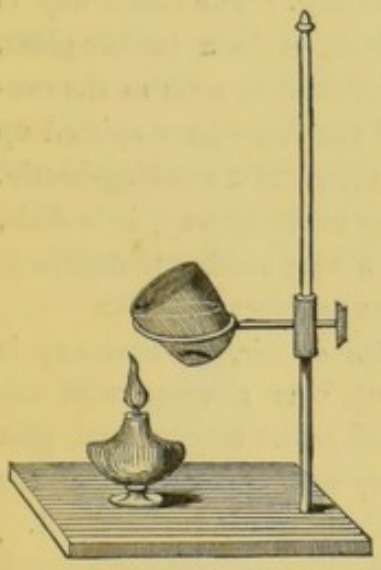


Fig. 23.

Where a fluid has to be evaporated to absolute dryness, as is so often the case, the operation should always, if possible, be concluded in the water-bath. In cases where from the nature of the dissolved substance, the application of the water-bath is inadmissible, the object in view may often be attained most readily by heating the contents of the evaporating-dish from the top, which is effected by placing the dish in a proper position, in a drying case, of which the upper plate is heated by a flame passing over it.

In cases where the heat has to be applied from the bottom, a method must be chosen which admits of an equal distribution, and ready graduation and moderation of the heat.

An air-bath is well adapted for this purpose; the apparatus illustrated in Fig. 20 may be used, although I must not omit to mention, that this mode of application will tend to injure it in the long run. If the operation has to be conducted over the flame of a lamp, the dish should be placed high above the flame; best on a wire-net, since this will greatly contribute to an equal distribution of the heat. The use of the sand-bath is objectionable here, because with that apparatus we cannot reduce the heat so speedily as may be desirable. But no matter which method, or apparatus be employed, this rule applies equally to all of them: that the operator must watch the process, from the moment that the residue begins to thicken, in order to prevent spirting, by reducing the heat, and by breaking the pellicles and crusts which form on the surface, with a glass rod, a platinum wire, or spatula.

Saline solutions that have a tendency upon their evaporation to ascend along the sides of the vessel, and may thus finally overflow the edge of the latter, which, of course, involves the risk of a loss of substance, should be heated from the top, in the way just indicated (Fig. 23); since by that means the sides of the vessel will get heated sufficiently to cause the instantaneous evaporation of the ascending liquid, preventing

thus its overflowing the edge. The inconvenience just alluded to may, however, be obviated also, in most cases, by covering the edge, and the uppermost part of the inner side of the vessel, with the very slightest possible coating of tallow, thus diminishing the adhesion between the fluid and the vessel.

In the case of liquids evolving gas bubbles upon evaporating, particular caution is required to guard against loss from spirting. The safest way is to heat such liquids in an obliquely-placed flask, or in a beaker-glass, covered with an evaporating dish; the latter is removed as soon as the evolution of gas bubbles has ceased, and the fluid that may have spirted up against it, is carefully rinsed into the glass, by means of a washing-bottle. If the evaporation has to be conducted in the common way, in a dish, a rather capacious one should be selected, and a very moderate degree of heat applied at first, and until the evolution of gas has ceased.

If a fluid has to be evaporated *with exclusion of air*, the best way is to place the dish under the bell of an air-pump, over a vessel with sulphuric acid, and to exhaust rapidly; or a tubulated retort may be used, with a long tube fixed into it, reaching down to very near the surface of the liquid, and through which hydrogen or carbonic acid gas is transmitted.

The respective materials of the evaporating vessels may exercise a much greater influence on the results of an analysis than is generally believed. Many rather startling phenomena that are observed in analytical processes may arise simply from the evaporated liquid having dissolved particles of the material of the evaporating vessel; this must, of course, lead also to great errors in the appreciation of the results of an analysis.

The importance of this point has induced me to subject it to a new and searching investigation (see experiments, 1—4), of which I will here briefly intimate the results.

Distilled water kept boiling for some length of time in flasks of Bohemian glass, dissolves appreciable traces of that material; this is the case still more with water containing a slight admixture of potassa, soda, or carbonate of potassa, or soda; a boiling solution of chloride of ammonium also attacks glass vessels. Boiling dilute acids dissolve glass less readily than water. Porcelain (Berlin dishes) is much less affected by boiling water than glass; but more than glass by boiling hydrochloric acid. Boiling solution of chloride of ammonium acts on porcelain strongly, boiling solution of carbonate of soda perceptibly. It results from these data, that in analyses pretending to a high degree of accuracy, silver and platinum dishes should always be preferred.

§ 25.

We come now to the *weighing of the residues remaining upon the evaporation of fluids*. We allude here simply to such as are soluble in water;

those which are separated by filtration, will be treated of in the next paragraph (Precipitation). Residues are generally weighed in the same vessel in which the evaporation has been completed, for which purpose platinum dishes, of from two to three inches in diameter, or large platinum crucibles are best adapted, since they are lighter than porcelain vessels, of the same capacity.

However, in most cases, the amount of liquid to be evaporated is too large for so small a vessel, and its evaporation in portions would occupy too much time. The best way, in cases of this kind, is to concentrate the liquid first in a larger vessel, and to terminate the operation afterwards in the smaller weighing vessel.

In transferring the fluid from the larger to the smaller vessel, the lip of the former is slightly greased with tallow, and the liquid made run down a glass rod. (See Fig. 24.)

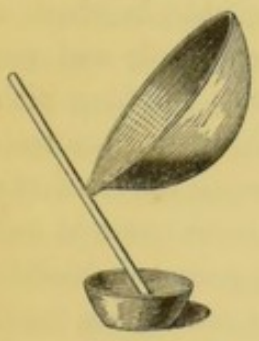


Fig. 24.

Finally the large vessel is carefully rinsed with a washing-bottle, until a drop of the last rinsing leaves no longer a residue upon evaporation on a platinum knife. When the fluid has thus been transferred to the weighing vessel, the evaporation is completed in the water-bath, and the residuary substance finally exposed to a red-heat, provided always it will admit of this process. For this purpose the dish is covered with a lid of thin platinum foil, or, in want of such, with a thin glass plate, and then placed high over the flame of a lamp, and heated gently until all the water which may still adhere to the substance is expelled; the dish is now exposed to a stronger, and finally to a red-heat. If a glass plate be used as a cover, this must, of course, be first removed before the application of red-heat can be resorted to. The dish is then allowed to cool; if the contents are liable to absorb water, the process of cooling must be conducted under a bell-glass over a vessel containing concentrated sulphuric acid. (See Fig. 8.) After cooling, the covered dish is weighed with its contents. When we have to operate upon substances which decrepitate, such as chloride of sodium, for instance, it is very advisable to expose them,—after their removal from the water-bath, and previously to the application of a free flame,—to a temperature somewhat above 212°, either in the air-bath, in a sand-bath, or on a common stove.

If the residue does not admit of the application of a red-heat, as in the case, for instance, with organic substances, ammoniacal salts, &c., the residuary mass is simply dried, at a temperature suited to its nature. In many cases the temperature of the water-bath is sufficiently high for this purpose, for the drying of chloride of ammonium, for instance; in others, the air-bath, or oil-bath must be resorted to. (Vide § 15.) Under any

circumstances, the desiccation is to be continued until the substance ceases to suffer the slightest diminution in weight after renewed exposure to heat, for from fifteen to thirty minutes. The dish should invariably be covered during the process of weighing.

If, as will frequently happen, we have to deal with a fluid containing a small quantity of a salt of potassa, or soda, the weight of which we want to ascertain, in presence of a comparatively large amount of a salt of ammonia, which has been mixed with it in the course of the analytical process, I prefer the following method. The saline mass is thoroughly dried in a large dish, in the water-bath, or, towards the end of the process, at a temperature somewhat exceeding 212°. The dry mass is then, with the aid of a platinum spatula, transferred to a small glass dish, which is put aside for a time under the bell-glass of an air-pump. The last traces of the salt left adhering to the sides and bottom of the large dish are rinsed off with a little water into the smaller dish, or the large crucible, in which it is intended to weigh the salt; the water is then evaporated, and the contents of the glass dish are added to the residue in the weighing dish or crucible: the ammonia salts are now expelled by heat, and the residuary fixed salts are then finally weighed. Should some traces of the saline mass adhere to the smaller glass dish, they ought to be removed and transferred to the weighing vessel, with the aid of a little pounded chloride of ammonium, or some other salt of ammonia, as the moistening them again with water would involve an almost certain loss of substance.

§ 26.

b. PRECIPITATION.

Precipitation is resorted to in quantitative analysis far more frequently than evaporation, since it serves not merely to convert substances into forms adapted for weighing, but also, and more especially, to separate them from one another. The principal intention in precipitation, for the purpose of quantitative estimations, is to convert the substance in solution into a form in which it is insoluble in the menstruum present. The result will, *cæteris paribus*, be the more accurate, the more the precipitated body deserves the epithet *insoluble*, and in cases where a substance may be precipitated in several different forms, possessing all the same degree of insolubility, *that* form will be the least liable to loss in which the smallest amount of liquid is required.

Hence it follows, first, that in all cases where other circumstances do not interfere, it is preferable to precipitate substances in their most insoluble form; thus, for instance, baryta had better be precipitated as a sulphate than as a carbonate; secondly, that when we have to deal with precipitates that are not quite insoluble in the menstruum present, we

must endeavour to remove that menstruum as far as may be practicable by evaporation; thus a dilute solution of strontia should be concentrated, before proceeding to precipitate the strontia with sulphuric acid; and, thirdly, that when we have to deal with precipitates slightly soluble in the liquid present, but altogether insoluble in another menstruum, into which the former may be converted by the addition of some substance or other, we ought to endeavour to bring about this modification of the menstruum. Thus, for instance, alcohol may be added to water, to induce complete precipitation of chloride of platinum and ammonium, chloride of lead, sulphate of lime, &c.; thus again, the phosphate of magnesia and ammonia may be rendered insoluble in an aqueous menstruum by adding ammonia to the latter, &c.

Precipitation is generally effected in beaker glasses. In cases, however, where we have to precipitate from fluids in a state of ebullition, or where the precipitate requires to be kept boiling for some time with the menstruum, flasks, or dishes are substituted for beaker-glasses.

The separation of precipitates, from the fluid in which they are suspended, is effected either by *decantation*, or *filtration*, or by both. But, before proceeding to the separation of the precipitate by any of these methods, the operator must know whether the precipitate is completely formed. To determine this most important point, an accurate knowledge of the properties of the various precipitates must be attained, which we shall endeavour to supply in the third section. As a general rule, the precipitated liquid should be allowed to stand at rest for several hours before proceeding to the separation of the precipitate. This rule applies more particularly to crystalline, pulverulent, and gelatinous precipitates, whilst curdy and flocculent precipitates, more particularly when thrown down by boiling, may often be filtered off immediately. However, we must observe here, that all general rules, in this respect, are of very limited application only.

§ 27.

a. SEPARATION OF PRECIPITATES BY DECANTATION.

When a precipitate subsides so completely and speedily in a fluid that the latter may be decanted off perfectly clear, and that the washing of the precipitate does not require a very long time, decantation is resorted to for its separation; this is the case, for instance, with chloride of silver, metallic mercury, &c.

Decantation will always be found a very expeditious, and accurate method of separation, if the process be conducted properly, and carefully; it is necessary, however, in most cases, to promote and assist the speedy and complete subsidence of the precipitate; and it may be laid down as a general rule in this respect, that heating the precipitate with its men-

struum will produce the desired effect. Nevertheless, there are instances in which the simple application of heat will not cause the precipitate to subside so speedily and completely as may be desirable; in some cases, as with chloride of silver, for instance, agitation of the fluid must be resorted to; in other cases, some re-agent, or other is to be added—hydrochloric acid, for instance, in the precipitation of mercury, &c. We shall have occasion, subsequently, in the fourth section, to discuss this point more fully, when we shall likewise treat of the vessels best adapted for the performance of this process in its various modifications, according to the nature of the precipitate.

After having washed the precipitate repeatedly with fresh quantities of the proper fluid, until there is no trace of a dissolved substance to be detected in the last rinsings, the precipitate is placed in a crucible, or dish, if it is not already in a vessel of that description; the fluid still adhering to it is poured off as far as is practicable, and the precipitate, is then, according to its nature, either simply dried, or heated to redness.

A far larger amount of water being required for washing precipitates separated by decantation than is the case with precipitates washed upon filters, the former process can be expected to yield *accurate* results only in cases where the precipitates are *absolutely insoluble*. For the same reasons, decantation is not ordinarily resorted to in cases where, besides the amount of the precipitated substance, we have to determine the amount of other constituents contained in the decanted fluid.

The decanted fluid must be allowed to stand at rest from twelve to twenty-four hours, to make quite sure that it contains no minute traces of the precipitated substances; if, after the lapse of twelve or twenty-four hours, according to circumstances, not a trace of sediment is to be discovered at the bottom of the vessel, the fluid may be thrown away except, of course, it should happen to be required for other purposes; but if a sediment has subsided, the amount of this had better be estimated by itself, and added to the gross amount; the sediment may, in such cases, be separated from the supernatant fluid by decantation, or by filtration.

§ 28.

β. SEPARATION OF PRECIPITATES BY FILTRATION.

This operation is resorted to whenever decantation is impracticable; and, consequently, in the great majority of cases; provided always the precipitate is of a nature to admit of its being completely freed, by mere washing on the filter, from all foreign particles adhering to it. Where this is not the case, the combined operations of decantation, and filtration are resorted to (§ 31).

α α. FILTERING APPARATUS. Filtration, as a process of quantitative

analysis, is almost exclusively effected by means of paper filters, supported by glass funnels.

Smooth and perfectly circular filters are invariably selected. Much depends upon the quality of the paper. To be perfect, this ought to combine the three following properties:—1. It must completely retain the finest precipitates; 2. It must filter rapidly; and 3. It must be as free as possible from any admixture of inorganic bodies, but more especially from such as are soluble in acid, or alkaline fluids.

It is a matter of some difficulty, however, to procure paper fully answering these conditions. The best is *Swedish filtering paper;* it bears that name in the watermark; and even this answers the purpose only so far as the first two conditions are concerned, but is by no means sufficiently pure for very accurate analyses, since it leaves upon incineration about 0·3 per cent of ashes, and yields to acids perceptible traces of lime, magnesia, and sesquioxide of iron. It is always advisable, therefore, to treat even the Swedish filtering paper, when intended for minute and accurate investigation, with dilute hydrochloric acid, in order to free it from inorganic matter; after this process, the paper is carefully washed with water, to remove all traces of the acid, and dried. In the case of very fine filtering paper, the best way to perform this operation, is to place the ready cut filters, either singly, or several together in a funnel, exactly the same way as if intended for immediate filtration; they are then moistened with a mixture of one part of pure hydrochloric acid with three parts of water, which is allowed to act on them for about ten minutes; after this, all traces of the acid are carefully removed by washing the filters (still in the funnel) repeatedly with warm water. The funnel is now covered with a piece of paper, turned over the edges, and is then put in a warm spot until the filters inside are dry.

Ready-cut filters of various sizes should always be kept on hand. Filters are either cut by a pattern of circular pieces of pasteboard or tin, or the paper is folded doubly together, with the border at right angles, and placed between two tin plates cut in the shape of segments (Fig. 25).

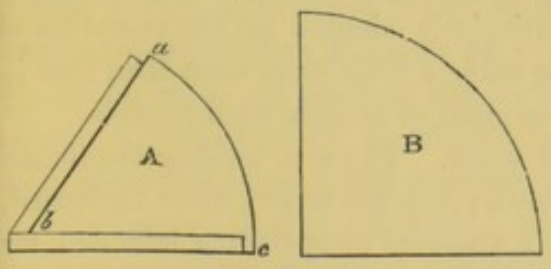


Fig. 25.

The portion of the paper which projects from between the two plates is cut off with the scissors. Filters cut in this way are perfectly circular and of equal size.

Several pairs of tin plates of various sizes, should be procured for this purpose. The filter ought always to be sufficiently large to afford room for double the quantity of precipitate remaining on it after the filtration of the fluid.

In the selection of funnels, care should be taken that they be straight

and regular, and inclined at the proper angle (60°). Glass is the most suitable material for funnels.

The filters must never reach over the brim of the funnel; the best way is to select filters the respective radii of which are one or two lines shorter than those of the funnels into which they are to be inserted.

The filter is firmly pressed into the funnel, to bring the paper closely contiguous, at every point, to the side of the latter; it is then moistened with water, which is allowed to pass through the tube; but must, on no account, be poured off by inverting the funnel.

The stands shown in Figs. 26 and 27, complete the apparatus for filtering.

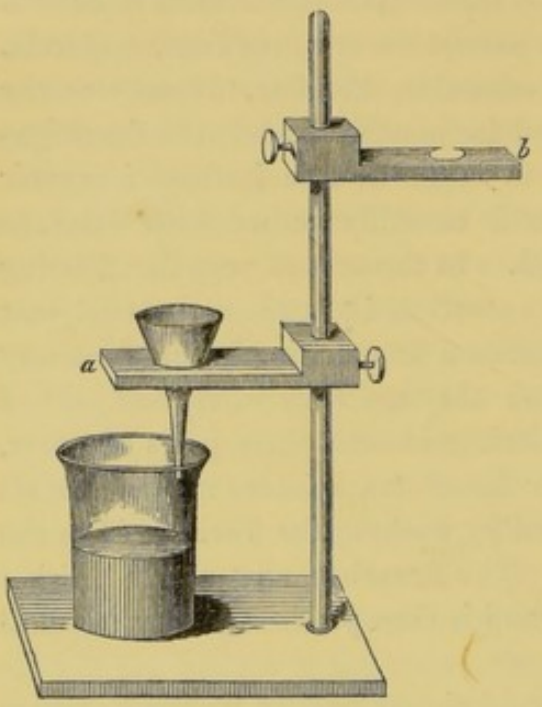


Fig. 26.

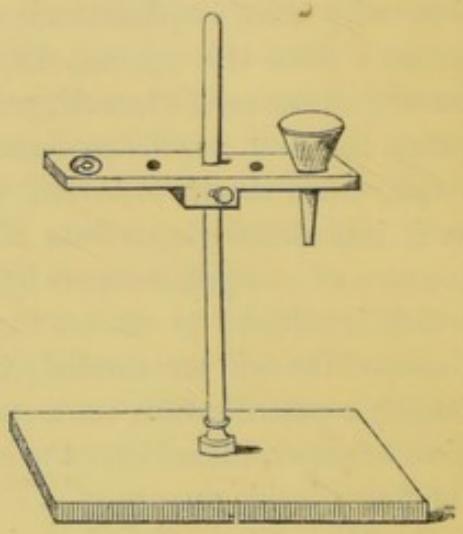


Fig. 27.

The stand in Fig. 26 is more particularly adapted for the reception of larger funnels, and should therefore be made a little more solid than that in Fig. 27, which is intended for the reception of smaller sized funnels.

The stands are made of solid hard wood. The arm holding the funnel or funnels must slide easily up and down; but the screw, when tightened, must retain it firmly in position. The aperture or apertures intended for the reception of the funnels, must be cut sloping conically downwards, to keep the funnels steadily in their places. The arm *b* (Fig. 26) serves for the reception of a washing bottle.

These stands are very convenient and may be readily moved without interfering with the operation.

§ 29.

b b. RULES TO BE OBSERVED IN THE PROCESS OF FILTRATION.

In the case of curdy, flocculent, gelatinous, or crystalline precipitates there is no great danger of any particles of the precipitate passing through the filter. But, in cases where we have to deal with fine pulverulent precipitates, it is generally *necessary*, and always *advisable*, to let the precipitate subside, and then filter the supernatant liquid, before proceeding to place the precipitate upon the filter. Substances which have been precipitated hot, are most properly filtered before cooling (provided always there be no objection to this course), since hot fluids run through the filter more speedily than cold ones. Some precipitates have a tendency to be carried though the filter with their menstruum; this may be prevented in some instances by modifying the latter. Thus sulphate of baryta, when filtered from an aqueous solution, passes rather easily through the filter—the addition of chloride of ammonium prevents this in a great measure.

Should the operator find, during the filtration of a precipitate, that he has taken too small a filter to hold the precipitate conveniently, and so as to admit of its being properly washed, he had always best use an additional filter, and thus distribute the precipitate over the two.

The fluid ought never to be poured directly upon the filter, but always down a glass rod, as represented in Fig. 24; and the lip or brim of the vessel from which the fluid is poured, may be greased with tallow.* The stream ought invariably to be directed towards the sides of the filter, never to the centre, since this might occasion some loss by splashing. In cases where the fluid has to be filtered off, with the least possible disturbance of the precipitate, the glass rod must not be placed, during the intervals, into the vessel containing the precipitate; but it may conveniently be put into a clean glass, which is finally rinsed with water upon the filter.

The filtrate is received either in flasks, beaker-glasses, or dishes, according to the various purposes for which it may be intended. Strict care should be taken to conduct the filtrate down the side of the receiving vessel; it should never be allowed to fall into the centre of the collecting fluid, since this again might occasion loss by splashing. The best method in this respect is that illustrated in Fig. 26, viz., to place the tube of the funnel against the upper part of the inner wall of the receiving vessel.

If the process of filtration is conducted in a place perfectly free from

* The tallow for this purpose may conveniently be kept in a small glass tube fitted with a piston, by means of which the tallow is pushed forward in proportion as it is required for use.

dust, there is no necessity to cover the funnel, nor the vessel receiving the filtrate; but since this is but rarely the case, it is generally indispensable to cover both the funnel, and the receiving vessel. This is best effected with round plates of glass; a small aperture for the tube of the funnel is cut out at the edge of the plates intended to cover the receiving vessel; —plates perforated in the centre are of no use for this purpose.

After the fluid and precipitate have been poured upon the filter, and the vessel which originally contained them has been washed repeatedly with water (of course, likewise, upon the filter), it happens generally that small particles of the precipitate remain adhering to the vessel, which cannot be removed with the glass rod. From beaker-glasses, or dishes these particles may be readily removed by means of a quill prepared for the purpose, by tearing off nearly the whole of the feather, leaving only a small piece, which should be cut perfectly straight. But if the minute remainder of the precipitate happens to stick to the inner walls of a flask, as is sometimes the case with substances precipitated from fluids in a state of ebullition (sesquioxide of iron, for instance); or, in short, wherever its removal cannot be accomplished by mechanical means, solution must be resorted to, followed by re-precipitation. In cases, therefore, where we have to deal with substances for which we possess no solvent, such as sulphate of baryta, for instance, we must avoid precipitating in vessels from which the precipitate cannot be readily and completely removed by mechanical means.

§ 30.

c c. WASHING OF PRECIPITATES.

After having transferred the precipitate completely to the filter, we have next to perform the operation of washing; this is effected by means of a washing-bottle, such as Figs. 28 and 29 represent.



Fig. 28.



Fig. 29.

I prefer the one illustrated in Fig. 29. The handle to it serves to render its use more easy and convenient, more particularly in washing with hot water; it is made of wood, and fastened with wire to the bottle.

Care must always be taken to regulate the stream properly, since too impetuous a stream of water might occasion some loss of substance.

In cases where a precipitate has to be washed with great care and caution, the apparatus illustrated in Fig. 30, will be found to answer very well.

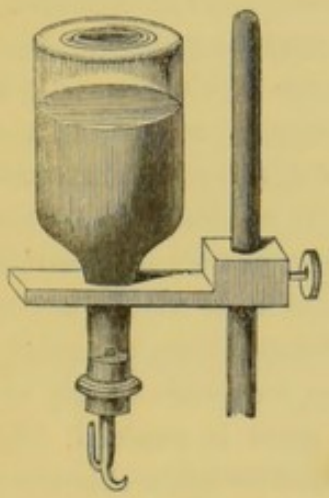


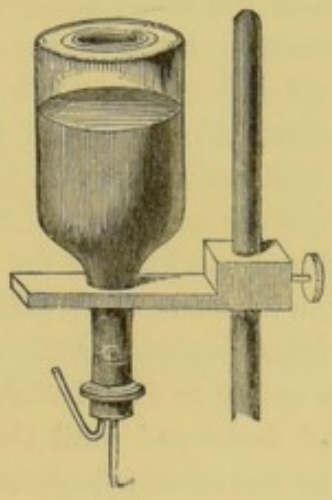
Fig. 30.

The construction of this apparatus does not require much explaining. The point *a* is drawn out at the end, and nipped off. When the flask is inverted, it supplies a fine continuous stream of water.

Precipitates requiring washing, are washed most expeditiously with hot water, provided always, there be no special reason against the application of it. The washing bottle, illustrated in Fig. 29, is particularly well adapted for this purpose.

In cases where the washing of a precipitate has to be continued very long, we employ sometimes bottles of a peculiar construction, which save us the trouble of repeated application. Figs. 31 and 32, illustrate washing-bottles of this kind.


Fig. 31.


Fig. 32.

It will at once be clearly apparent from the engravings that the principle is the same in both. There is only this difference between them, that in 31, the two tubes are joined together in one piece, whilst in 32, they are separate. The construction of 31 is somewhat more difficult of illustration than that of 32. A brief exposition of the principle will show this clearly enough. Fig. 33 represents the cork with the tubes, apart from the bottle. The arrangement is so contrived that no water can flow out of the bottle upon a simple inversion of the same; but it begins to flow imme-

diately upon bringing the finger, or a small piece of paper, or some other substance, in contact with the water in the point *c*; the water now flows constantly, whilst air passes into the bottle, through the tube *a b*; the efflux of the water stops the moment the finger, or the piece of paper, &c., is removed from *c*.

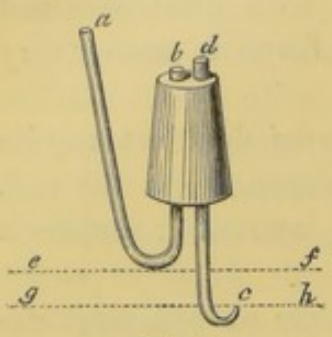


Fig. 33.

I deem it of great importance, for the proper construction and use of this washing apparatus, that the student should possess a clear and correct notion of the principle upon which its properties depend. I will, therefore, now briefly explain this principle. In the first place, the non-efflux of water from *c*, is owing to the circumstance that the pressure of the column of water occupying the space between the lines *e f* and *g h*, is not *altogether* but *nearly* sufficiently powerful to overcome the capillary attraction which the tube *a b* exercises upon the fluid;—in the second place, the efflux of water from *c* ensuing upon its being brought into contact with a body to which it may adhere, is owing to the pressure of the water column *f h*, assisted as it is now by the power of adhesion of the moistened body, overcoming the capillary attraction in *a b*. If the point *c* is put completely under water, the efflux will likewise cease, since this shortens the column *f h*. If the tube *d c* is lowered, so as to place *c* below *g h*, the water will flow incessantly, the pressure of the increased column of water overcoming by itself the capillary attraction in *a b*. But if, on the contrary, *c d* is moved upwards, the pressure of the column *f h*, together with the force of adhesion of the substance in contact with it, will no longer be sufficiently powerful to overcome the capillary attraction in *a b*, and consequently no water will flow out. It will be readily conceived from the preceding remarks, that the construction, as well as illustration, of the joint-tube in 31 offers some difficulties, since it is not by any means easy to fit the point *c exactly* at the required distance from the point where the tube *a b* is united to *c d*. In 32, the tube *c d* requires simply to be turned upward and downward until the desired point is attained. In the construction of the latter apparatus, care should be taken that the aperture *a* of *a b* be situated somewhat higher than *b*; if this precaution be neglected, water will be forced out every time the air passes through this tube; moreover, *d* must abut somewhat higher than *b*, or, as soon as the surface of the water ceases to close *b*, the remainder will flow out in a continued stream.

The process of washing by means of either of these bottles is easily performed. The bottle is placed inverted into the aperture contrived for its reception in the second arm of the filter-stand (*vide* Fig. 26, *b*), and kept suspended over the funnel in such a manner that *c just*

dips under the surface of the fluid. If the apparatus is well arranged, the water will now flow out of *c* in the same measure as it runs off through the funnel. To substitute for these washing bottles, narrow-necked flasks, inverted directly into the funnel, is quite inadmissible in cases where we intend to determine the exact amount of the precipitated substance, since the ascending bubbles of air would invariably carry minute particles of the precipitate up into the flask.

Care should be taken, whilst washing the precipitate, no matter whether with, or without a washing apparatus, to prevent the formation of channels in it, through which the water might flow off, without pervading the whole mass of the substance. If such channels have formed, the precipitate must be carefully stirred with a glass rod, or a platinum spatula.

The operation of washing may be considered completed when all soluble matter has been removed; whether this end has been attained may generally be ascertained by evaporating a drop of the last washings upon a clean platinum knife, and observing whether or not this leaves any residue behind. But in cases where the precipitate is not altogether insoluble in water (sulphate of strontia, for instance), recourse must be had to more special tests, which we shall have occasion to point out in the course of the work.

The operation of washing precipitates requires the greatest care and attention at the hands of the analytical chemist; it is self-evident that the imperfect washing of a precipitate must materially interfere with the accuracy of the results. The operation should, therefore, never be deemed concluded on the mere impression and judgment to that effect of the operator, the information elicited by the application of the appropriate test, or tests alone can safely be relied on.

§ 31.

SEPARATION OF PRECIPITATES BY DECANTATION, AND FILTRATION COMBINED.

In the case of precipitates which, from their gelatinous nature, or from an admixture of certain salts that have been thrown down together with them, appear to oppose insuperable, or, at all events, considerable obstacles to perfect washing on the filter, the following method will be found to answer perfectly. Let the precipitate subside as far as practicable, pour the nearly clear supernatant liquid on the filter, stir the precipitate up with the washing fluid (in certain cases, where such a course is indicated, the mixture of the washing fluid with the precipitate may besides be heated to boiling), let it subside again, and repeat this operation until the precipitate is nearly washed. Place

it now upon the filter, and complete the operation with the washing bottle.

§ 32.

FURTHER TREATMENT OF PRECIPITATES PREPARATORY TO THE PROCESS OF WEIGHING.

Before we proceed to weigh a precipitate, it is indispensable first to convert it into a form of perfectly, and accurately known composition. This is done either by drying the precipitate, or by heating it to redness. The former proceeding is more protracted and tedious in its application than the latter, and is, moreover, liable to give less accurate results. The process of drying is, therefore, generally confined to precipitates which cannot bear exposure to a red heat without undergoing total, or partial volatilization, and when ignition leaves residues not of a kind admitting of correct inference as to the exact original composition of the precipitate; thus, for instance, drying is resorted to in the case of sulphide of mercury, sulphide of lead, and other metallic sulphides, and also in the case of cyanide of silver, bichloride of platinum and chloride of potassium, &c., &c.

But whenever the nature of the precipitated substance leaves the operator at liberty to choose between drying and heating to redness, the latter is almost invariably preferred to the former; thus precipitates of sulphate of baryta, sulphate of lead, and a great many other compounds, are heated to redness.

§ 33.

A. *Drying of precipitates.*

When a precipitate has been collected, washed, and dried on a filter, minute particles of it adhere so firmly to the paper that it is found impossible to remove them. The weighing of dried precipitates involves, therefore, in all accurate analyses, the drying, and weighing of the filter. Formerly, chemists used to collect the precipitate upon two filters of equal size, the one placed within the other; after the precipitate had been dried, the outer filter was taken off, and placed on the balance as a counterpoise to the inner filter which contained the precipitate. It was at the time assumed that filters of equal size were likewise of equal weight. This assumption, however, is inadmissible in minute and accurate analyses, since every experiment shows that even small filters, although of equal size, differ in weight to the extent of twenty, thirty, and even more millegrammes. To obtain accurate results, it is necessary to dry and to weigh the filter previously to using it; the temperature at which the filter is dried must be the same as that at which it is intended subsequently to expose the precipitate. Another condition is that the filtering paper

must not contain any substance liable to be dissolved by the fluid passing through it.

The process of drying filters is conducted either in the water-bath, air-bath, or oil-bath, according to the degree of heat required. The dried filter is always weighed in a covered vessel, mostly between two watch-glasses, pressed together with a clasp (§ 15), or in a platinum crucible, or small test-tube. When the filter appears dry, it is placed between the heated watch-glasses, or in the heated crucible, or test-tube, allowed to cool under a bell-glass, over sulphuric acid, and weighed. The crucible, or the watch-glasses, or test-tube, together with the filter, are then again exposed for some time to the required degree of heat, and after cooling, weighed once more. If the weight does not differ from that found at first the filter may be considered dry, and we have simply to note the collective weight of the watch-glasses, clasp, and filter, or of the crucible and filter, or test-tube and filter.

After the washing of the precipitate has been concluded, and the water allowed to run off as far as practicable, the filter with the precipitate is taken off the funnel, folded up, and placed upon blotting-paper, which is then kept for some time in a moderately warm place, protected from dust; this serves to dry the precipitate in some measure, and thus facilitates the further process. The filter, with the precipitate in it, is now put into one of the watch-glasses, or into the uncovered platinum crucible, in which it had been weighed previously to the filtration, and is then exposed to the appropriate degree of heat, either in the water, air, or oil-bath, according to the nature of the precipitate. When it is judged that the precipitate is dry, the lid of the crucible is put on, or where a watch-glass has been used, the second watch-glass, with the clasp pushed over the two, and the crucible or the watch-glasses are then placed under a bell-glass, over sulphuric acid, where they are left to cool. After cooling they are weighed. The filter and the precipitate are then again exposed in the same way, to the proper drying temperature, allowed to cool, and weighed again, the same process being repeated until the weight remains constant, or differs only to the extent of a few deci-milligrammes. By subtracting from the weight found, the known weight of the crucible, or watch-glasses, with clasp, and filter, we obtain the weight of the dry precipitate.

It happens sometimes that the precipitate nearly fills the filter, or retains a considerable amount of the water; or sometimes the paper is so thin that its removal from the funnel cannot well be effected without tearing it. In all such cases, the best way is to let the filter and precipitate get nearly dry in the funnel, which may be effected readily enough by covering the funnel with a piece of blotting-paper turned down over the brim, and placing it on the sand-bath, or on a stove, supported on a broken beaker-glass (Fig. 34), or some similar vessel, most appropriately on a tin-plate cone, open at both ends, from ten to twelve centimeters



Fig. 34.



Fig. 35.

high, and from seven to eight centimeters in diameter at the lower, from four to six at the upper end (see Fig. 35).

§ 34.

B. *Heating precipitates to redness.*

It was customary formerly in this process to dry the precipitate jointly with the filter, then to scrape the latter clean and remove it, previously to heating the precipitate to redness. This proceeding inevitably gave rise to the loss of the minute particles which, however clean the filter may be scraped, will always adhere to it. Experience has shown that more accurate results are obtained if the filter is left with the precipitate, and the weight of the ashes remaining upon the incineration of a *clean* filter of the same size, be subtracted from the weight of the precipitate after the process of ignition; this, of course, involves the incineration of the filter.

If care be taken to make the filters always of the same paper, and to have for every size a pattern to cut them by, the quantity of ashes which they respectively yield upon incineration may be readily determined once for all, for every size. To this end we need simply take ten filters of the same size, to burn them in an obliquely placed platinum crucible, or in a platinum dish, to continue the application of a red heat until every trace of carbon is removed, and then to weigh the ashes, and to divide the amount found by 10; the quotient expresses, with sufficient precision, the average quantity of ashes which every individual filter of the same size, and of the same paper leaves upon incineration.

In the ignition of precipitates, the following four points have to be more particularly regarded.

1. That no loss of substance be incurred.
2. That the ignited precipitates do not alter during the operation.
3. That the incineration of the filters be complete.
4. That the crucibles be not affected.

The following two methods of heating precipitates to redness, seem to me the simplest and most appropriate of all that have as yet been proposed. The respective selection depends upon certain circumstances, which I shall immediately have occasion to point out. But no matter which method may be resorted to, the precipitate must always be thoroughly dried first, before it can properly be exposed to a red heat. The application of a red heat to moist precipitates, more particularly

to such as are very light and loose in the dry state (silicic acid, for instance), involves always a risk of loss from the impetuously escaping aqueous vapors carrying away with them minute particles of the substance. Some other substances, as hydrate of alumina, or hydrated sesquioxide of iron, for instance, have a tendency to concrete into small hard lumps: if such substances are not thoroughly dried previously to exposure to a red heat, they are liable, upon the application of the latter process, to fly about in the crucible with great violence. The best way of effecting the preliminary operation of drying, in such cases, is to leave the filter with the precipitate in the funnel; to cover the latter with a piece of blotting-paper turned over the brim, and to expose the whole to the heat of the sand-bath, or of a stove, in the manner illustrated by Figs. 34, 35.

Respecting the *degree* of heat to be applied, and the *duration* of the process, these must, of course, depend upon the nature, and properties of the precipitate operated upon, and upon its deportment at a red heat. As a general rule, a moderate red heat, applied for about five minutes, is found sufficient to effect the purpose in view; the exceptions from the rule we shall have occasion to point out hereafter.

Whenever the choice is permitted between porcelain, and platinum crucibles, the latter are always preferred, on account of their comparative lightness and superior solidity, and because they are more readily heated to redness. The crucible selected should always be of sufficient capacity, as the use of crucibles deficient in size involves the risk of loss of substance. The proper size, in most cases, is four centimeters in height, and 3·5 centimeters in diameter. That the crucible must be perfectly clean, both inside and outside, need hardly be mentioned. Dirt or impurities adhering to it may be removed by boiling with water, hydrochloric acid, or solution of soda. Where this fails to attain the desired end, a little bisulphate of potassa is fused in the crucible, the fluid mass is shaken about inside, allowed to cool, and the crucible is then finally boiled with water. There are two ways of cleaning crucibles soiled outside; either the crucible is placed in a larger one, and the interstices between the two are filled up with bisulphate of potassa, which is then heated to fusion; or, the crucible is placed on a platinum wire triangle, heated to redness, and then sprinkled over with pulverised bisulphate of potassa.

When the crucible is clean, it is placed upon a clean platinum wire triangle, and heated to redness; it is then allowed to cool under the bell-glass, and afterwards weighed. This operation, though not indispensable, is still always advisable, to insure perfect correctness of the results, in so far as the weight of the crucible is concerned. The empty crucible may, indeed, also be weighed after the ignition of the precipitate; still it is always better to weigh it previously.

We will now proceed to the description of the two methods.

§ 35.

FIRST METHOD. (*Heating the precipitate to redness, with simultaneous incineration of the filter.*)

This method is resorted to in cases where there is no danger of a reduction of the precipitate by the action of the carbon of the filter. The mode of proceeding is as follows:—

The perfectly dry filter, with the precipitate, is removed from the funnel, and its sides are gathered together at the top, so that the precipitate lies inclosed as in a small bag. The filter is now put into the crucible, which is then covered and exposed over a gas, or spirit-lamp with double draught, to a moderate heat, to effect the slow charring of the filter; the cover is now removed, the crucible placed obliquely over the flame, and a stronger degree of heat applied, until complete incineration of the filter is effected; the lid, which had in the meantime best be kept on a porcelain plate, or in a porcelain crucible, is put on again, and a red heat applied for some time longer, if needed; the crucible is now allowed to cool a little, and is then, while still hot, though no longer red hot,* taken off with a pair of tongs of brass or polished iron (Fig. 36), and put under the bell-glass, where it is left to cool; it is then finally weighed.

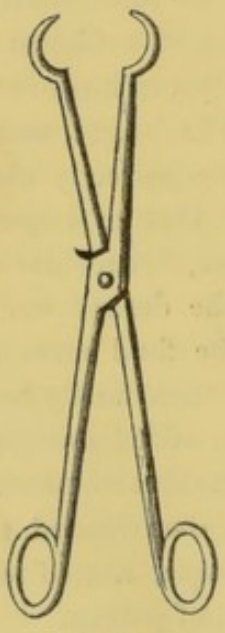


Fig. 36.

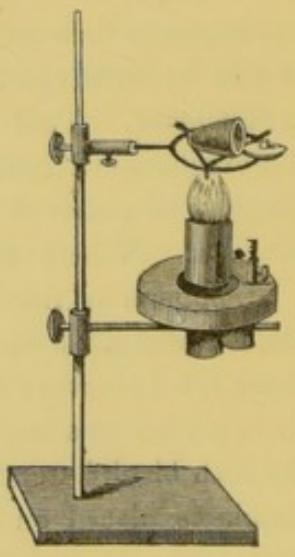


Fig. 37.

The combustion of the carbon of the filter may be promoted, in cases where it proceeds too slowly, by pushing the non-consumed particles with a smooth and rather stout platinum wire, within the focus of the strongest action of the heat and air. Or the operator may also increase the draught

* Taking hold of a *red-hot* platinum crucible with a pair of brass pincers, might cause the formation of black rings round it.

of air by leaning the lid of the crucible against the latter in the manner illustrated in Fig. 37.

It will occasionally happen, that particles of the carbon of the filter obstinately resist incineration. In such cases the operation may be promoted by putting a small lump of fused and dry nitrate of ammonia into the crucible, placing the lid on the latter, and applying a gentle heat at first, which is gradually increased.

In cases where the precipitate may be easily detached from the filter, the preceding method is occasionally modified in this, that the precipitate is put into the crucible, and the filter, with the still adhering particles, folded loosely together, and laid over the precipitate. In other respects, the operation is conducted in the manner above described.

§ 36.

SECOND METHOD. (*Heating the precipitate to redness, and incinerating the filter separately.*)

This method is resorted to in cases where a reduction of the precipitate from the action of the carbon of the filter is apprehended; and also where the ignited precipitate is required for further investigation, in which the ashes of the filter might form a disturbing element. The mode of proceeding is as follows:—

The crucible intended to receive the precipitate, is placed upon a sheet of glazed paper; the perfectly dry filter with the precipitate is taken out of the funnel, and gently pressed together over the paper, to detach the precipitate from the filter; the precipitate is now placed in the crucible, and the particles still adhering to the filter are removed from it, as far as practicable, by gentle scraping and friction, and are then likewise thrown into the crucible. The filter is then cut into eight or ten small pieces, with a pair of clean scissors over the glazed paper; the lid of the crucible is heated to redness over a Berzelius-lamp, or gas-flame, and the pieces are placed one by one upon the red-hot cover, with a pair of small pincers —the application of a gentle red heat being continued until the last trace of carbon is completely consumed.

If the lid of the crucible happens to be large, and the filter small, there is no need of cutting up the latter; it is in that case simply folded together and burnt in the usual way upon the lid. The lid is then laid on a porcelain crucible, and covered over with a beaker-glass. As has already been stated, certain precipitates, the phosphate of magnesia and ammonia, for instance, are not altogether insoluble in the rinsing water. In the case of precipitates of this kind, the filter gets soaked with a saline solution, though an extremely dilute one; and the subsequent incineration, consequently, often requires a long protracted application of a red heat. In such cases, the incineration of the filter may be promoted

by gently pressing the still unconsumed particles with a smooth platinum wire, or platinum spatula, against the red-hot lid, to bring them into the most intimate contact with it. Much patience is required for this operation. It need hardly be mentioned, that it must always be conducted in a spot entirely protected from currents of air.

When perfect incineration of the filter has been effected, the particles of the precipitate that may have chanced to fall upon the sheet of glazed paper, are transferred to the crucible, and the precipitate is now heated to redness. The lid, with the ashes, is then finally put on—(in cases where the precipitate is required for further investigation, in which the presence of the ashes might prove a disturbing element, the cover must, of course, be put on in a manner to prevent the filter ashes falling into the crucible) —the application of red heat being continued for a moment longer; the crucible is then allowed to cool a little, and placed, still hot, under the bell-glass, where it is left to cool. It is then finally weighed.

Certain precipitates suffer some essential modification in their properties, in their solubility, for instance, from the application of a red heat. In cases where a portion of a substance of the kind is required after the weighing, for some other purpose with which the effects of a red heat would interfere, the two operations of drying and heating to redness may be combined in the following way:—the precipitate is collected on a filter dried at 212°; it is then dried, likewise, at 212°, and weighed. A portion of the dry precipitate is then put into a weighed crucible, and its exact weight ascertained; it is now exposed to a red heat, allowed to cool in the usual way, and weighed again; the diminution of weight which it has undergone is then calculated on the whole amount of the precipitate in hand.

§ 37.

5. ANALYSIS BY MEASURE.

It may be readily gathered from the preceding paragraph that the quantitative estimation of a substance in the usual way, viz., by converting it, by evaporation, or precipitation, into a weighable form, is always rather a protracted task; evaporation, subsidence of precipitates, filtration, washing, drying, heating to redness, weighing, being all of them operations requiring much time.

Certain methods in which all, or nearly all of these operations are dispensed with, and which are accordingly much more expeditious, have, therefore, of late been frequently resorted to, and with the best success, particularly in quantitative estimations for technical purposes. The principle of these methods may best be illustrated by a few examples.

Suppose we have prepared a solution of chloride of sodium, containing in 100 parts 0·7307 parts of the salt; with this solution we may pre-

cipitate exactly 1·3496 grm. of silver from its solution in nitric acid—the equivalent of chloride of sodium being 730·7, that of silver 1349·6. Now, suppose we have an alloy before us, consisting of unknown quantities of silver and copper, we want to determine the amount of silver present. In this case, we need simply weigh off 1·3496 grm. of the alloy, dissolve carefully in nitric acid, and add to the solution our solution of chloride of sodium, drop by drop, until the whole of the silver is thrown down, and an additional drop fails to produce a further precipitate. The amount of silver present may now simply be calculated from the amount of solution of chloride of sodium used. Thus, supposing we had used 80 parts of our solution, the amount of silver present in the alloy would be 80 per cent; as 100 parts of our solution of chloride of sodium will throw down 1·3496 of pure silver, it follows that every one hundredth part of our chloride of sodium solution corresponds to one per cent of silver.

Another example. It is well known that iodine and sulphuretted hydrogen cannot exist together: whenever these two substances are brought in contact, decomposition immediately ensues, the hydrogen separating from the sulphur and joining the iodine (I + HS = HI + S). Hydriodic acid exercises no action on starch paste, whereas the least trace of free iodine imparts to the latter substance a blue tint. Now, if we prepare an alcoholic solution, containing in 100 parts, 17·463 of iodine, we may with this decompose exactly one gramme of sulphuretted hydrogen, for 212·5 : 1586 : : 1 : 7·463. Let us suppose, then, we have before us a fluid containing an unknown amount of sulphuretted hydrogen, which it is our intention to determine. We need simply add to it a little starch paste, and then add drop by drop our solution of iodine, until a persistent blue coloration of the fluid indicates the formation of iodide of starch, and hence the absolute and complete decomposition of the sulphuretted hydrogen. The amount of the latter originally present in the fluid may now be readily calculated from the amount of solution of iodine used. Every one-hundredth part of the latter corresponding to 00·1 grm. of sulphuretted hydrogen.

The principle of these methods consists accordingly in this, that a chemical decomposition is effected, of which the exact point of termination may be clearly and distinctly observed; and that this decomposition is effected by means of a fluid of accurately known composition, the action and combining proportions of the active agent in it being likewise accurately known, so that the quantity used of the latter may be determined with the greatest precision.

Whether the quantitative estimation be made here by weight, or by measure is a matter of perfect indifference. But as the process of measuring, from its greater expedition and convenience, is mostly resorted to in

preference to that of weighing, these methods are usually comprised under the collective name of analysis by measure.

The details of the various methods of analysis by measure will be treated of hereafter. I will simply point out here the conditions on which the accuracy of the results depends.

a. The decomposition which forms the leading point of the analysis must always remain the same; thus, for instance, a precipitate forming must present exactly the same composition throughout, no matter whether it forms at the commencement of the operation, when one of the substances is still predominant, or at the end when that predominance has ceased.

b. The termination of the process of decomposition must be most clearly and unmistakeably discernible.

c. The decomposing fluid must admit of the most accurate preparation, either by dissolving a weighed quantity of a substance of perfectly and accurately known nature and composition, in a definite volume of fluid; or by preparing in the first place a solution of approximately known composition, determining then, by experiments, the exact and proportionate amount of the active agent in it, and diluting it finally to the required degree. If the test fluid keeps unaltered, this is a great advantage, as, in the contrary case, we have to determine the proportionate amount of the active agent in it anew, on the occasion of every fresh analysis.

d. The quantitative estimation must be as rigorously precise as may be practicable. To enable us to achieve the utmost in this respect, we prepare in very accurate analyses by measure, besides the actual test fluid, another solution, ten times more dilute, by adding to the former nine parts of water, spirits of wine, or some other fluid, as the case may be. We now effect the decomposition of the solution under examination, partially only, though very near to completion, with a most accurately measured quantity of the concentrated test fluid, and complete the operation then finally with the dilute test fluid. By this means we guard in a great measure against the risk of adding too much of the test fluid, and gain, moreover, a higher degree of accuracy in the measuring.

e. The decomposition must, of course, always be conducted, so as to guard against loss of any of the active agents.

SECTION II.

REAGENTS.

§ 38.

For general information respecting reagents, I refer the student to my volume on Qualitative Analysis.

The instructions given here will be confined to the preparation, testing, and most important application of those chemical substances which subserve principally and more exclusively the purposes of quantitative analysis. Those reagents which are equally applied in qualitative investigations, and that have accordingly been treated of already in the volume on the qualitative branch of the analytical science, will be simply enumerated.

The classification adopted in my qualitative analysis has been retained here, not because it is free from objection, but because, upon the whole, it may be considered the most convenient.

The mode of preparing and testing those reagents which—as the test acids, for instance, used in analyses by measure—simply subserve some specific purpose, will be found where we shall have occasion to speak of their application.

A. REAGENTS IN THE HUMID WAY.

I. GENERAL REAGENTS.

a. Reagents principally used as simple solvents.

§ 39.

1. DISTILLED WATER (see Qualitative Analysis).

Water intended for quantitative investigations must be perfectly pure. Water distilled from glass vessels leaves a residue upon evaporation (see experiment, No. 1), and is therefore inapplicable for many purposes; thus, for instance, we cannot use it to determine the exact degree of solubility of sparingly soluble substances. For certain uses it is necessary to free the water by ebullition from atmospheric air, and carbonic acid.

2. ALCOHOL.

1. Absolute alcohol. 2. Spirits of wine of various degrees of strength.

3. ETHER.

The application of ether as a solvent is very limited. It is more frequently used mixed with spirits of wine, in order to diminish the solvent power of the latter for certain substances, *e. g.* bichloride of platinum and chloride of ammonium.

b. Reagents which are principally used as chemical solvents.

§ 40.

1. HYDROCHLORIC ACID.

An acid of 1·12 sp. gr. suffices for most purposes; in some cases, however, it is required stronger.

2. NITRIC ACID.

An acid of 1·2 sp. gr. suffices for most purposes.

3. FUMING-NITRIC ACID.

Preparation.—Two parts of pure and dry nitrate of potassa are introduced into a capacious retort, and one part of hydrated sulphuric acid is poured upon this salt, either through the tube of the retort, or if a common non-tubulated retort is used, through the neck of the latter by means of a long funnel tube bent at the lower end, carefully avoiding soiling the neck of the retort. The latter is then placed in a sand-bath, and connected with a receiver, but not quite air-tight. The distillation is conducted at a gentle heat, and carried to dryness. The cooling of the receiver must be properly attended to during the distillation.

Red fuming nitric acid intended for analytical purposes, must be in a state of the greatest possible concentration, and perfectly free from any admixture of sulphuric acid.

Uses.—This acid is a powerful dissolving and oxidising agent; it serves more especially to convert sulphur and the sulphides into sulphuric acid, and sulphates.

4. NITROHYDROCHLORIC ACID.

5. ACETIC ACID.

6. CHLORIDE OF AMMONIUM.

c. Reagents which serve principally to separate substances into general classes, or groups.

§ 41.

1. SULPHURIC ACID.

a. CHEMICALLY PURE, CONCENTRATED SULPHURIC ACID.

Preparation.—From three to four pounds of common sulphuric acid are introduced into a capacious glass retort, coated externally with a mortar of clay and cow-hair; a coil of platinum wire, or a few fragments of platinum, are thrown into the retort, and the latter is placed deep into a wind furnace (which is subsequently covered with a cap); the neck of the retort is introduced into the body of a large globular receiver, without luting. The contents of the retort are then gradually heated to boiling, by surrounding the latter with red-hot charcoal, taking care in the course of the operation to make the fire act principally upon the top and sides, and less upon the bottom, of the retort.

If these instructions be strictly followed, the distillation will proceed quietly, and the operator need be under no apprehension of danger. The acid which passes over first contains an admixture of nitric acid; to obtain a perfectly pure acid, therefore, the receiver is changed after some time, and the distillation is then continued until about three-fourths of the acid in the retort has passed over.

The distillation may be conducted also in a sand-bath, with a large amount of sand at the bottom, but so narrow that only a small space is left intervening between its sides and the walls of the retort; the latter is covered with sand, and a very inclined position given to the neck. The distillation is then conducted as above. In this manner (*i. e.* in the sand-bath) ten pounds and more of sulphuric acid may be distilled at a time without danger.

Testing.—Chemically pure sulphuric acid leaves no residue upon evaporation upon a platinum knife. See also Qualitative Analysis.

b. COMMON SULPHURIC ACID.

c. DILUTE SULPHURIC ACID.

Dilute sulphuric aid is prepared by mixing concentrated sulphuric acid, pure, or common, according to the requirements of the case, with five parts of water.

2. SULPHURETTED HYDROGEN (HYDROSULPHURIC ACID).

a. Sulphuretted hydrogen gas.

For the mode of preparing, &c., sulphuretted hydrogen gas for occasional use, I refer the student to my volume on Qualitative Analysis.

For large laboratories, and to chemists who have occasion to make considerable and frequent use of this reagent, I would recommend my new lead apparatus,* illustrated in Fig. 38, and which I use in my own laboratory with the best success.

a b c d and *e f g h* are two cylindrical leaden vessels, soldered with pure lead. They are both of the same size (in my own apparatus 33 centimeters high, and 30 centimeters in diameter). *i* is a false bottom of lead, perforated with numerous holes, of 1½ millimeters diameter, and placed from 4 to 5 centimeters above the actual bottom of the vessel; this false bottom rests on leaden feet, which support it not only on the sides, but more particularly in the centre; at *k* is the opening, where the sulphide of iron is put in. In my own apparatus, this opening is 7 centimeters in diameter. It has a broad smooth rim, on which the corresponding rim of the smooth-turned cover is fastened down with three handle screws of iron, or brass, a greased leather ring being first interposed. At *l* is the opening where the solution of sulphate of iron is let off. The engraving shows that this aperture, which is 3 centimeters in diameter, is made at a somewhat deepened part of the bottom *g h;* it has a broad smooth rim, on which the corresponding rim of a smooth-turned leaden cover is fastened down with a handle screw; the female screw is set in a semi-elliptical bar, hinged to the sides of *l* in a manner to admit of its being bent out of reach of the liquid, on the drawing off of the latter. The engraving shows with sufficient clearness the construction of the filling tube *m*, and also that of the tube *d h*, which is intended to convey the acid from the upper to the lower vessel, and *vice versâ*. It will be seen that this latter tube reaches down to the deepened part of the bottom *g h*, but without touching the latter. The tube *c e* is closed at the top, and thus has no communication whatever with the upper vessel; it is intended to let off the gas evolved in *e f g h*, and is to that end furnished with a branch tube *o*, provided with a stop-cock *n*. The tube *q* is then closed at both ends, and serves simply as a support. The tubes in my apparatus have a diameter of 16 millimeters.

The operation of filling is performed as follows, the quantities here given referring to an apparatus of the same dimensions as my own:—3·3 killogrammes of fused sulphide of iron in large lumps are put, through *k*, on the perforated bottom *i*; the covers are then carefully screwed down on *k* and *l*, the stop-cock *n* is closed, and seven litres † of water are poured in through the funnel of *m*, followed by one litre of concentrated sulphuric acid, and then again seven litres of water. The air in *a b c d* escapes during this operation through *p*, even though that tube be already connected with the bottles *r*, *s*, *t*.

* Made after my own design, by Mr. Stumpf, of Wiesbaden, of excellent workmanship, and at a reasonable price.

† One litre = 1 pint, 15 F. ounces, 1 F. dr. 43 minims, imperial measure.

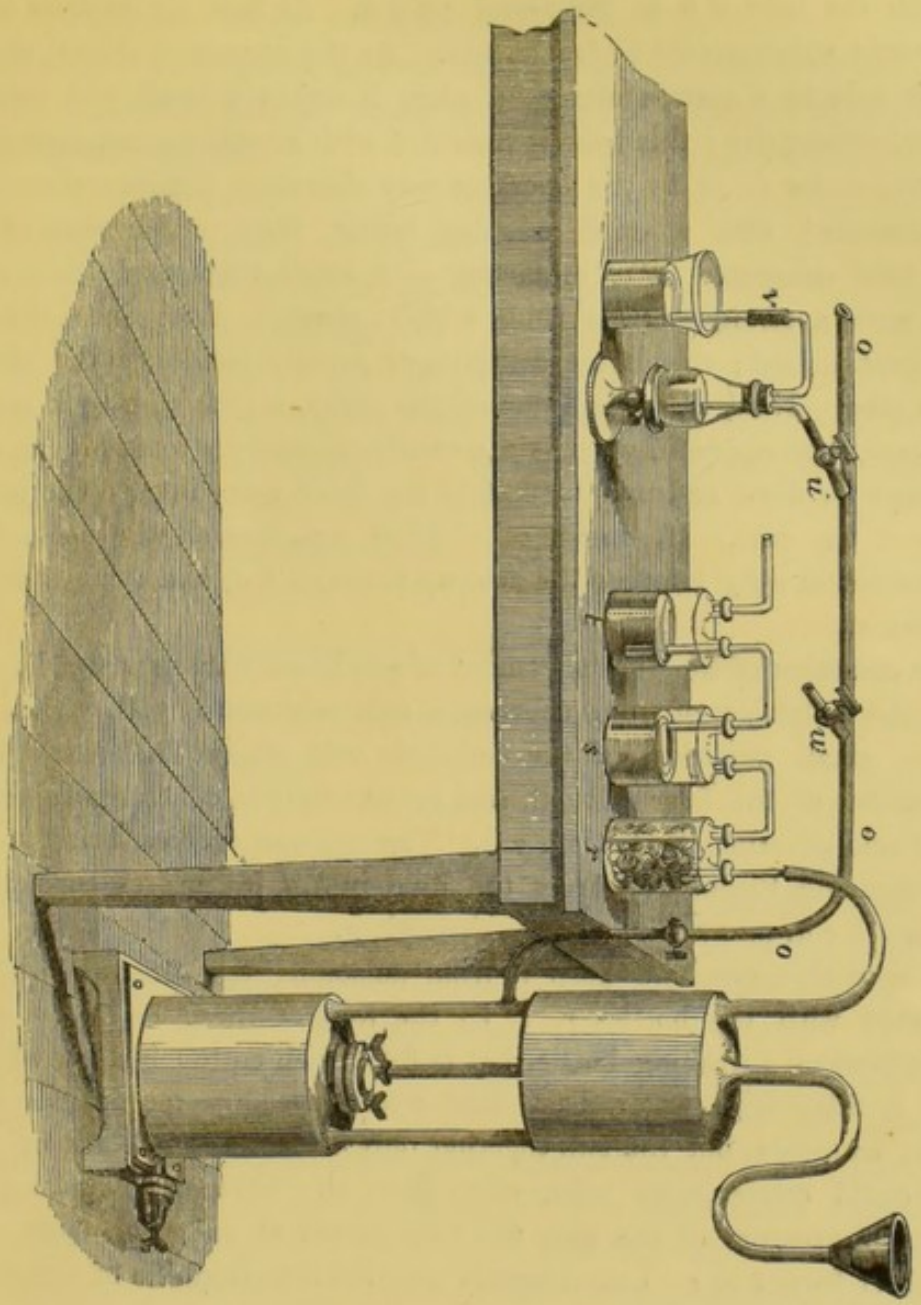


Fig. 38.

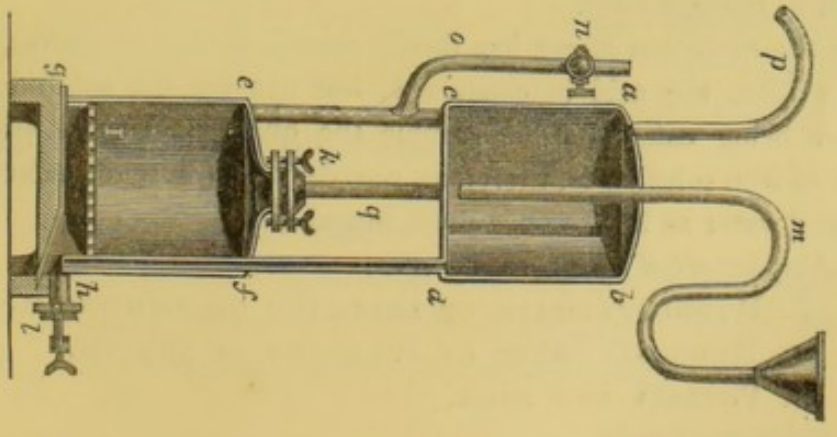


Fig. 39.

If we now open the cock *n* and one of the cocks *u*, the acid will flow through the tube *d h* to the vessel *e f g h*. At first air escapes from *o*, afterwards sulphuretted hydrogen gas. As the engraving shows, the tube *o* rises only to a certain elevation, when it makes a bend, and continues thence horizontally; this tube is provided with as many close-fitting brass gas stop-cocks (*u u*) as the operator may choose to put on; these cocks are connected with a small washing bottle, from which rises a bent glass tube connected at *v*, by means of a small vulcanized India-rubber tube, with a straight glass tube which reaches down into the fluid to be precipitated; this latter contrivance greatly facilitates the cleaning of the tube. Now, if we open one of the cocks, *u* (the stop-cock *n* being, of course, also opened), we obtain a constant, steady stream of gas which continues for days, and may be readily regulated according to the requirements of the case. If, on the other hand, we close all the cocks *u*, the gas evolved in *e f g h* forces the acid up through *h d*, and the evolution of gas ceases.

The cessation of the disengagement of gas is not instantaneous, however, since the sulphide of iron continues still moistened with acid; and, besides, small particles of the sulphide will always fall through the perforations of the false bottom, and remain thus in contact with the rest of the acid covering the bottom *g h*. The gas now evolved being stopped from escaping through *o*, forces the fluid in *h d* up, passes through the acid in *a b c d*, and finally escapes through *p*.

To save this gas, and keep it from poisoning the air, the tube *p* is connected with the bottles *r*, *s*, *t*; the first of these bottles, *r*, serves the purpose of a washing bottle, but is filled with cotton instead of water (were it filled with water, that fluid would speedily recede); *s* and *t* contain ammonia, but the two together only as much as either of them alone could conveniently hold, since from the alternate increasing and decreasing pressure of the gas, the fluid passes at one time from *s* to *t*, at another from *t* to *s*. I need hardly mention that sulphide of ammonium is formed in these bottles.

When the evolution of gas has finally ceased, that is, of course, with the cocks *u u* open, the acid is consumed, but not yet the sulphide of iron, the latter being calculated for double the quantity of acid used. The sulphate of iron solution is, therefore, now drawn off, and the same quantity of acid and water as before once more introduced.

b. Sulphuretted hydrogen water.

3. Hydrosulphate of sulphide of ammonium.

4. Hydrosulphate of sulphide of sodium.

5. Potassa and soda.

a. Solution of soda.

b. Hydrate of potassa purified with alcohol.

c. Hydrate of potassa prepared with baryta.

6. Carbonate of soda.

This reagent is required both in solution and in pure crystals; in the latter form to neutralize an excess of acid in a fluid which it is desirable not to dilute overmuch.

7. Ammonia.

8. Carbonate of ammonia.

9. Chloride of barium.

10. Nitrate of baryta.

11. Cyanide of potassium.

This substance is extensively used in quantitative analysis to separate certain metals from one another. The aqueous solution of it must be prepared fresh every time it is required for use.

12. Nitrate of silver.

13. Chlorine.

II. SPECIAL REAGENTS IN THE HUMID WAY.

a. Reagents which serve principally to determine, or to separate certain bases.

§ 42.

1. Phosphate of ammonia.

Preparation.—Mix pure dilute phosphoric acid (prepared from phosphorus) of 1·13 sp. gr. with an equal quantity of water, add pure ammonia to the mixture until it shows a strongly alkaline reaction, let it stand some time, filter, if necessary, and keep for use.

Tests.—Phosphate of ammonia must be free from any admixture of arsenic acid, nitric acid, and sulphuric acid, but more particularly of potassa, or soda. The presence of either of these alkalies may be detected by adding pure solution of acetate of lead, until the formation of a precipitate ceases, filtering, precipitating the excess of lead with sulphuretted hydrogen, filtering again, evaporating to dryness, and igniting the residue. If there now remains a residue soluble in water, and of alkaline reaction, this may be considered a conclusive proof of the original presence of soda, or potassa.

In most cases phosphate of soda (see Qualitative Analysis) may be substituted for phosphate of ammonia.

2. Oxalate of ammonia.

3. Succinate of ammonia.

Preparation.—Saturate succinic acid, which has been purified by recrystallization from its solution in nitric acid, with dilute solution of ammonia. The reaction of the new compound should be rather slightly alkaline than acid.

Uses.—This reagent serves occasionally to separate sesquioxide of iron from other metallic oxides.

4. Baryta water.
5. Carbonate of baryta.
6. Protosulphate of iron.
7. Oxide of mercury.

This latter reagent serves, in quantitative investigations, principally to decompose chloride of magnesium in the process of separating magnesia from the alkalies.

8. Chloride of mercury.
9. Protochloride of tin.
10. Terchloride of gold.
11. Bichloride of platinum.
12. Hydrofluosilicic acid.
13. Tartaric acid.
14. Sulphite of soda.
15. Copper.

The copper of commerce, with the exception of Japanese copper, which it is not always easy to procure, is rarely sufficiently pure for analytical purposes. The following is the most convenient mode of preparing pure copper: precipitate the metal from a solution of sulphate of copper by a clean plate of iron, free the precipitated copper from the iron by boiling with hydrochloric acid; wash, dry, and fuse the pure copper obtained, and roll it into thin sheets.

Tests.—Pure copper must dissolve completely in nitric acid, and addition of ammonia in excess to this solution must not, even after long standing, produce in it the faintest trace of a precipitate (iron, lead, &c.); neither should the addition of hydrochloric acid render the solution turbid (silver). Sulphuretted hydrogen must precipitate the copper completely from a neutral solution of the nitrate.

Uses.—This metal serves us occasionally in *indirect* analysis; thus it is used, for instance, to determine the amount of copper present in a fluid, and also the amount of protoxide of iron existing in the presence of the sesquioxide of that metal, &c.

b. Reagents which serve principally to determine, or to separate, certain acids.

§ 43.

1. Acetate of soda.
2. Molybdate of ammonia.

Preparation.—Dissolve one part of molybdic acid in eight parts of ammonia, and add to the solution 30 parts of nitric acid; keep the fluid in a well closed bottle. (See qualitative analysis.)

Uses.—The molybdate of ammonia supersaturated with nitric acid, serves, in certain difficult cases, to effect the separation of phosphoric acid.

3. Chloride of calcium.

4. Fluoride of calcium.

This substance is used in quantitative analysis to displace and determine boracic acid; none but perfectly pure fluor-spar (like that of Derbyshire), free from any admixture of silicic acid, is applicable for this purpose. The hydrofluoric acid used in analytical investigations for the decomposition of silicates, may be prepared from a less pure kind of fluor-spar than that of Derbyshire.

Tests.—The best way of testing the purity of fluor-spar, in case of doubt, is to pulverise it finely, and to treat a weighed amount of the powder with pure concentrated sulphuric acid, in a platinum crucible, at a gentle heat, which is gradually increased to redness; the same operation being repeated until the weight of the residue remains constant. The fluor-spar may be considered pure if the calculated amount of sulphate of lime is obtained by this process.

5. Sulphate of magnesia.

6. Sesquichloride of iron.

7. Oxide of lead.

Preparation.—Precipitate solution of pure nitrate, or acetate of lead with carbonate of ammonia, wash the precipitate, dry it, and expose the residue to a gentle red heat until complete decomposition is effected.

Uses.—Oxide of lead is occasionally used to fix an acid, so as to prevent its expulsion at a red heat.

8. Neutral acetate of lead.

9. Protochloride of palladium and sodium.

B.—REAGENTS IN THE DRY WAY.

§ 44.

1. Carbonate of soda.

2. Carbonate of soda and potassa.

3. Hydrate of baryta.

4. Bisulphate of potassa.

Preparation.—Mix 87 parts of neutral sulphate of potassa (see qualitative analysis) in a platinum crucible, with 49 parts of pure concentrated sulphuric acid, and heat to gentle redness, until the mass is in a state of uniform and calm fusion. Pour the fused salt into a platinum dish, standing in cold water. After cooling, break the mass into pieces, and preserve for use.

Uses.—This reagent serves as a flux for certain native compounds of alumina and oxide of chromium. Bisulphate of potassa is used also, as we have already had occasion to state, for the cleansing of platinum crucibles; for this latter purpose, however, the salt which is obtained as a collateral product in the preparation of nitric acid, will be found sufficiently pure.

5. Nitrate of potassa.

6. Nitrate of soda.

7. Carbonate of ammonia.

This reagent serves to convert the bisulphates of the alkalies into neutral salts. It must completely volatilize when heated in a platinum dish.

8. Biborate of soda (fused).

Preparation.—Heat crystallized biborate of soda (see qualitative analysis) in a platinum, or porcelain dish, until it ceases to swell; reduce the porous mass to powder, and heat the latter in a platinum crucible till it is fused to a transparent mass; pour the more fluid portion of the mass into a platinum dish, and remove the rest from the crucible with a platinum spatula. Keep the biborate of soda thus obtained in a well stoppered bottle.

Uses.—This reagent serves to expel carbonic acid, and other volatile acids, at a red heat.

9. Hydrogen gas.

Preparation.—Hydrogen gas is evolved when dilute sulphuric acid is added to granulated zinc. It may be procured absolutely pure by transmitting it, in the first place, through a long glass tube loosely filled with cotton, soaked with solution of chloride of mercury; afterwards through a solution of potassa; and finally through hydrated sulphuric acid. In most cases, however, it is only necessary to dry it, by transmission through sulphuric acid, or through a tube filled with chloride of calcium.

Tests.—Pure hydrogen gas is inodorous. It ought to burn with a colorless flame, which, when cooled by depressing a porcelain dish upon it, must deposit nothing on the surface of the dish except pure water, free from acid reaction.

Uses.—Hydrogen gas is frequently used, in quantitative analysis, to reduce oxides, chlorides, sulphides, &c., to the metallic state.

10. Chlorine.

Chlorine gas is purified and dried by transmitting it, first, through a washing bottle containing concentrated sulphuric acid, and, finally, through a tube filled with chloride of calcium; the latter may, however, be omitted.

Uses.—Chlorine gas serves principally to produce chlorides, and to separate the volatile from the non-volatile chlorides; it is also used to displace, and indirectly to determine, bromine, and iodine.

C.—REAGENTS APPLIED IN ORGANIC ELEMENTARY ANALYSIS.

§ 45.

1. Oxide of copper.

Preparation.—Mix pure copper scales with pure nitric acid, in a porcelain dish, to a thick paste; after the effervescence has ceased, heat gently in the sand-bath until the mass is perfectly dry. Transfer the green basic

salt produced into a Hessian crucible, and heat to moderate redness, until no more red fumes escape, which may be readily ascertained by introducing a small portion of the mass into a test tube, closing the latter with the finger, heating to redness, and then looking through the tube lengthwise; in most instances, however, the smell will sufficiently indicate whether the evolution of nitrous vapors continues or not. The uniform decomposition of the salt in the crucible may be promoted by stirring the mass from time to time with a hot glass rod. When the crucible has cooled a little, reduce the mass, which now consists of pure oxide of copper, to a tolerably fine powder, by triturating it in a brass or porcelain mortar; pass the powder through a metal sieve, and keep the sifted portion in a well-stoppered bottle for use. It is always advisable to leave a small portion of the oxide in the crucible, and to expose this again to an intense red heat. This portion is not pounded, but simply broken into small fragments, which are kept in a separate bottle.

Tests.—Pure oxide of copper is a compact, heavy, deep black powder, gritty to the touch, and absolutely insoluble in water; upon exposure to a red heat, it must evolve no nitrous acid fumes, nor carbonic acid, the latter would indicate contamination with fragments of charcoal, or with dust. That portion of the oxide which has been exposed to an intense red heat, should be hard, and have a grayish black appearance.

Uses.—Oxide of copper serves to oxidize the carbon, and hydrogen of organic substances, yielding up its oxygen wholly, or in part according to circumstances. That portion of the oxide which has been heated to the most intense redness, is particularly useful in the analysis of volatile fluids.

The reduced copper may be again oxidized with nitric acid, and may thus be used again and again, for the same purpose. Should it have become mixed with alkaline salts in the course of the analytical process, it may be freed from such admixture by digesting it with very dilute, cold nitric acid, and washing it afterwards with water.

2. CHROMATE OF LEAD.

Preparation.—Precipitate a clear filtered solution of acetate of lead, slightly acidulated with acetic acid, with bichromate of potassa slightly in excess; decant, and wash the precipitate thoroughly on a linen strainer; dry the washed precipitate, put it into a Hessian crucible, and heat to bright redness until the mass is fairly in fusion. Pour the fused mass upon a stone slab or iron plate, let it cool, break and pulverize it, and pass the powder through a fine metallic sieve.

Tests.—Chromate of lead is a heavy powder, of a dirty yellowish brown color; it is insoluble in water. It must evolve no carbonic acid upon the application of a red heat; the evolution of carbonic acid would indicate contamination with organic matter, dust, &c.

Uses.—Chromate of lead serves, the same as oxide of copper, for the

combustion of organic substances. It is converted, in the process of combustion, into chromic acid, and basic chromate of lead. It suffers the same decomposition, with evolution of oxygen, when heated by itself beyond its point of fusion. The property of chromate of lead to fuse at a red heat, renders it preferable to oxide of copper as an oxidizing agent, in cases where we have to act upon difficultly combustible substances.*

Chromate of lead which has been used once may be used a second time. For this purpose it is fused again, and the mass reduced to powder, in the same way as stated before. Should it be deemed necessary, the second fusion may be preceded by washing.

3. Chlorate of potassa.

Preparation.—Heat commercial chlorate of potassa in a platinum, or porcelain dish, until the mass is fairly in fusion; but no longer; pour the fused mass into a platinum dish, and break it, whilst still hot, into small pieces. Preserve in a well-stoppered bottle for use.

Uses.—Chlorate of potassa yields up all its oxygen at a high temperature; it is used, accordingly, to effect the complete oxidation of difficultly combustible organic substances. For the *modus operandi, vide infrâ* (organic elementary analysis).

4. Soda-lime (mixture of caustic lime and hydrate of soda).

Preparation.—Dissolve commercial crystallized carbonate of soda, in the manner described in the Qualitative Analysis; ascertain the strength of the solution, and then add a weighed amount of the best caustic lime, in the exact proportion of two parts of anhydrous caustic lime to one part of hydrate of soda contained in the solution, and evaporate to dryness. Heat the mixture in a Hessian crucible, keep it for some time at a moderate red heat, and reduce the mass, whilst still warm, to a tolerably fine powder. Keep the powder in a well-stoppered bottle.

Tests.—Soda-lime must not effervesce much, when treated with hydrochloric acid in excess; but more particularly, it must not evolve ammonia, when mixed with pure sugar, and heated to redness.

Uses.—Soda-lime serves in the analysis of nitrogenous organic substances. For the *rationale* of its action, *vide infrâ,* organic elementary analysis.

5. Bicarbonate of soda.

In certain processes of organic elementary analysis of nitrogenous substances, bicarbonate of soda serves to evolve the carbonic acid, by means of which the atmospheric air is expelled from the combustion tube. The commercial bicarbonate is sufficiently pure for this purpose, but it must be perfectly dry.

6. Metallic copper.

Metallic copper serves, in the analysis of nitrogenous substances, for the

* Chromate of lead should be always employed in the combustion of organic compounds containing chlorine.

reduction of the nitric oxide gas that may form in the course of the analytical process.

It is used either in the form of turnings, or in that of close spiral wire; or of small rolls made of thin sheet copper. A length of from seven to ten centimeters is given to the spirals, or rolls, and just sufficient thickness to admit of their being inserted into the upper end of the combustion tube. To have it perfectly free from any admixture of dust, oxide, &c., it is first heated to redness in the open air, in a crucible, until the surface is oxidized; it is then put into a glass, or porcelain tube, through which an uninterrupted current of dry hydrogen gas is transmitted; finally, when all atmospheric air has been expelled from the evolution apparatus, and the tube, the latter is in its whole length heated to redness. The operator should make sure that the atmospheric air has been thoroughly expelled, before he proceeds to apply heat to the tube: neglect of this precaution may lead to an explosion.

7. Potassa.

a. Solution of potassa.

Dissolve one part of purified carbonate of potassa in 12 parts of water, and add to it a paste made of two-third parts of lime mixed with three times the quantity of warm water. The mode of preparing the solution is the same as that given in the qualitative analysis for the preparation of soda.

Allow the mixture to stand some time in a covered jar, decant the fluid, and evaporate it in an iron vessel, over a strong fire, down to a specific gravity of 1·27; pour it, still warm, into a bottle, close the latter well, and wait until all solid particles have subsided. Draw the clear solution off from the sediment, and keep for use.

b. Hydrate of potassa.

The commercial hydrate of potassa may answer the purpose. If you wish to prepare it yourself, evaporate solution of potassa (*a*) in a silver vessel, over a strong fire, until the residuary hydrate flows like oil, and white fumes begin to escape from the surface. Pour the fused mass out on a clean iron plate, and break it up into small pieces. Keep in a well-stoppered bottle for use.

Uses.—Solution of potassa serves for the absorption, and hence quantitative estimation of carbonic acid. In many cases, a tube filled with hydrate of potassa, is used in addition to the apparatus filled with solution of potassa.

8. Chloride of calcium.

a. Crude fused chloride of calcium.

Preparation.—Digest with warm water the residuary mixture of chloride of calcium, and lime which remains after the preparation of ammonia; filter, and evaporate the filtrate to dryness, in an iron vessel; fuse the residue in a Hessian crucible, pour the fused mass out, and break it up into pieces. Preserve in well-stoppered bottles.

b. Pure chloride of calcium.

Preparation.—Dissolve the crude chloride of calcium of *a*, in water, filter the solution, and, should it shew an alkaline reaction, saturate it with a few drops of hydrochloric acid ; evaporate it, in a porcelain dish, to dryness, and expose the residue for several hours to a tolerably strong heat (about 392°), in the sand-bath. The white and porous mass obtained by this process consists of Ca Cl + 2 aq.

Uses.—The crude fused chloride of calcium serves to dry moist gases and to abstract water from fluids; the pure chloride is used in organic elementary analysis for the absorption and estimation of the water formed from the hydrogen evolved from the analysed substance. The solution of the pure chloride of calcium must not possess an alkaline reaction.

SECTION III.

ON THE COMPOSITION AND PROPERTIES OF THE FORMS AND COMBINATIONS IN WHICH SUBSTANCES ARE SEPARATED FROM EACH OTHER, OR IN WHICH THEIR WEIGHT IS DETERMINED.

§ 46.

The quantitative analysis of a compound substance requires, as the first and most indispensable condition, a correct and accurate knowledge of the composition and properties of the new combinations, into which it is intended to convert its several individual constituents, for the purpose of separating them from one another, and determining their respective weight. Regarding the properties of the new compounds and their deportment, we have to inquire more particularly, in the first place, how they comport themselves with solvents ; secondly, what is their deportment in the air ; and, thirdly, what phenomena do they manifest when exposed to the action of a red heat ? It may be laid down as a general rule that compounds are the better adapted for quantitative determination the more insoluble they are, and the less alteration they undergo upon exposure to the air, or to a high temperature.

The composition of bodies is expressed either in percentage proportions, or in stœchiometrical, or symbolic formulæ ; by means of the latter, the constitution of the more frequently recurring compounds may be more easily committed to memory. In this section the composition of the substances treated of is given in four different ways, in as many columns : the first column gives the composition of the substance in symbols ; the

second, in equivalents (O = 100); the third, in equivalents (H = 1); the fourth, in percentage proportions. With respect to its composition, a compound is the better adapted for quantitative determination, the less it contains relatively of the substance which it is intended to determine; since the less the relative proportion of the latter, the less influence will any error, or loss of substance that may occur in the course of the analytical process exercise upon the accuracy of the results. Thus, bichloride of platinum and chloride of ammonium, for instance, is, in this respect, better adapted for the determination of nitrogen than chloride of ammonium; since 100 parts of the former contain only 6·27 of that element, whilst 100 parts of the latter contain 26·2 of it.

Suppose we have to analyse a nitrogenous substance:—we convert its nitrogen into bichloride of platinum and chloride of ammonium. The process, conducted with absolute accuracy, yields from 0·300 grm. of the analysed body, 1·000 grm. of bichloride of platinum and chloride of ammonium: 100 parts of this double chloride contain 6·27 parts of nitrogen, 1·000 contains therefore 0·0627 of that element. These 0·0627 have been derived from 0·300 of substance; 100 parts of the analysed body, consequently, contain 20·90 of nitrogen.

We now make a second analysis, in which we convert the nitrogen of the substance to be analysed into chloride of ammonium, instead of bichloride of platinum and chloride of ammonium; we again conduct the process with absolute accuracy, and obtain from 0·300 of the substance under examination, 0·2394 of chloride of ammonium, corresponding to 0·0627 of nitrogen, or 20·90 per cent.

Now, let us assume a loss of 10 milligrammes to have occurred in each process:—this will alter the result, in the first instance, from 1·000 to 0·990 of bichloride of platinum and chloride of ammonium, corresponding to 0.062073 of nitrogen, or 20·69 per cent; the loss of nitrogen will therefore be 20·90 minus 20:69 = 0·21.

In the second instance the result will be altered from 0·2394 to 0·2294 of chloride of ammonium, corresponding to 0·0601 of nitrogen, or 20·03 per cent. The loss in this case will consequently amount to 0·87.

We see here that the same error occasions, in the one case, a loss of 0·21 per cent, with respect to the amount of nitrogen; whilst, in the other case, the loss amounts to 0·87 per cent.

We will now proceed to enumerate and examine those combinations of various substances which are best adapted for their quantitative determination. The description given here of the external form and appearance of the new compounds, relates to the state in which they are obtained in our analyses. With regard to the properties of the new compounds, we shall confine ourselves to the enumeration of those which bear upon the special object we have here more immediately in view.

A.—FORMS AND COMBINATIONS IN WHICH THE VARIOUS BASES ARE SEPARATED FROM OTHER BODIES, OR IN WHICH THEIR WEIGHT IS DETERMINED.

BASES OF THE FIRST GROUP.

§ 47.

1. POTASSA.

The combinations best suited for the weighing of potassa are, SULPHATE OF POTASSA, NITRATE OF POTASSA, CHLORIDE OF POTASSIUM, BICHLORIDE OF PLATINUM AND CHLORIDE OF POTASSIUM.

a. Sulphate of potassa crystallizes usually in small, hard, oblique, four-sided prisms, or in double six-sided pyramids; in the analytical process it is obtained as a white crystalline mass. It dissolves pretty readily in water; it is almost absolutely insoluble in pure alcohol, but slightly more soluble in alcohol containing an admixture of sulphuric acid (Experiment No. 6). It does not affect vegetable colors; it is unalterable in the air. The crystals decrepitate strongly when heated, yielding up at the same time a little water, which they hold mechanically confined. The decrepitation of crystals that have been kept long drying is less marked. At a strong heat sulphate of potassa fuses unaltered, and without volatilizing. When exposed to a red heat, mixed with chloride of ammonium, sulphate of potassa is partly, and, upon repeated application of the process, wholly, converted, with effervescence, into chloride of potassium. (*H. Rose.*)

COMPOSITION.

KO	= 588·86	= 47·11	= 54·08
SO_3	= 500·00	= 40·00	= 45·92
	1088·86	= 87·11	= 100·00

Bisulphate of potassa, (KO, SO_3 + HO, SO_3), is always produced when neutral sulphate of potassa, is mixed with free sulphuric acid in excess and evaporated to dryness. It is fusible even at a moderate heat. At a red heat, it loses half its sulphuric acid, together with the basic water, but not readily—the complete reconversion of the acid into the neutral salt requiring the long continued application of an intense red heat. When heated, however, in an atmosphere of carbonate of ammonia—which may be readily procured by repeatedly throwing small lumps of pure carbonate of ammonia into a crucible heated to slight redness, and putting the lid on—the acid salt changes readily and quickly to the neutral sulphate. The transformation may be considered complete as soon as the salt, which was so readily fusible before, re-assumes the solid state, at a moderate red heat.

b. Nitrate of potassa crystallizes generally in long striated prisms. In

analysis it is obtained as a white crystalline mass; it is readily soluble in water, nearly insoluble in absolute alcohol, and scantily soluble in spirits of wine. It does not affect vegetable colors, and is unalterable in the air. On being exposed to a gentle heat, far below redness, it fuses unaltered and without any diminution of weight; upon the application of a stronger heat, it changes into nitrite of potassa, with evolution of oxygen; and if the heat be increased to intense redness, it becomes converted into caustic potassa, and binoxide of potassium, with evolution of oxygen, and of nitrogen. When exposed to a red heat, in conjunction with chloride of ammonium, it is readily and completely converted into chloride of potassium.

COMPOSITION.

KO	=	588·86	=	47·11	= 46·59
NO_5	=	675·06	=	54·00	= 53·41
		1263·92	=	101·11	= 100·00

c. Chloride of potassium crystallises usually in cubes, often lengthened to columns, rarely in octohedrons. In the analytical process, we obtain it either in the former shape, or as an amorphous mass. It is readily soluble in water, nearly insoluble in absolute alcohol, and but slightly soluble in spirits of wine. It does not affect vegetable colors, and is unalterable in the air. When heated, it decrepitates, unless it has been kept long drying, with expulsion of a little water mechanically confined in it. At a moderate red heat, it fuses unaltered and without diminution of weight; when exposed to a higher temperature, it volatilizes in white fumes; this volatilization proceeds the more slowly, the more effectually the access of air is prevented. (Experiment No. 7.)

COMPOSITION.

K	=	488·86	=	39·11	= 52·44
Cl	=	443·28	=	35·46	= 47·56
		932·14	=	74·57	= 100·00

d. Bichloride of platinum and chloride of potassium present either small reddish yellow octohedrons, or a lemon-colored powder. It is difficultly soluble in cold, but more readily so in hot water; nearly insoluble in absolute alcohol, and but sparingly soluble in spirits of wine, one part requiring for its solution, respectively, 12083 parts of absolute alcohol—3775 parts of spirits of wine of 76 per cent.—1053 parts of spirits of wine of 55 per cent. (Experiment No. 8, *a.*) Presence of free hydrochloric acid sensibly increases its solubility. (Experiment No. 8, *b.*) In solution of potassa it dissolves completely to a yellow fluid. It is unalterable in the air, and at 212°. On exposure to an intense red heat, the whole of the chlorine which is in combination with the platinum escapes, metallic platinum and chloride of potas-

sium being left behind; but even after long continued fusion, there remains still a little bichloride of platinum and chloride of potassium resisting decomposition. Complete decomposition is effected, however, by heating the double salt to redness in a current of hydrogen gas.

According to *Andrews*, the bichloride of platinum and chloride of potassium, even though dried at a temperature considerably exceeding 212°, retains still 0·0055 of its weight of water.

COMPOSITION.

K =	488·86 =	39·11 =	16·00
Pt =	1236·75 =	98·94 =	40·48
3 Cl =	1329·84 =	106·38 =	43·52
	3055·45 =	244·43 =	100·00

K Cl =	932·14 =	74·57 =	30·51
$PtCl_2$ =	2123·31 =	169·86 =	69·49
	3055·45 =	244·43 =	100·00

§ 48.

2. SODA.

Soda is usually weighed as SULPHATE OF SODA, NITRATE OF SODA, CHLORIDE OF SODIUM, OR CARBONATE OF SODA.

a. The anhydrous neutral *sulphate of soda* is a white powder, or a white, very friable mass. It dissolves readily in water; it is sparingly soluble in absolute alcohol, but somewhat more readily in dilute alcohol (Experiment No. 9). The presence of free sulphuric acid increases its solubility in absolute alcohol. It does not affect vegetable colors; upon exposure to moist air, it slowly absorbs water (Experiment No. 10). The application of a gentle heat leaves it unaltered; upon exposure to an intense red heat, it fuses, without decomposition, or diminution of weight. When heated to redness, mixed with chloride of ammonium, it comports itself the same as sulphate of potassa under similar circumstances.

COMPOSITION.

NaO =	387·44 =	31 =	43·66
SO_3 =	500·00 =	40 =	56·34
	887·44 =	71 =	100·00

Bisulphate of soda ($NaO, SO_3 + HO, SO_3$), is uniformly produced upon the evaporation of a solution of the neutral salt mixed with sulphuric acid in excess; this acid salt fuses even at a gentle heat; it may be readily converted into the neutral salt in the same manner as the bisulphate of potassa is reconverted into the neutral sulphate (vide § 47 *a*).

b. Nitrate of soda crystallizes in obtuse rhomboids. In analysis it is mostly obtained as an amorphous mass. It dissolves readily in water, but is nearly altogether insoluble in absolute alcohol, and but little more soluble in spirits of wine. It does not affect vegetable colors, and is unalterable in a dry atmosphere; but when exposed to very moist air, it absorbs water. It fuses without decomposition at a temperature far below red heat; at a higher temperature it undergoes the same decomposition as nitrate of potassa. (Vide § 47 *b*.) (Comp. Experiment No. 11.) When heated to redness, in conjunction with chloride of ammonium, it comports itself the same as the corresponding salt of potassa under similar circumstances.

COMPOSITION.

NaO	= 387·44	= 31	= 36·47
NO_5	= 675·06	= 54	= 63·53
	1062·50	= 85	= 100·00

c. Chloride of sodium crystallizes in cubes, octohedrons, and hollow four-sided pyramids. In the analytical process it is frequently obtained as an amorphous mass. It dissolves readily in water; it is but slightly soluble in absolute alcohol, and but sparingly so in spirits of wine. It is neutral to vegetable colors. Exposed to a somewhat moist atmosphere, it slowly absorbs water. (Experiment No. 12.) Crystals of this salt that have not been kept drying a considerable time, decrepitate when heated, yielding a little water, which they hold mechanically confined. At a red heat, it fuses without decomposition; at a white heat, and in open vessels, even at a bright red heat, it volatilizes in white fumes. (Experiment No. 13.)

COMPOSITION.

Na	= 287·44	= 23·00	= 39·34
Cl	= 443·28	= 35·46	= 60·66
	730·72	= 58·46	= 100·00

d. Anhydrous *carbonate of soda* is a white powder, or a white, very friable mass. It dissolves readily in water, but is insoluble in alcohol. Its reaction is strongly alkaline. Exposed to the air, it absorbs water very slowly. At a strong red heat, it fuses without decomposition, and without volatilizing.

COMPOSITION.

NaO	= 387·44	= 31	= 58·49
CO_2	= 275·00	= 22	= 41·51
	662·44	= 53	= 100·00

§ 49.

3. AMMONIA (NH_4O).

Ammonia is most advantageously weighed as CHLORIDE OF AMMONIUM, or as BICHLORIDE OF PLATINUM AND CHLORIDE OF AMMONIUM.

Under certain circumstances, ammonia may likewise be estimated from the volume of the nitrogen eliminated from it.

a. Chloride of ammonium crystallizes in cubes and octohedrons, but more frequently in feathery crystals. In analysis we obtain it uniformly as a white mass. It dissolves readily in water, but is difficultly soluble in spirits of wine. It does not alter vegetable colors, and is persistent in the air. Solution of chloride of ammonium when evaporated in the water-bath, loses a small quantity of ammonia, and becomes slightly acid. The diminution of weight occasioned by this loss of ammonia is very trifling. (Experiment No. 14.) At 212° chloride of ammonium loses nothing, or next to nothing, of its weight. (Experiment No. 14.) At a higher temperature it volatilizes readily, and without undergoing decomposition.

COMPOSITION.

NH_4	= 225·06	= 18·00	= 33·67
Cl	= 443·28	= 35·46	= 66·33
	668·34	= 53·46	= 100·00

NH_3	= 212·56	= 17·00	= 31·80
CHl	= 455·78	= 36·46	= 68·20
	668·34	= 53·46	= 100·00

b. Bichloride of platinum and chloride of ammonium occurs either as a heavy lemon-colored powder, or in small, hard, octohedral crystals of a bright yellow color. It is difficultly soluble in cold, but more readily in hot water. It is very sparingly soluble in absolute alcohol, but more readily in spirits of wine, one part requiring—of absolute alcohol, 26535 parts ; of spirits of wine of 76 per cent., 1406 parts ; of spirits of wine of 55 per cent., 665 parts. The presence of free acid sensibly increases its solubility. (Experiment No. 15.) It remains unaltered in the air, and at 212°. Upon exposure to a red-heat, chlorine and chloride of ammonium escape, leaving the metallic platinum behind as a porous mass (spongy platinum).

COMPOSITION.

NH_4	= 225·06	= 18·00	= 8·06
Pt	= 1236·75	= 98·94	= 44·30
3Cl	= 1329·84	= 106·38	= 47·64
	2791·65	= 223·32	= 100·00

NH_4Cl	= 668·34 =	53·46 =	23·94
$PtCl_2$	= 2123·31 =	169·86 =	76·06
	2791·65 =	223·32 =	100·00

NH_3	= 212·56 =	17·00 =	7·61
HCl	= 455·78 =	36·46 =	16·33
$PtCl_2$	= 2123·31 =	169·86 =	76·06
	2791·65 =	223·32 =	100·00

N	= 175·06 =	14·00 =	6·27
H_4	= 50·00 =	4·00 =	1·79
Pt	= 1236·75 =	98·94 =	44·30
Cl_3	= 1329·84 =	106·38 =	47·64
	2791·65 =	223·32 =	100·00

c. Nitrogen gas is colorless, tasteless, and inodorous; it mixes with air, without producing the slightest coloration; it does not affect vegetable colors. The specific gravity is 0·9706 (air = 1). One litre (one cubic decimeter), weights at 32°, and 29·8 of the barometer, 1.2609 gramme. It is difficultly soluble in water, one volume of gas requiring 24 volumes of water at a temperature of 64°·4.

BASES OF THE SECOND GROUP.

§ 50.

1. BARYTA.

Baryta is generally weighed as SULPHATE OF BARYTA, CARBONATE OF BARYTA, and SILICO-FLUORIDE OF BARIUM.

a. Artificially prepared *sulphate of baryta* presents the appearance of a fine white powder. It is almost absolutely insoluble, both in cold and hot water; the presence of free acid hardly increases its solubility. Nitro-hydrochloric acid dissolves a perceptible amount of it. It remains quite unaltered in the air at 212°, and even at a red heat. When heated to redness, mixed with charcoal, in a covered crucible, it is reduced to sulphide of barium; free access of air prevents this reduction taking place. Upon exposure to a red heat, mixed with chloride of ammonium, sulphate of baryta undergoes partial decomposition.

COMPOSITION.

BaO	= 957·32 =	76·59 =	65·69
SO_3	= 500·00 =	40·00 =	34·31
	1457·32 =	116·59 =	100·00

b. Artificially prepared *carbonate of baryta* presents the appearance of a white powder. It dissolves in 14137 parts of cold, and in 15421 parts of boiling water. (Experiment No. 16.) It dissolves far more readily in solution of chloride of ammonium, or of nitrate of ammonia; from these solutions it is, however, precipitated again, though not completely, by caustic ammonia. In water containing free carbonic acid, carbonate of baryta dissolves, being converted into bicarbonate. In water impregnated with ammonia and carbonate of ammonia, it is nearly insoluble, one part requiring 141000 parts. (Experiment No. 17.)

Solution of carbonate of baryta has a feebly alkaline reaction. Carbonate of baryta is unalterable in the air, and at a red-heat. Upon heating it to redness, in conjunction with charcoal, caustic baryta is formed, with evolution of carbonic oxide gas.

COMPOSITION.

BaO	= 957·32	= 76·59	= 77·69
CO_2	= 275·00	= 22·00	= 22·31
	1232·32	= 98·59	= 100·00

c. Silico-fluoride of barium forms small, hard, and colorless crystals, or a fine crystalline powder. It dissolves in 3800 parts of cold water; in hot water it is more readily soluble. (Experiment No. 18.) The presence of free hydrochloric acid increases its solubility considerably. (Experiment No. 19.) In spirits of wine, it is almost insoluble. It is unalterable in the air, and at 212°; when heated to redness, it is decomposed into bifluoride of silicon, which escapes, and fluoride of barium, which remains behind.

COMPOSITION.

Ba Fl	= 1094·82	= 87·59	= 62·39	Ba	= 857·32	= 68·59	= 48·85
$Si Fl_2$	= 660·18	= 52·81	= 37·61	Si	= 185·18	= 14·81	= 10·55
				Fl_3	= 712·50	= 57·00	= 40·60
	1755·00	= 140·40	= 100·00		1755·00	= 140·40	= 100·00

§ 51.

2. STRONTIA.

Strontia is weighed either as SULPHATE OF STRONTIA, or as CARBONATE OF STRONTIA.

a. Sulphate of strontia, artificially prepared, is a white powder. It dissolves in 6895 parts of cold, and 9638 parts of boiling water (Experiment No. 20.) In water containing sulphuric acid, it is still more difficultly soluble, requiring from 11000 to 12000 parts of it. (Ex-

periment No. 21.) It dissolves in solution of chloride of sodium, but is precipitated again from this solution by sulphuric acid. It is nearly insoluble both in alcohol and in spirits of wine. It does not alter vegetable colors; and is unalterable in the air, and at a red heat. When exposed to a most intense red heat, it fuses without undergoing decomposition. When mixed with charcoal, and heated to redness, in a close-covered crucible, it is reduced to sulphide of strontium.

COMPOSITION.

SrO	= 645·93	= 51·67	= 56·37
SO_3	= 500·00	= 40·00	= 43·63
	1145·93	= 91·67	= 100·00

b. Carbonate of strontia, artificially prepared, is a white, light, loose powder. It dissolves at the common temperature in 18045 parts of water. (Experiment No. 22.) Presence of ammonia diminishes its solubility. (Experiment No. 23.) It dissolves pretty readily in solutions of chloride of ammonium and of nitrate of ammonia, but is precipitated again from these solutions by ammonia, and more completely than carbonate of baryta is under similar circumstances. Water impregnated with carbonic acid dissolves it as a bicarbonate. Its reaction is very feebly alkaline. It remains unaltered in the air, and even at a red heat, but when exposed to an intense red heat, it fuses and gradually loses its carbonic acid. Upon heating it to intense redness, in conjunction with charcoal, caustic strontia is formed, with evolution of carbonic oxide.

COMPOSITION.

SrO	= 645·93	= 51·67	= 70·14
CO_2	= 275·00	= 22·00	= 29·86
	920·93	= 73·67	= 100·00

§ 52.

3. LIME.

Lime is weighed either as SULPHATE OF LIME, or as CARBONATE OF LIME; to convert it into the latter form, it is first precipitated as oxalate of lime.

a. Artificially prepared anhydrous *sulphate of lime* is a loose, white powder. It dissolves at the common temperature in 430 parts, at 212°, in 460 parts of water (*Poggiale*). Presence of chloride of ammonium, sulphate of soda, and chloride of sodium, increase its solubility. The aqueous solution of sulphate of lime does not alter vegetable colors. In alcohol and in spirits of wine it is almost insoluble. Exposed to the air, it slowly absorbs water. It remains unaltered at a dull red heat. Heated to bright redness, it fuses without undergoing decomposition. When mixed with

charcoal, and heated to redness, in a covered crucible, it is reduced to sulphide of calcium.

COMPOSITION.

CaO	= 350	= 28	= 41·18
SO_3	= 500	= 40	= 58·82
	850	= 68	= 100·00

b. Artificially prepared *carbonate of lime* is a fine white powder. It dissolves in 10601 parts of cold (Experiment No. 24), and in 8834 parts of boiling water (Experiment No. 25). The aqueous solution has a barely perceptible alkaline reaction. In water, containing ammonia and carbonate of ammonia, it dissolves still more sparingly, one part of the salt requiring 65000 parts of the solvent (Experiment No. 26); this solution is not precipitated by oxalate of ammonia. It dissolves more readily in solutions of chloride of ammonium, and of nitrate of ammonia, but is precipitated again from these solutions by ammonia, and more completely than carbonate of baryta is under similar circumstances. Neutral salts of potassa and of soda likewise increase its solubility. Water impregnated with carbonic acid dissolves carbonate of lime as a bicarbonate. Carbonate of lime remains unaltered in the air, at 212°, and even at a red heat; but upon the application of an intense red heat, more particularly with free access of air, it gradually loses its carbonic acid. Attempts at reducing the carbonate completely to caustic lime, in a platinum crucible, over a spirit-lamp with double draught have, however, failed (Experiment No. 27). It is decomposed far more readily when mixed with charcoal and heated to redness, giving off its carbonic acid, in the form of carbonic oxide gas).

COMPOSITION.

CaO	= 350·00	= 28	= 56·00
CO_2	= 275·00	= 22	= 44·00
	625·00	= 50	= 100·00

c. Oxalate of lime is a fine white powder, almost absolutely insoluble in water. Presence of free oxalic acid and acetic acid slightly increases its solubility; but ammoniacal salts exercise no influence in this respect. The stronger acids (hydrochloric acid, nitric acid) dissolve oxalate of lime readily; from these solutions it is precipitated again unaltered, by alkalies; and also by alkaline oxalates or alkaline acetates added in excess (provided always, the excess of acid be not too great). It is unalterable in the air, and at 212°. Dried at the latter temperature, it has the following composition (Experiment No. 28).

CaO	= 350·00	= 28	= 38·36
C_2O_3	= 450·00	= 36	= 49·32
1 aq.	= 112·50	= 9	= 12·32
	912·50	= 73	= 100·00

At a temperature of from 356° to 392°, oxalate of lime loses its water without undergoing decomposition; at a somewhat higher temperature, still scarcely reaching incipient dull redness, it is decomposed, without actual separation of carbon, into carbonic oxide, which escapes, and carbonate of lime, which remains behind. The powder, which was previously of snowy whiteness, transiently assumes a gray color in the course of this process, even though the oxalate be of the most perfect purity. Upon the continued application of heat this gray color disappears again. If the oxalate of lime is heated in small coherent fragments, such as are obtained upon drying the precipitated salt upon a filter, the commencement and progress of the decomposition can be readily marked by this transient appearance of gray. If the process of heating be conducted properly, the residue will not contain a trace of caustic lime.

§ 53.

4. MAGNESIA.

Magnesia is weighed as SULPHATE OF MAGNESIA, PYROPHOSPHATE OF MAGNESIA, OR PURE MAGNESIA. To convert it into the pyrophosphate it is precipitated as BASIC PHOSPHATE OF AMMONIA AND MAGNESIA.

a. Anhydrous sulphate of magnesia presents the appearance of a white opaque mass. It dissolves readily in water. It is nearly altogether insoluble in absolute alcohol, and but very sparingly soluble in spirits of wine. It does not alter vegetable colors. Exposed to the air, it absorbs water rapidly. At a moderate red heat, it remains unaltered; but when heated to intense redness, it undergoes partial decomposition, losing part of its acid and is no longer perfectly soluble in water (Experiment No. 29). Ignited with chloride of ammonium, sulphate of magnesia is not decomposed.

COMPOSITION.

MgO	= 250·19	= 20	= 33·33
SO_3	= 500·00	= 40	= 66·67
	750·19	= 60	= 100·00

b. Basic phosphate of magnesia and ammonia is a white crystalline powder. It dissolves at the common temperature, in 15293 parts of cold water (Experiment No. 30.) In water containing ammonia, it is much more difficultly soluble—one part of the salt requiring 45000 parts of the solvent (Experiments No. 31). Chloride of ammonium slightly increases its solubility (Experiments No. 33 and 34). Presence of alkaline phosphates exercises no influence in this respect. The basic phosphate of magnesia and ammonia dissolves readily in acids, even in acetic acid. Its composition is expressed by the formula

$$2\,MgO,\,NH_4O,\,PO_5 + 12\,aq.$$

10 of these 12 equivalents of water escape at 212°, the remaining two, together with the ammonia, at a red heat, leaving behind $2MgO, PO_5$. The transition of the phosphoric acid into pyrophosphoric acid, is indicated by a vivid incandescence of the whole mass.

Ammonia precipitates phosphate of magnesia and ammonia from its solution in dilute hydrochloric, or dilute nitric acid, to the extent compatible with the degree of solubility of that salt in water impregnated with ammonia (or with ammonia and its salts). *Weber* (Pogg. 73, p. 152) having questioned the correctness of this fact, I was induced to test it again by experiment (No. 32) which, however, yielded exactly the same results as the former.

c. Pyrophosphate of magnesia presents the appearance of a white mass, often slightly inclining to gray. It is barely soluble in water, but readily so in hydrochloric acid, and in nitric acid. It remains unaltered in the air, and even at a red heat; at a very intense red heat it fuses unaltered. It leaves the color of moist turmeric and of reddened litmus paper unchanged.

If we dissolve pyrophosphate of magnesia in hydrochloric acid, or in nitric acid, add water to the solution, boil it for some time, and then precipitate with ammonia in excess, we obtain a precipitate of phosphate of magnesia and ammonia which, after ignition, gives less weight than corresponds to the amount of substance used. *Weber* gives the loss as from 1·3 to 2·3 per cent. My own experiments (No. 35) confirm this statement and point out the circumstances under which the loss is the least considerable (compare also § 106). By long continued fusion, in conjunction with carbonate of potassa and soda, pyrophosphate of magnesia is completely decomposed, the phosphoric acid being reconverted into the tribasic state. If, therefore, we treat the fused mass with hydrochloric acid, and add water and ammonia, and heat the precipitate to redness, we re-obtain the whole quantity of the salt used.

COMPOSITION.

$2MgO$ =	500·38 =	40·00 =	35·94
PO_5 =	892·04 =	71·36 =	64·06
	1392·42 =	111·36 =	100·00

d. Pure magnesia is a white, light, loose powder. It dissolves in 55368 parts of cold, and in the same proportion of boiling water. (Experiment No. 36.) Its aqueous solution has a very slightly alkaline reaction. Magnesia dissolves in hydrochloric acid, and in other acids, without evolution of gas. Exposed to the air, it slowly absorbs carbonic acid and water. Magnesia is highly infusible, remaining unaltered at a strong red heat, and fusing superficially only at the very highest temperature.

COMPOSITION.

Mg	= 150·19	= 12	= 60·03
O	= 100·00	= 8	= 39·97
	250·19	= 20	= 100·00

BASES OF THE THIRD GROUP.

§ 54.

1. ALUMINA.

Alumina is usually precipitated as HYDRATE OF ALUMINA, and uniformly weighed in the pure state.

a. Hydrate of alumina, recently precipitated, is a gelatinous mass which invariably retains a minute proportion of the acid with which the alumina was combined previously to its precipitation, as well as of the alkali which has served as the precipitant; it is freed with difficulty from these admixtures by repeated washing.

Hydrate of alumina is insoluble in pure water; but readily soluble in solutions of soda and potassa, and in acids; it is sparingly soluble in caustic ammonia, and altogether insoluble in carbonate of ammonia; presence of ammoniacal salts renders it almost insoluble also in caustic ammonia. (Experiment No. 37.) The correctness of this statement of mine in the first edition of the present work, has been amply confirmed since by *Malaguti* and *Durocher* (Ann. de Chim. et de Phys., 3, Ser. 17, 421 ;) and also by experiments made by my assistant, *Mr. J. Fuchs*. The former chemists (*Malaguti* and *Durocher*) state that when a solution of alumina is precipitated with sulphide of ammonium, the fluid may be filtered off five minutes after without a trace of alumina in it. *Fuchs* did not find this to be the case. (Experiment No. 38.)

Hydrate of alumina shrinks considerably upon desiccation, and when dry, becomes a hard, transparent, yellowish, or a white earthy mass. When heated to redness it loses its water, and this loss of water is frequently attended with slight decrepitation, and invaribly with considerable diminution of bulk.

b. Alumina, prepared by heating the hydrate to a moderate degree of redness, is a loose and soft mass; but upon the application of a very intense degree of redness, it concretes into small hard lumps. At the most intense degree of white heat, it fuses to a colorless glass. Ignited alumina is dissolved by acids with very great difficulty. Placed upon moist reddened litmus paper it does not turn the color of that paper blue. Upon igniting alumina, with chloride of ammonium, chloride of aluminium escapes.

COMPOSITION.

2 Al	= 340·84	= 27·26	= 53·19
3 O	= 300·00	= 24·00	= 46·81
	640·84	= 51·26	= 100·00

§ 55.

2. SESQUIOXIDE OF CHROMIUM.

Sesquioxide of chromium is usually precipitated as HYDRATED SESQUIOXIDE OF CHROMIUM, and uniformly weighed in the pure state.

a. Hydrated sesquioxide of chromium, recently precipitated, is a greenish-gray gelatinous mass, insoluble in water; it dissolves readily at a low temperature, in solutions of potassa, or of soda, imparting a dark green tint to the fluid; it dissolves also, at a low temperature, but rather sparingly, in solution of ammonia, imparting to the fluid a bright red tint. In acids it dissolves readily, imparting a dark green tint to the fluid. Presence of chloride of ammonium exercises no influence upon the greater or less solubility of hydrated sesquioxide of chromium in ammonia. Boiling effects the separation of the sesquioxide from its solutions in potassa, soda, or ammonia. (Experiment No. 39.) Dried hydrated sesquioxide of chromium is a greenish blue powder; it loses its water of hydration at a gentle red heat.

b. Sesquioxide of chromium, produced by heating the hydrate to dull redness, is a dark green powder; upon the application of a higher degree of heat, it assumes a lighter tint, but suffers no diminution of weight; the transition from the darker to the lighter tint is marked by a vivid incandescence of the powder. The feebly ignited sesquioxide is difficultly soluble in hydrochloric acid, and the strongly ignited sesquioxide is altogether insoluble in that acid. Mixed with chloride of ammonium, and exposed to a red heat, sesquioxide of chromium remains unaltered.

COMPOSITION.

2 Cr	= 669·40	= 53·56	= 69·05
3 O	= 300·00	= 24·00	= 30·95
	969·40	= 77·56	= 100·00

BASES OF THE FOURTH GROUP.

§ 56.

1. OXIDE OF ZINC.

The oxide of zinc is uniformly weighed in that form; but it is usually precipitated as BASIC CARBONATE OF ZINC, or as SULPHIDE OF ZINC.

a. Basic carbonate of zinc, recently precipitated, is a white, flocculent

mass, nearly insoluble in water—(one part requiring 44600 parts, Experiment No. 40)—but readily soluble in solutions of potassa, ammonia, carbonate of ammonia, and in acids. When a neutral solution of zinc is precipitated with carbonate of potassa (or carbonate of soda), carbonic acid is evolved, under all circumstances, since the precipitate formed is not Zn O, CO_2, but consists of a mixture of $2(ZnO, CO_2) + 3(ZnO, HO)$ with carbonate of zinc and potassa. (Potassio-carbonate of zinc.) Owing to the presence of this carbonic acid, as well as to the circumstance that *the carbonate of zinc and potassa* is not insoluble in water, part of the oxide of zinc remains in solution; the cold filtered fluid yields, therefore, a precipitate when acted upon by sulphide of ammonium.

If, however, the solution of zinc be heated to boiling, previously to the addition of the carbonate of potassa, and then kept boiling for some time after (which will prevent the formation of *carbonate of zinc and potassa*, and will, moreover, cause the expulsion of every trace of free carbonic acid from the fluid), the precipitation of the zinc will be complete, in so far that the filtrate will not be rendered turbid by the addition of sulphide of ammonium; still, if the filtrate, mixed with sulphide of ammonium, be allowed to stand at rest for many hours, minute and almost imponderable flakes of sulphide of zinc will separate from the fluid. The precipitate of carbonate of zinc, obtained in the manner just now described, may be completely freed from all admixture of potassa by washing with hot water. If ammoniacal salts be present, every trace of ammonia must be expelled first, before the complete * precipitation of the zinc can be achieved. If the solution of a zinc salt is mixed with carbonate of potassa in excess, and the mixture is evaporated to dryness, at a gentle heat, and the residue treated with cold water, a perceptible proportion of the zinc is obtained in solution as *carbonate of zinc and potassa;* but if the mixture is evaporated to dryness, at boiling heat, and the residue is treated with hot water, the whole of the zinc, with the exception of an extremely minute proportion, as we have already had occasion to observe, is obtained as carbonate of zinc.

The dried basic carbonate of zinc is a pure white, loose powder; exposure to a red heat converts it into oxide of zinc.

b. Oxide of zinc, produced from the carbonate by the application of a red heat, is a white light powder, with a slightly yellow tint in it. When heated, it acquires a yellow color, which disappears again on cooling. Upon exposing oxide of zinc, mixed with charcoal, to a red heat, carbonic oxide gas and zinc fumes escape. Oxide of zinc is insoluble in water. Placed on moist turmeric paper, it does not change

* That is, complete within the limits indicated just now, so that sulphide of ammonium occasions no turbidity in the filtrate, although it may produce subsequently and after long standing some slight and almost imponderable flakes of sulphide of zinc.

the color of that paper to brown. In acids, oxide of zinc dissolves readily, and without evolution of gas. Heated to redness, in conjunction with chloride of ammonium, it is decomposed, and fused chloride of zinc obtained, which volatilizes with very great difficulty, if the air is excluded; but readily and completely, if free access is given to the air.

COMPOSITION.

Zn	= 406·59	= 32·53	= 80·26
O	= 100·00	= 8·00	= 19·74
	506·59	= 40·53	= 100·00

c. Sulphide of zinc, recently precipitated, is a white loose mass (ZnS, HO), insoluble in water, in caustic alkalies, carbonated alkalies, and alkaline sulphides. It dissolves readily and completely in hydrochloric acid and in nitric acid, but very sparingly only in acetic acid. When dried, the precipitated sulphide of zinc is a white powder; at 212° it loses half, and at a red heat the whole of its water. During the latter process some sulphuretted hydrogen escapes, and the remaining sulphide of zinc contains an admixture of oxide of zinc.

§ 57.

2. PROTOXIDE OF MANGANESE.

Manganese is weighed either as PROTOSESQUIOXIDE OF MANGANESE (red oxide of manganese) [$MnO + Mn_2O_3) = Mn_3O_4$], or as SULPHATE OF PROTOXIDE OF MANGANESE. For the purpose of converting it into the first form, it is precipitated as CARBONATE OF PROTOXIDE OF MANGANESE, HYDRATED PROTOXIDE OF MANGANESE, or SULPHIDE OF MANGANESE.

a. Carbonate of protoxide of manganese, recently precipitated, forms a white, flocculent mass, nearly insoluble in pure water, but somewhat more soluble in water impregnated with carbonic acid. Presence of carbonate of soda or potassa does not increase its solubility. Recently precipitated carbonate of protoxide of manganese dissolves pretty readily in solution of chloride of ammonium; it is owing to this property that a solution of protoxide of manganese cannot be completely precipitated by carbonate of potassa or soda, in presence of chloride of ammonium (or of any other ammoniacal salt), until the latter is completely decomposed. If the precipitate, while still moist, is exposed to the air, or washed with water impregnated with air, it slowly assumes a dirty brownish-white color, part of it becoming converted into hydrated sesquioxide of manganese. If the precipitate is dried, removed from the contact of air, it forms a delicate white powder, persistent in the air [$2(MnO, CO_2) + 1$ aq.]; but when dried, with free access of air, the powder is of a more or less dirty white, or brownish color. When heated to redness, with access of air, this powder first turns black, and changes subsequently to brown protosesquioxide of manganese.

b. Hydrated protoxide of manganese, recently prepared, forms a white, flocculent precipitate, insoluble in water and in the alkalies, but soluble in chloride of ammonium; this precipitate immediately absorbs oxygen from the air, and turns brown, owing to the formation of hydrated sesquioxide of manganese. On drying it in the air, a brown powder (hydrated sesquioxide of manganese) is obtained; when heated to intense redness, with free access of air, this hydrated sesquioxide is converted into protosesquioxide of manganese.

c. Sulphide of manganese, prepared in the humid way, forms a flesh-colored precipitate; it is insoluble in water and in solutions of the alkalies. It is not altogether insoluble in the colorless hydrosulphate of sulphide of ammonium, but absolutely so in the yellow hydrosulphate, which contains pentasulphide of ammonium. Presence of chloride of ammonium does not increase its solubility. In dilute acids (hydrochloric acid, sulphuric acid, &c.,) it dissolves with evolution of sulphuretted hydrogen. When the precipitate, while still moist, is exposed to the air, is washed with water impregnated with air, its fleshy tint changes to brown, hydrated sesquioxide of manganese being formed, together with a small portion of sulphate of protoxide of manganese. To guard against this, some yellow sulphide of ammonium must be added to the washing water.

*d. Protosesquioxide of manganese** (red oxide of manganese), artificially produced, is a reddish-brown powder. Whenever it is exposed to the action of heat, it assumes a black tint, but its weight remains unaltered. It is insoluble in water, and does not alter vegetable colors. Heated to redness, in conjunction with chloride of ammonium, it is converted into protochloride of manganese.

COMPOSITION.

3 Mn	= 1034·05	= 82·71	= 72·10
4 O	= 400·00	= 32·00	= 27·90
	1434·05	= 114·71	= 100·00

e Anhydrous sulphate of protoxide of manganese, produced by exposing the crystallized salt to the action of heat, is a white, friable mass, readily soluble in water. It resists the protracted application of a faint red heat; but upon exposure to a more intense degree of red heat it suffers more or less complete decomposition—oxygen, sulphurous acid, and anhydrous sulphuric acid being evolved, and red oxide of manganese remains behind.

COMPOSITION.

MnO	= 444·68	= 35·57	= 47·07
SO_3	= 500·00	= 40·00	= 52·93
	944·68	= 75·57	= 100·00

* All the oxides of manganese finally change to the red oxide, upon ignition with free access of air.

§ 58.

3. PROTOXIDE OF NICKEL.

Nickel is precipitated as HYDRATED PROTOXIDE OF NICKEL, and as SULPHIDE OF NICKEL. It is uniformly weighed in the form of PROTOXIDE.

a. Hydrated protoxide of nickel forms an apple-green precipitate, almost absolutely insoluble in water, but soluble in solution of ammonia and of carbonate of ammonia. From these solutions it is completely precipitated again by potassa added in excess; application of heat promotes the precipitation. It is unalterable in the air; exposure to a red heat converts it into protoxide of nickel.

b. Protoxide of nickel is a dirty greyish-green powder, insoluble in water, but readily soluble in hydrochloric acid. It does not affect vegetable colors. It suffers no variation of weight upon ignition with free access of air. Mixed with chloride of ammonium and exposed to a red heat, it is reduced to metallic nickel.

COMPOSITION.

Ni	= 369·33	= 29·55	= 78·69
O	= 100·00	= 8·00	= 21·31
	469·33	= 37·55	= 100·00

c. Hydrated sulphide of nickel, prepared in the humid way, forms a black precipitate insoluble in water. It is insoluble in an excess of sulphide of ammonium, perfectly saturated with sulphuretted hydrogen; but it is slightly soluble in ammonia, and still more so in ammonia not fully saturated with sulphuretted hydrogen. When these solutions, which are of a more or less brown color, are exposed to the air, the sulphide of nickel, contained in them, precipitates gradually. (*Vide* Experiments sub. No. 41). If sulphide of nickel, in a moist state, is exposed to the air, it oxidises slowly, and is converted into sulphate of protoxide of nickel. It is very sparingly soluble in acetic acid, but somewhat more so in hydrochloric acid. It is more readily soluble still in nitric acid, and most so in nitrohydrochloric acid. It loses its water upon the application of a red heat; when ignited in the air, it is transformed into a basic compound of sesquioxide of nickel with sulphuric acid.

§ 59.

4. PROTOXIDE OF COBALT.

Cobalt is weighed in the PURE METALLIC state; or as PROTOSESQUIOXIDE OF COBALT, or as SULPHATE OF PROTOXIDE OF COBALT. Besides the properties of these substances, we have to study here also those of HYDRATED PROTOXIDE OF COBALT, and of SULPHIDE OF COBALT.

a. Hydrated protoxide of cobalt.—Upon precipating a solution of pro-

toxide of cobalt with potassa, a blue precipitate (a basic salt) is formed at first, which, upon boiling with potassa in excess, removed from the contact of air, changes to pale red hydrated protoxide of cobalt; if, on the contrary, this process is conducted with free access of air, the precipitate becomes discolored, part of the hydrated protoxide being converted into hydrated sesquioxide. But the hydrated protoxide of cobalt, prepared in this way, retains always a certain quantity of the acid: and, even after the most thorough washing with hot water, still a considerable amount of the alkaline precipitant. (*Fremy*, J. pr. Chem. 57, 81.) The result of my own experiments fully confirm this statement of Fremy. (Experiment No. 42). The metallic cobalt, therefore, which we obtain upon the ignition of the precipitate in hydrogen gas, manifests a strongly alkaline reaction when placed on moist turmeric paper. This unavoidable alkaline admixture renders the oxide, or metal obtained in this way, unfit for the quantitative estimation of cobalt.

Hydrated protoxide of cobalt is insoluble in water, and likewise in potassa; it dissolves in solution of ammoniacal salts; when dried in the air, it absorbs oxygen, and assumes a brownish color.

b. When pure chloride of cobalt, or nitrate of protoxide of cobalt, is heated to redness in a current of hydrogen gas, pure *metallic cobalt* is obtained, in the form of a grayish black metallic powder, which is attracted by the magnet, and is more difficultly fusible than gold. If the reduction has been effected at a faint heat, the finely divided metal oxidises in the air, to protosesquioxide of cobalt, which is not the case if the reduction has been effected at an intense red heat. Cobalt does not decompose water, neither at the common temperature, nor upon ebullition—except sulphuric acid be present, in which case decomposition will ensue. Heated in conjunction with hydrated sulphuric acid, it forms sulphate of protoxide of cobalt, with evolution of sulphurous acid. In nitric acid it dissolves readily to the nitrate of protoxide of cobalt.

c. Upon ignition of the nitrate of protoxide of cobalt, a black residue is left of constant composition; this residue consists of protosesquioxide of *cobalt*, a compound corresponding to the protosesquioxide of iron, and which, accordingly, has the formula $CoO + Co_2O_3$, or Co_3O_4 (*Rammelsberg, Fremy*). This oxide is insoluble in water; in hot hydrochloric acid it dissolves to protochloride of cobalt, with evolution of chlorine. When heated to redness, in conjunction with chloride of ammonium, it suffers reduction to metallic cobalt.

COMPOSITION.

Co_3	= 1105·95	= 88·47	= 73·42
O_4	= 400·00	= 32·00	= 26·58
	1505·95	= 120·47	= 100·00

d. *Sulphide of cobalt*, produced in the humid way, forms a black pre-

cipitate, insoluble in water, in alkalies, and in alkaline sulphides. It is but sparingly soluble in acetic acid and in dilute mineral acids, but more readily so in concentrated mineral acids, and most readily in hot nitrohydrochloric acid. When sulphide of cobalt, in a moist state, is exposed to the air, it slowly absorbs oxygen, and is converted into sulphate of protoxide of cobalt.

e. Sulphate of protoxide of cobalt crystallizes, in combination with 7 aq., slowly in oblique rhombic prisms, of a fine red color. The crystals yield the whole of the 7 equivalents of water, at a moderate heat, and are converted into a rose-colored anhydrous salt, which bears the application of a gentle red heat without losing acid. It dissolves rather difficultly in cold, but more readily in hot water. Ignition in a current of hydrogen gas fails to effect its reduction.

COMPOSITION.

38·0	48·72	CoO	= 468·65 = 37·49 =	48·39
40.0	51.28	SO_3	= 500·00 = 40·00 =	51·61
78.0	100.00		968·65 = 77·49 =	100·00

§ 60.

5. PROTOXIDE OF IRON; and 6, SESQUIOXIDE OF IRON.

Iron is uniformly weighed in the form of SESQUIOXIDE. Besides the sesquioxide, we have to study the HYDRATED SESQUIOXIDE OF IRON, SULPHIDE OF IRON, and SUCCINATE OF SESQUIOXIDE OF IRON.

a. Hydrated sesquioxide of iron, recently prepared, is a reddish-brown precipitate, insoluble in water, in the alkalies, and in ammoniacal salts, but readily soluble in acids; the process of drying reduces the bulk of this precipitate amazingly. When dry, it presents the appearance of a brown hard mass, the fracture of which exhibits a shining appearance similar to shell. In the precipitation of salts of sesquioxide of iron by the alkalies, a portion of the precipitant alkali is invariably carried down in combination with the sesquioxide of iron,—on which account ammonia alone can properly be used in analysis, as a precipitant for salts of sesquioxide of iron.

b. The hydrated sesquioxide of iron is, upon ignition, converted into the *anhydrous sesquioxide.* If the hydrated sesquioxide has not been most carefully and thoroughly dried, and the small solid lumps, though outside dry, retain still a portion of water confined within, the sudden conversion of that water into steam, upon the application of a red heat, will cause particles of the sesquioxide to fly about, and may thus lead to loss of substance. Pure sesquioxide of iron, when placed upon moist reddened litmus paper, does not color the latter blue. It dissolves slowly in dilute, but more rapidly in concentrated hydrochloric acid; the application of a moderate degree of heat promotes this solution more than that of boiling heat.

Its weight does not vary, upon ignition in the air; when ignited together with chloride of ammonium, sesquichloride of iron escapes. Ignition in conjunction with charcoal, shielded from the access of air, reduces it more or less.

COMPOSITION.

2 Fe =	700·00	= ·56 =	70·00
3 O =	300·00	= ·24 =	30·00
	1000·00	= ·80 =	100·00

c. Sulphide of iron, produced in the humid way, forms a black precipitate, slightly soluble in aërated water, (with decomposition), insoluble in water containing alkaline sulphides, but readily soluble in mineral acids, both concentrated and dilute. When precipitated from a highly dilute solution, it remains suspended a long time, imparting a blackish green tint to the fluid; it subsides, however, completely, after the lapse of some time. When moistened and exposed to the air, it absorbs oxygen, and assumes a brown tint, hydrated sesquioxide of iron and sulphate of protoxide of iron being formed.

d. When a neutral solution of a salt of sesquioxide of iron is mixed with a neutral solution of a succinate of ammonia, a cinnamon-colored precipitate of a brighter or darker hue is formed; this is *succinate of sesquioxide of iron* ($Fe_2O_3, \overline{S}_2$). It results from the nature of this precipitate, that its formation must set free an equivalent of acid (of succinic acid, if the succinate of ammonia is used in excess); *e. g.*, $Fe_2O_3, 3\,SO_3 + 3\,NH_4O, \overline{S} = Fe_2O_3, \overline{S}_2 + 3\,(NH_4O, SO_3) + \overline{S}$. This free succinic acid does not exercise a clearly perceptible solvent action upon the precipitate, in a cold and highly dilute solution, but it redissolves the precipitate more copiously in a hot solution. The precipitate must therefore be filtered cold, if we want to guard against its re-solution. Formerly the precipitate was erroneously supposed to consist of a neutral salt, decomposable by hot water into an insoluble basic and soluble acid compound. Succinate of sesquioxide of iron is insoluble in cold, and but sparingly soluble in hot water. It dissolves readily in mineral acids. Ammonia deprives it of the greater portion of its acid, leaving compounds similar to the hydrated sesquioxide of iron, and which contain from nine to fifteen equivalents of sesquioxide of iron to one equivalent of succinic acid. (Döpping.) Hot ammonia withdraws the acid more completely than cold ammonia.

BASES OF THE FIFTH GROUP.

§ 61.

1. OXIDE OF SILVER.

Silver may be weighed in the METALLIC state, or as CHLORIDE OF SILVER, SULPHIDE OF SILVER, and CYANIDE OF SILVER.

a. Metallic silver, obtained by the ignition of salts of silver with organic acids, &c., is a light, white, glittering mass of metallic lustre; but, when obtained by reducing chloride of silver, &c., in the humid way, by the agency of zinc, it forms a dull gray powder. It is not fusible over a Berzelius' lamp. Ignition leaves its weight unaltered. It dissolves readily and completely in dilute nitric acid.

b. Chloride of silver, recently precipitated, forms a white curdy mass, which, upon drying, assumes a pulverulent character. It is wholly insoluble in water and in nitric acid, and but very sparingly soluble in concentrated hydrochloric acid, from which solution it is almost completely thrown down again by addition of water. It is slightly soluble also in solutions (more particularly concentrated solutions), of chloride of ammonium (but of no other ammoniacal salt), chloride of sodium, and chloride of potassium. It dissolves readily in caustic ammonia. Exposed to the light, it acquires first a violet, finally a black tint, owing to the escape of chlorine. This modification of the chloride of silver is, however, so very superficial only, that the loss of chlorine cannot be noted, even on a very delicate balance. When heated, chloride of silver acquires a yellow tint; at about 500° it fuses to a transparent yellow liquid, which, after cooling, presents the appearance of a colorless or slightly yellowish mass. Exposed to a very intense degree of red heat, chloride of silver volatilizes unaltered. When fused in a current of chlorine gas, it absorbs a little of the latter, but yields it again completely upon cooling. Ignition in conjunction with charcoal fails to effect its reduction to the metallic state; but it may be readily reduced to metallic silver, by igniting it in a current of carbonic oxide gas.

COMPOSITION.

Ag	= 1349·66	= 107·97	= 75·28
Cl	= 443·28	= 35·46	= 24·72
	1792·94	= 143·43	= 100·00

c. Sulphide of silver, prepared in the humid way, forms a black precipitate, insoluble in water, dilute acids, alkalies, and alkaline sulphides. This precipitate is unalterable in the air, and may be dried at 212° without suffering decomposition. It dissolves in concentrated nitric acid, with separation of sulphur.

COMPOSITION.

Ag	= 1349·66	= 107·97	= 87·07
S	= 200·00	= 16·00	= 12·93
	1549·66	= 123·97	= 100·00

d. Cyanide of silver, recently precipitated, forms a white curdy mass, insoluble in water and dilute nitric acid, soluble in cyanide of potassium, and also in ammonia; exposure to the light fails to impart the slightest shade of black to it; it may be dried at 212°, without suffering decomposition. Upon ignition, it is decomposed into cyanogen gas, which escapes, and metallic silver, which remains behind, mixed with a little paracyanide of silver.

COMPOSITION.

Ag	= 1349·66	= 107·97	= 80·60
C_2N	= 325·06	= 26·00	= 19·40
	1674·72	= 133·97	= 100·00

§ 62.

2. PROTOXIDE OF LEAD.

Lead is weighed as PROTOXIDE, SULPHATE, CHROMATE, CHLORIDE, and SULPHIDE OF LEAD. Besides these compounds, we have likewise to study here the CARBONATE and the OXALATE OF LEAD.

a. Neutral carbonate of lead forms a heavy white pulverulent precipitate. It is but very slightly soluble in perfectly pure water (one part requiring 50550 parts of pure water; (vide Experiment No. 43 *a*); but it dissolves somewhat more readily in water containing ammonia and its salts. (Experiments No. 43 *b* and *c*.). It dissolves likewise somewhat more readily in water impregnated with carbonic acid, than in pure water. It loses its carbonic acid when ignited.

b. Oxalate of lead is a white powder, very sparingly soluble in water. The presence of ammonia salts slightly increases its solubility. (Experiment No. 44.) When heated in close vessels, it leaves suboxide of lead behind, but when heated, with access of air, yellow oxide (protoxide).

c. Protoxide of lead, produced by igniting the carbonate or oxalate of this metal, is a lemon-yellow powder, inclining sometimes to a reddish yellow, or to a pale yellow. Whenever this yellow protoxide of lead is heated, it assumes a brownish red color, without the slightest variation in its weight. It fuses at an intense red heat. Ignition in contact with charcoal reduces it. When exposed to a white heat, it rises in vapor. Placed upon moist, reddened litmus-paper, it changes the color of this paper to blue. When exposed to the air, it slowly absorbs carbonic acid Mixed with chloride of ammonium and ignited, it is converted into chloride of lead.

COMPOSITION.

Pb	= 1294·64	= 103·57	= 92·83
O	= 100·00	= 8·00	= 7·17
	1394·64	= 111·57	= 100·00

d. Sulphate of lead forms a heavy, white powder. It dissolves, at the common temperature, in 22800 parts of pure water (Experiment No. 45); it is less soluble still in water containing sulphuric acid (one part requiring 36500 parts—Experiment No 46); it is far more readily soluble in water containing ammoniacal salts; from this solution it may be precipitated again by adding sulphuric acid in excess (Experiment No. 47). It is nearly altogether insoluble in alcohol and spirits of wine. It dissolves in concentrated hydrochloric acid, upon heating. In nitric acid it dissolves the more readily, the more concentrated and hotter the acid; water fails to precipitate it from its solution in nitric acid; but the addition of a copious amount of dilute sulphuric acid causes its precipitation from this solution. The more nitric acid the solution contains, the more sulphuric acid is required to throw down the sulphate of lead from it. Sulphate of lead dissolves sparingly in concentrated sulphuric acid, and the dissolved portion precipitates again upon diluting the acid with water (and more completely still, upon the addition of alcohol). It dissolves readily in hot solutions of potassa or soda. It is unalterable in the air, and at a gentle red heat; when exposed to a higher degree of heat, it fuses without suffering decomposition. (Experiment No 48.) When sulphate of lead is ignited in conjunction with charcoal, sulphide of lead is formed at first, and the sulphur of this reduces the sulphuric acid of the undecomposed portion of the sulphate, to sulphurous acid, giving thus, on both sides, rise to the separation of metallic lead.

COMPOSITION.

PbO	= 1394·64	= 111·57	= 73·56
SO_3	= 500·00	40·00	= 26·44
	1894·64	= 151·57	= 100·00

e. Chloride of lead appears either in the form of small brilliant crystalline needles, or as a white powder; it dissolves, at the common temperature, in 135 parts of water; and is still more soluble in hot water. It dissolves less readily in water mixed with nitric acid, one part requiring 1636 parts, (*Bishof*); it dissolves copiously in concentrated hydrochloric acid, from which solution it may be precipitated again by the addition of water. It is extremely sparingly soluble in spirits of wine of from 70 to 80 per cent, and altogether insoluble in absolute alcohol. It is unalterable in the air. It fuses at a temperature below red heat, without suffering any diminution of weight. When exposed to a higher temperature, with access of air, it volatilizes slowly, with partial decomposition: chlorine gas escaping, and a mixture of protoxide and chloride of lead remaining behind.

COMPOSITION.

Pb	= 1294·64	= 103·57	= 74·49
Cl	= 443·28	= 35·46	= 25·51
	1737·92	= 139·03	= 100·00

f. Sulphide of lead, prepared in the humid way, is a black precipitate, insoluble in water, dilute acids, alkalies, and alkaline sulphides. This precipitate is unalterable in the air, and may be dried at 212° without suffering decomposition. It dissolves in concentrated hot hydrochloric acid, with evolution of sulphuretted hydrogen. In moderately concentrated nitric acid, sulphide of lead dissolves, upon the application of heat, with separation of sulphur,—if the acid is rather concentrated, a small portion of sulphate of lead is also formed. Fuming nitric acid acts energetically upon sulphide of lead, and converts it into sulphate of lead, without separation of sulphur. (Experiment No. 49.)

COMPOSITION.

Pb	= 1294·64	= 103·57	= 86·61
S	= 200·00	= 16·00	= 13·39
	1494·64	= 119·57	= 100·00

For the composition and properties of *chromate of lead*, see *chromic acid*, § 72.

§ 63.

3. SUBOXIDE OF MERCURY; and 4. OXIDE OF MERCURY.

Mercury is weighed either in the METALLIC state, or as SUBCHLORIDE, or as SULPHIDE OF MERCURY, or occasionally also as OXIDE.

a. Metallic mercury is liquid at the common temperature; it has a tin-white color. When pure, it presents a perfectly bright surface. It is unalterable in the air at the common temperature. It boils at 680°. Mercury emits a sensible vapor at from between 68° and 80°; but at this temperature it volatilizes very slowly. Upon long boiling with water, a small portion of mercury volatilizes, and traces of it escape in conjunction with the aqueous vapor, whilst a very minute proportion remains suspended in the water. (Experiment No. 50.) This suspended portion of mercury subsides completely after long standing at rest. When metallic mercury is precipitated from a fluid, in a very minutely divided form, the small globules will readily unite into a large one, if the mercury be perfectly pure; but if even the slightest trace of extraneous matter, such as fat, &c., should adhere to the mercury, the union of the minute globules of this metal will be prevented. Mer-

cury does not dissolve in hydrochloric acid, not even in concentrated; it is barely soluble in dilute cold sulphuric acid, but dissolves readily in nitric acid, and in concentrated boiling sulphuric acid.

b. Subchloride of mercury, prepared in the humid way, is a heavy white powder. It is almost absolutely insoluble in cold water; in boiling water it is gradually decomposed into chlorine and mercury; upon continued boiling, the residue acquires a gray color. Highly dilute hydrochloric acid fails to dissolve the subchloride of mercury, at the common temperature, but dissolves it slowly at a higher temperature; upon ebullition, with access of air, the whole of the subchloride is gradually dissolved by the dilute acid: the solution contains chloride of mercury ($Hg_2Cl + HCl + O = 2HgCl + HO$). Subchloride of mercury, when acted upon by boiling concentrated hydrochloric acid, is rather speedily decomposed into mercury, which remains undissolved, and chloride of mercury, which dissolves in the menstruum. Boiling nitric acid dissolves subchloride of mercury and converts it into chloride and nitrate of mercury. Chlorine water and nitrohydrochloric acid transforms it into chloride, even at a low temperature. Solutions of chloride of ammonium, chloride of sodium, and chloride of potassium, decompose subchloride of mercury into metallic mercury and chloride of mercury, which latter dissolves in the menstruum; at a low temperature, this decomposition is confined to a small portion of the subchloride, but the application of heat promotes the decomposing action of the alkaline solutions. Subchloride of mercury does not affect vegetable colors; it is unalterable in the air, and may be dried at 212° without suffering any diminution of weight; when exposed to a higher degree of heat, though still below redness, it volatilizes completely, without previous fusion.

COMPOSITION.

2 Hg	= 2501·20	= 200·10	= 84·95
Cl	443·28	= 35·46	= 15·05
	2944·48	= 235·56	= 100·00

c. Sulphide of mercury, prepared in the humid way, is a black powder, insoluble in water. Dilute hydrochloric acid, and dilute nitric acid, fail to dissolve it, and it remains insoluble even in boiling hydrochloric acid; it is only very slightly soluble in hot concentrated nitric acid, but it is dissolved by nitrohydrochloric acid. In solution of potassa, it is insoluble, even though the solution be boiling; but it dissolves readily in sulphide of potassium. (Experiment No. 51.) Sulphide of ammonium and cyanide of potassium fail to dissolve it. In the air it is unalterable, even in the moist state, and so it remains at 212°. When exposed to a higher temperature, it sublimes completely and unaltered.

COMPOSITION.

Hg	= 1250·6	= 100·05	= 86·21
S	= 200·0	= 16·00	= 13·79
	1450·6	= 116·05	= 100·00

d. Oxide of mercury is a crystalline brick-colored powder, which, when it is exposed to the action of heat, changes to the color of cinnabar, and subsequently to a violet black tint. It bears a tolerably strong heat without suffering decomposition; but, when heated to incipient redness, it is decomposed into mercury and oxygen; perfectly pure oxide of mercury leaves no residue, upon continued exposure to a red heat.

COMPOSITION.

Hg	= 1250·6	= 100·05	= 92·59
O	= 100·0	= 8·00	= 7·41
	1350·6	= 108·05	= 100·00

§ 64.

5. OXIDE OF COPPER.

Copper is usually weighed in the form of OXIDE. Besides the oxide, we have to examine here SULPHIDE OF COPPER, METALLIC COPPER, and SUBOXIDE OF COPPER.

a. Oxide of copper. When a dilute, cold, aqueous solution of a salt of copper is mixed with solution of potassa in excess, a light blue precipitate of hydrated oxide of copper is formed; this precipitate is very liable to carry down with it a little of the precipitant, which it is found difficult to wash out. If the precipitate be left in the fluid from which it has been precipitated, it will, even at a temperature of from 68° to 80°, gradually acquire a rusty black tint, yielding up nearly the whole of its water of hydration.

This transformation is immediate upon heating the fluid nearly to boiling. The fluid filtered off from the black precipitate is free from copper. If the solutions of the salt of copper, and of potassa, are mixed in a concentrated state, the fluid, in addition to the formation of the blue precipitate, will acquire a blue color, owing to a portion of very minutely divided hydrated oxide remaining suspended in it. From a fluid of this description, even protracted boiling will fail to precipitate all the copper which it contains; after previous dilution with water, however, the desired object is readily attained. If the solution of a salt of copper happens to contain non-volatile organic substances in admixture, potassa in excess will, even upon boiling, fail to precipitate the whole of the copper as oxide. The oxide of copper precipitated with potassa from hot dilute solutions of

salts of copper, retains a portion of the precipitant, with great force; it may, however, be completely freed from this by washing with boiling water. Oxide of copper, prepared by the ignition of carbonate or nitrate of copper, is a brownish black, or black powder, the weight of which remains unalterable, upon strong ignition over the spirit-lamp. (Experiment No. 52.) The same powder is produced by igniting the oxide of copper prepared in the humid way. But if the oxide of copper, either prepared in the dry or humid way, is exposed to a heat approaching the fusing point of metallic copper, it fuses, yields up oxygen, and becomes converted into Cu_5O_3. (*Favre* and *Maumené*.) It is readily reduced by ignition in contact with charcoal; heated in the air, the reduced metallic copper re-oxidizes. Oxide of copper, in contact with the atmosphere, absorbs water; oxide that has been but slightly ignited, absorbs the water more rapidly than such as has been strongly ignited. (Experiment No. 53.) Oxide of copper, is nearly insoluble in water, but it dissolves readily in hydrochloric acid, nitric acid, &c.; it dissolves less readily in ammonia. It does not affect vegetable colors.

COMPOSITION.

Cu	= 396·00	= 31·68	= 79·84
O	= 100·00	= 8·00	= 20·16
	496·00	= 39·68	= 100·00

b. *Sulphide of copper*, prepared in the humid way, is a brownish black, or black precipitate, insoluble in water; when this precipitate, in a moist state, is exposed to the air, it acquires a greenish tint, and the property of reddening litmus paper, and becomes gradually altogether converted into sulphate of copper. Sulphide of copper dissolves readily in boiling nitric acid, with separation of sulphur. Hydrochloric acid dissolves it with difficulty. It does not dissolve in solutions of potassa and of sulphide of potassium, even if these solutions be boiling; but it dissolves perceptibly in sulphide of ammonium, and readily in cyanide of potassium.

c. *Copper* in its pure state, is a metal of a peculiar reddish-brown color. It requires a white heat for its fusion. Exposure to dry, or moist air, free from carbonic acid, leaves it unaltered; but upon exposure to moist air impregnated with carbonic acid, it becomes gradually tarnished and coated with a film, first of a dark gray, finally of a blueish green color. Upon ignition in the air, a layer of black oxide forms on its surface. Hydrochloric acid fails to dissolve it, even upon boiling, if the air is excluded; but with free access of air, it dissolves it slowly. Copper dissolves readily in nitric acid. In ammonia it dissolves slowly if free access is given to the air; but it remains insoluble in that menstruum, if the air is excluded. Metallic copper brought into contact with solution of chloride of copper in

hydrochloric acid, or with solution of oxide of copper in ammonia, reduces the chloride to subchloride, and the black oxide to red oxide (suboxide), one equivalent of metal being dissolved for every one equivalent of chloride, or oxide.

d. When the blue solution which is obtained upon the addition of paratartaric acid, and subsequently of a solution of soda in excess, to solution of oxide of copper, is mixed with solution of grape sugar, or sugar of milk, and the mixture is heated, there speedily forms an orange-yellow precipitate of hydrated suboxide of copper, which contains the whole of the copper originally present in the solution, and after a short time, more particularly upon the application of a stronger heat, turns red, owing to the conversion of the hydrate into simple suboxide (Cu_2O.) The precipitate, which is insoluble in water, retains a portion of alkali with great force. When acted upon with dilute sulphuric acid, it yields sulphate of copper, which dissolves in the menstruum, and metallic copper, which separates.

§ 65.

6. TEROXIDE OF BISMUTH.

Bismuth is invariably weighed in the form of teroxide. Besides this compound, we have to study here the BASIC CARBONATE and the TERSULPHIDE OF BISMUTH.

a. Teroxide of bismuth, prepared by igniting the carbonate, or nitrate of that metal, is a pale lemon-yellow powder which, under the influence of heat, assumes transiently a dark yellow, or reddish-brown tint. When heated to intense redness, it fuses, without any alteration in its weight. Ignition in conjunction with charcoal, or in a stream of carbonic oxide gas, reduces it to the metallic state. It is insoluble in water, and does not affect vegetable colors. It dissolves readily in those acids which form soluble salts with it.

COMPOSITION.

Bi	= 2599·95	= 208	= 89·655
O_3	= 300·00	= 24	= 10·345
	2899·95	= 232	= 100·000

b. Carbonate of teroxide of bismuth.—Upon adding carbonate of ammonia in excess to the solution of a salt of bismuth, free from hydrochloric acid, a white precipitate of carbonate of bismuth (BiO_3,CO_2) is immediately formed; part of this precipitate, however, redissolves in the excess of the precipitant. But if the fluid with the precipitate be heated previous to filtration, the filtrate will be perfectly free from any trace of bismuth. Carbonate of potassa likewise precipitates solutions of salts of bismuth completely; but the precipitate in this case invariably contains traces of potassa, which it is

very difficult to remove by washing. Carbonate of soda precipitates solutions of salts of bismuth less completely than the carbonate of ammonia, and that of potassa. The precipitate obtained by means of carbonate of ammonia, is easily washed; it is nearly insoluble in water, but dissolves readily, with effervescence, in hydrochloric acid and nitric acid. Upon ignition it loses its carbonic acid, leaving teroxide of bismuth behind.

c. Tersulphide of bismuth, prepared in the humid way, is a brownish black, or black precipitate, insoluble in water, dilute acids, alkalies, alkaline sulphides, and cyanide of potassium. In moderately concentrated nitric acid it dissolves, at a high temperature, as a nitrate, with separation of sulphur. It is unalterable in the air, and may be dried at 212°, without undergoing any change.

COMPOSITION.

Bi	= 2599·95	= 208	= 81·25
3 S	= 600·00	= 48	= 18·75
	3199·95	= 256	= 100·00

§ 66.

7. OXIDE OF CADMIUM.

Cadmium is weighed either as OXIDE, or as SULPHIDE OF CADMIUM. Besides these substances, we have to examine CARBONATE OF CADMIUM.

a. Oxide of cadmium, produced by igniting the carbonate, or nitrate of cadmium, is a powder, the color of which varies from yellowish brown to reddish brown. The application of a white heat fails to fuse, to volatilize, or to decompose it; it is insoluble in water, but dissolves readily in acids; it does not alter vegetable colors. Ignition, in conjunction with charcoal, reduces it readily, the metallic cadmium escaping in the form of vapor.

COMPOSITION.

Cd	= 696·77	= 55·74	= 87·45
O	= 100·00	= 8·00	= 12·55
	796·77	= 63·74	= 100·00

b. Carbonate of cadmium is a white precipitate, insoluble in water and in the fixed alkaline carbonates, and extremely sparingly soluble in carbonate of ammonia. It loses its water completely upon desiccation. Ignition converts it into oxide of cadmium.

c. Sulphide of cadmium, produced in the humid way, is a lemon-yellow, or orange-yellow precipitate, insoluble in water, dilute acids, alkalies, alkaline sulphides, and cyanide of potassium. (Experiment No. 54.) It dissolves in concentrated hydrochloric acid, with evolution of

sulphuretted hydrogen, and in moderately concentrated hot nitric acid, with separation of sulphur. It may be dried at 212°, without undergoing decomposition.

COMPOSITION.

Cd	= 696·77	= 55·74	= 77·78
S	= 200·00	= 16·00	= 22·22
	896·77	= 71·74	= 100·00

METALLIC OXIDES OF THE SIXTH GROUP.

§ 67.

1. TEROXIDE OF GOLD.

Gold is invariably weighed in the metallic state. Besides METALLIC GOLD, we have to consider here TERSULPHIDE OF GOLD.

a. Metallic gold, obtained by precipitation, presents the appearance of a blackish-brown powder, destitute of metallic lustre, which it assumes, however, upon pressure, or friction; when coherent in a compact mass, it exhibits the characteristic bright yellow color peculiar to it. It fuses only at a white heat, and resists, accordingly, all attempts at fusion over a spirit-lamp. It remains wholly unaltered in the air and at a red heat, and is not in the slightest degree affected by water, nor by any single acid. Nitrohydrochloric acid dissolves it to terchloride of gold.

b. Tersulphide of gold.—When sulphuretted hydrogen is transmitted through a dilute cold solution of terchloride of gold, the whole of the gold separates as tersulphide ($Au\ S_3$), in the form of a brownish-black precipitate. If this precipitate be left in the fluid, it will gradually be transformed into metallic gold and free sulphuric acid. Upon transmitting sulphuretted hydrogen through a *hot* solution of terchloride of gold, a protosulphide (Au S) precipitates, with simultaneous formation of sulphuric acid and of hydrochloric acid.

$$(2\ AuCl_3 + 3\ HS + 3\ HO = 2\ AuS + 6\ HCl + SO_3.)$$

The tersulphide ($Au\ S_3$) is insoluble in water, hydrochloric acid, and nitric acid, but dissolves in nitrohydrochloric acid. The colorless sulphide of ammonium fails to dissolve it; but it dissolves almost completely in the yellow sulphide of ammonium, and completely upon addition of potassa. It dissolves in potassa, with separation of gold. Yellow sulphide of potassium dissolves it completely. Exposure to a moderate heat reduces it to metallic gold.

§ 68.

2. BINOXIDE OF PLATINUM.

Platinum is invariably weighed in the METALLIC STATE; it is generally precipitated as BICHLORIDE OF PLATINUM AND CHLORIDE OF AMMO-

NIUM, or as BICHLORIDE OF PLATINUM AND CHLORIDE OF POTASSIUM, rarely as BISULPHIDE OF PLATINUM.

a. *Metallic platinum*, produced by igniting the bichloride of platinum and chloride of ammonium, or the bichloride of platinum and chloride of potassium, presents the appearance of a gray, lustreless, porous mass (spongy platinum). The fusion of platinum can be effected only at the very highest degrees of heat. It remains wholly unaltered in the air, and even the most intense heat of our furnaces fails to affect it. It is insoluble in water and in any single acid, and nearly insoluble in aqueous solutions of the alkalies. Nitrohydrochloric acid dissolves it to bichloride of platinum.

b. The properties of *bichloride of platinum and chloride of potassium*, and those of *bichloride of platinum and chloride of ammonium*, have been given already respectively in §§ 47 and 49.

c. *Bisulphide of platinum.* — When a concentrated solution of bichloride of platinum is mixed with sulphuretted hydrogen water, or when sulphuretted hydrogen gas is transmitted through a more dilute solution of the bichloride, no precipitate forms at first; after standing some time, however, the solution turns brown, and finally a precipitate subsides. But if the mixture of solution of bichloride of platinum with sulphuretted hydrogen in excess, is gradually heated to ebullition, the whole of the platinum separates as bisulphide (free from any admixture of bichloride of platinum). The bisulphide of platinum is insoluble in water and in any single acid; but it dissolves in nitrohydrochloric acid. It dissolves partly in caustic alkalies, with separation of platinum, and completely in alkaline sulphides. When sulphuretted hydrogen is transmitted through water holding minutely divided bisulphide of platinum in mechanical suspension, the bisulphide, absorbing sulphuretted hydrogen, acquires a grayish brown color (the sulphuretted hydrogen thus absorbed, separates again upon exposure to the air). When moist bisulphide of platinum is exposed to the air, it is gradually decomposed, being converted into metallic platinum and sulphuric acid. Ignition in the air reduces bisulphide of platinum to metallic platinum.

§ 69.

3. OXIDE OF ANTIMONY.

Antimony is most generally weighed as TERSULPHIDE OF ANTIMONY, more rarely as ANTIMONIOUS ACID, or in the METALLIC state.

a. Upon transmitting sulphuretted hydrogen through a solution of terchloride of antimony mixed with paratartaric acid, an orange-red precipitate of *hydrated tersulphide of antimony* is obtained, mixed at first with a small portion of basic terchloride of antimony. However, if the fluid

is thoroughly saturated with sulphuretted hydrogen, and a gentle heat applied, the terchloride of antimony mixed with the precipitate is decomposed, and the pure hydrated tersulphide of antimony is obtained; which, subsequently, in the process of drying, loses its water of hydration. Tersulphide of antimony is insoluble in water and dilute acids; it dissolves in concentrated hydrochloric acid, with evolution of sulphuretted hydrogen. Brought into contact with fuming nitric acid, containing a slight admixture of hydrochloric acid, it oxidizes with much violence, and is converted into sulphate of teroxide of antimony. It dissolves readily in solutions of potassa, sulphide of ammonium, and sulphide of potassium, but is only sparingly soluble in ammonia. It may be dried at 212°, without suffering decomposition; when dried, it is unalterable in the air. When recently precipitated tersulphide of antimony is long boiled with water, it becomes transformed into teroxide of antimony, which dissolves in the water, and into sulphuretted hydrogen. When tersulphide of antimony is exposed for some time to the air, water being present, it absorbs oxygen, and dissolves gradually as sulphate of teroxide of antimony. The higher sulphides of antimony, corresponding to antimonious and antimonic acid, are likewise insoluble in water; they dissolve, however, sparingly in water impregnated with sulphuretted hydrogen.

COMPOSITION.

Sb	= 1612·90	= 129	= 72·89	71·47
S_3	= 600·00	= 48	= 27·11	28·53
	2212·90	= 177	= 100·00	

b. Antimonious acid is a white powder which, when heated, acquires transiently a yellow tint; it is fixed and infusible. It is almost insoluble in water, and dissolves in hydrochloric acid with very great difficulty. It undergoes no alteration by the action of sulphide of ammonium. It manifests an acid reaction, when placed upon moist litmus paper.

COMPOSITION.

Sb	= 1612·90	= 129	= 80·13	78·98
4 O	= 400·00	= 32	= 19·87	21·02
	2012·90	= 161	= 100·00	

c. Metallic antimony, produced in the humid way, by precipitation, presents the appearance of a lustreless black powder. Metallic antimony is insoluble in water; however, when it is exposed to the action of air, in presence of water, it oxidizes slowly, and the oxide formed dissolves in the water present. The powder of antimony may be dried at 212°, without suffering any alteration. It fuses at a moderate red heat. Upon ignition

in a current of hydrogen gas it volatilizes (without formation of antimoniuretted hydrogen). Concentrated hydrochloric acid has no action on it, even upon ebullition. Nitric acid converts it into teroxide of antimony, mixed with a greater or less proportion of antimonious acid, according to the greater or less degree of concentration possessed by the oxidising acid.

§ 70.

4. PROTOXIDE OF TIN; and 5. BINOXIDE OF TIN.

Tin is generally weighed in the form of BINOXIDE; besides the binoxide, we have here to examine PROTOSULPHIDE and BISULPHIDE OF TIN.

a. Binoxide of tin—(*a* and *b*).—The hydrate of the binoxide *b* (*hydrated metastannic acid*), is obtained in the form of a white precipitate, by the action of nitric acid upon metallic tin, or by evaporating a solution of a salt of tin with nitric acid in excess. This precipitate is insoluble in water, nitric acid, and sulphuric acid, and dissolves but sparingly in hydrochloric acid. It reddens litmus, even when thoroughly washed. But if we precipitate solution of bichloride of tin, with an alkali, with sulphate of soda, or nitrate of ammonia, we obtain the hydrate of the binoxide *a*, which dissolves readily in hydrochloric acid. Both hydrates lose their water of hydration, upon ignition, and change to simple binoxide of tin.

Binoxide of tin is a straw-colored powder which, under the influence of heat, transiently assumes a different tint, varying from yellow to brown. It is insoluble in water and acids, and does not alter the color of litmus paper. Mixed with chloride of ammonium in excess, and exposed to the action of a red heat, it volatilizes completely as bichloride.

COMPOSITION.

Sn	= 735·30	= 58·82	= 78·62	58 = 78·38
2 O	= 200·00	= 16·00	= 21·38	16 21·62
	935·30	= 74·82	= 100·00	

b. Hydrated protosulphide of tin forms a brown precipitate, insoluble in water, sulphuretted hydrogen water, and dilute acids. Ammonia fails to dissolve it; but it dissolves pretty readily (as bisulphide) in the yellow sulphide of ammonium, and in the yellow sulphide of potassium; it dissolves readily in hot concentrated hydrochloric acid. Heated, with exclusion of air, it loses its water of hydration, and is converted into anhydrous protosulphide of tin; when it is exposed to the continued action of a gentle heat, with free access of air, it is transformed into sulphurous acid, which escapes, and binoxide of tin, which remains behind.

c. Hydrated bisulphide of tin forms a bright yellow precipitate, which, upon drying, assumes a darker tint. It is insoluble in water, but dissolves

slightly in water impregnated with sulphuretted hydrogen; it dissolves with difficulty in ammonia, but readily in potassa and alkaline sulphides, and likewise in hot concentrated hydrochloric acid. When heated, with exclusion of air, it loses its water of hydration, and, at the same time, according to the greater or less degree of heat applied, one-half, or one whole equivalent of sulphur, becoming converted either into sesquisulphide, or into protosulphide of tin; when heated very slowly, with free access of air, it becomes converted into binoxide of tin, whilst sulphurous acid escapes.

§ 71.

6. ARSENIOUS ACID; and 7. ARSENIC ACID.

TERSULPHIDE OF ARSENIC is weighed either as ARSENIATE OF LEAD, or as ARSENIC, or as ARSENIATE OF MAGNESIA AND AMMONIA, or as ARSENIATE OF SESQUIOXIDE OF IRON.

a. Arseniate of lead, in the pure state, is a white powder, which begins to agglutinate into a semi-fused mass, when exposed to a gentle red heat, at the same time transitorily acquiring a yellow tint; it fuses when exposed to a higher degree of heat. When strongly ignited, it suffers a slight diminution of weight, losing a small proportion of arsenic acid, which escapes as arsenious acid and oxygen. In analysis we have never occasion to operate upon the pure arseniate of lead, but upon a mixture of it with free oxide of lead.

b. Tersulphide of arsenic forms a precipitate of a rich yellow color; it is insoluble in water, and but very sparingly soluble in sulphuretted hydrogen water. When boiled with water, or left for several days in contact with that fluid, it undergoes a trifling decomposition: a trace of arsenious acid dissolves in the water, and a minute proportion of sulphuretted hydrogen is disengaged. This does not interfere, however, with the washing of the precipitate. The precipitate may be dried at 212°, without suffering decomposition; the whole of the water which it contains is expelled at that temperature. When exposed to a stronger heat, tersulphide of arsenic transitorily assumes a brownish-red color, fuses, and finally rises in vapor, without suffering decomposition. It dissolves readily in alkalies and alkaline sulphides, and likewise in nitrohydrochloric acid, but it is only slightly soluble in boiling concentrated hydrochloric acid. Fuming nitric acid converts it into arsenic acid and sulphuric acid.

COMPOSITION.

As =	937·5 =	75 =	60·98
3 S =	600·0 =	48 =	39·02
	1537·5 =	123 =	100·00

c. Arseniate of magnesia and ammonia forms a white, somewhat transparent, fine crystalline precipitate, which has the formula, $2\,MgO,NH_4O,AsO_5 + 12$ aq.

At 212° it loses 11 equivalents of water; the formula of the precipitate dried at that temperature, is accordingly $2\,MgO,NH_4O,AsO_5 + aq$. Upon ignition it loses its water and ammonia, and changes to $2\,MgO, AsO_5$. But as the ammoniacal gas exercises a reducing action upon the arsenic acid, the new compound suffers a loss of weight, which is the more considerable the longer the application of a red heat is continued; it amounts to from 4—12 per cent of the arsenic originally present in the salt. (*H. Rose*). Arseniate of magnesia and ammonia dissolves very sparingly in water, one part of the salt dried at 212°, requiring 4926, one part of the anhydrous salt, 5154 parts of water of 59°. It is still more sparingly soluble in ammoniated water, one part of the salt dried at 212°, requiring 9260, one part of the anhydrous salt, 9709 parts of a mixture of one part of liquor of ammonia (0·96 sp. gr.), and 7 parts of water at 59°. In water containing chloride of ammonium, it is much more readily soluble, one part of the anhydrous salt requiring 1600 parts of a solution of one part of chloride of ammonium in 70 parts of water; and 1044 parts of a solution of one part of chloride of ammonium in 7 parts of water. Presence of ammonia diminishes the solvent capacity of the chloride of ammonium solution: one part of the anhydrous salt requires 2790 parts of a mixture of 60 parts of water, 10 of solution of ammonia (0·96 sp. gr.), and one of chloride of ammonium; and 1810 parts of a mixture of one part of chloride of ammonium, one of caustic ammonia, and 6 of water. The experiments on the solubility of arseniate of magnesia and ammonia were made in my own laboratory by Mr. *Fränkel* (J. pr. Chem. 56, 33).

d. Arseniate of sesquioxide of iron.—The white, shining precipitate, produced by the action of arseniate of soda upon solution of sesquichloride of iron, has the composition $2\,Fe_2O_3, 3\,AsO_5$. It dissolves in solution of ammonia, imparting a yellow color to the fluid.

Besides this compound, there exist still several others, with larger proportions of sesquioxide of iron; thus we have, Fe_2O_3, AsO_5, which falls down + 5 aq. upon the precipitation of arsenic acid with acetate of sesquioxide of iron (*Kotschoubey*); $2\,Fe_2O_3, AsO_5$, which is obtained + 12 aq., when basic-arseniate of protoxide of iron is oxidized with nitric acid, and ammonia added;—$16\,Fe_2O_3, AsO_5$, which forms + 24 aq., upon boiling the less basic compounds with solution of potassa in excess (*Berzelius*). The two latter compounds are not soluble in ammonia; the last of them is quite like hydrated sesquioxide of iron. In *Berthier's* method of estimating arsenic acid, we obtain mixtures of these different salts. They are, on account of their insolubility in ammonia, the better adapted for the purpose, the more basic they are; and in the same measure, it is the easier to wash them.

Upon ignition the water alone is expelled, provided the heat be very gradually increased. But if the salt is suddenly exposed to a very strong heat before the adhering ammonia has escaped, part of the arsenic acid is thereby reduced to arsenious acid (*H. Rose*).

B.—FORMS AND COMBINATIONS IN WHICH THE VARIOUS ACIDS ARE SEPARATED FROM OTHER BODIES, OR IN WHICH THEIR RESPECTIVE WEIGHT IS DETERMINED.

ACIDS OF THE FIRST GROUP.

§ 72.

1. ARSENIOUS ACID and ARSENIC ACID.—See the preceding paragraph (§ 71).

2. CHROMIC ACID.

Chromic acid is weighed either in the form of SESQUIOXIDE OF CHROMIUM, or in that of CHROMATE OF LEAD.

a. Sesquioxide of chromium.—See § 55.

b. Chromate of lead forms a precipitate of an intensely yellow color; this precipitate is insoluble in water and acetic acid, and barely soluble in dilute nitric acid, but readily so in solution of potassa. When chromate of lead is boiled with concentrated hydrochloric acid, it is readily decomposed, and its elements transposing with those of the decomposing acid, chloride of lead and protochloride of chromium are formed. Addition of alcohol tends to promote this double decomposition. Chromate of lead is unalterable in the air; it dries thoroughly at 212°. Under the influence of heat, it transitorily acquires a reddish-brown tint; it fuses at a red heat; when heated beyond its point of fusion, it loses oxygen, and is transformed into a mixture of sesquioxide of chromium and basic chromate of lead. Heated in contact with organic substances, it readily yields up oxygen to the latter.

COMPOSITION.

PbO	= 1394·64	= 111·57	= 68·72
CrO_3	= 634·70	= 50·78	= 31·28
	2029·34	= 162·35	= 100·00

3. SULPHURIC ACID.

Sulphuric acid is determined best in the form of SULPHATE OF BARYTA, for the properties of which see § 50.

4. PHOSPHORIC ACID.

Phosphoric acid may be weighed as PHOSPHATE OF LEAD, PYROPHOSPHATE OF MAGNESIA, BASIC PHOSPHATE OF SESQUIOXIDE OF IRON, PHOSPHATE OF BINOXIDE OF TIN, PHOSPHATE and PYROPHOSPHATE OF SILVER. Besides these compounds, we have to examine here PHOSPHATE OF SUBOXIDE OF MERCURY, and PHOSPHO-MOLYBDATE OF AMMONIA.

a. The *phosphate of lead*, obtained in the course of analysis, is hardly ever quite pure, but is generally intermixed with free oxide of lead. The basic phosphate of lead ($3\,PbO,PO_5$) in the pure state, presents the appearance of a white powder; it is insoluble in water and in acetic acid, and equally so in ammonia; it dissolves readily in nitric acid. When exposed to the action of heat, it fuses, without undergoing decomposition.

b. Pyrophosphate of Magnesia.—See § 53.

c. Basic phosphate of sesquioxide of iron.

Räwsky states that upon the precipitation of phosphoric acid with acetate of sesquioxide of iron in excess, or with a mixture of iron alum, and acetate of soda, a phosphate of sesquioxide of iron is produced, of constant composition, viz., Fe_2O_3,PO_5. The correctness of this statement has been questioned, in *Liebig* and *Kopp's* Annual Report (Jahresbericht) 1847 and 1848, p. 946; and altogether disputed by *Way* and *Ogston* (*Liebig* and *Kopp's* Annual Report, 1849, p. 571). *Wittstein* obtained Fe_2O_3, PO_5, by exactly precipitating phosphoric acid with acetate of sesquioxide of iron; but upon adding the precipitant in excess, he obtained $4\,Fe_2,O_3$, $3\,PO_5$. *Rammelsberg* obtained Fe_2O_3, PO_5+4 aq. and *Wittstein* subsequently, the same compound $+8$ aq., upon mixing sulphate of sesquioxide of iron with phosphate of soda in excess; with an insufficient quantity of the phosphate of soda, the latter chemist obtained a more yellowish precipitate, which had the formula

$$3\,(Fe_2O_3,\,PO_5+8\,aq.)+(Fe_2O_3,\,3\,HO).$$

When an acid fluid containing a *considerable* excess of phosphoric acid, is mixed with a small portion of sesquioxide of iron, and afterwards with an alkaline acetate, a precipitate is formed, having the formula $2Fe_2O_3,3PO_5$, $3\,HO+10$ aq.; this precipitate leaves upon ignition $2Fe_2O_3$, $3PO_5$. (This statement is based upon an analysis made by *Will* and myself, "Annal. d. Chem. u. Pharm. 50, 379," and subsequently, at a different period, repeated by myself, with a freshly prepared salt.) To obtain a precipitate of this composition, there must, of course, be a *considerable* excess of phosphoric acid present. *Wittstein* obtained simply Fe_2O_3,PO_5, upon the precipitation of sulphate of sesquioxide of iron with phosphate of soda, in presence of acetic acid.

COMPOSITION.

PO_5	= 892·041 =	71·36 =	47·16
Fe_2O_3	= 1000·000 =	80·00 =	52·84
	1892·041 =	151·36 =	100·00

3 PO_5	= 2676·12 =	214·08 =	57·22
2 Fe_2O_3	= 2000·00 =	160·00 =	42·78
	4676·12 =	374·08 =	100·00

If we dissolve phosphate of sesquioxide of iron in hydrochloric acid, supersaturate the solution with ammonia, and apply heat, we obtain basic salts, as 3 Fe_2O_3, 2 PO_5 (*Rammelsberg*); 2 Fe_2O_3, PO_5 (*Wittstein*—after long washing). In *Wittstein's* experiment, the washing fluid contained phosphoric acid. The phosphate of sesquioxide of iron does not dissolve in acetic acid, but it dissolves in a solution of acetate of sesquioxide of iron.

Upon boiling the latter solution (that of the phosphate of sesquioxide of iron in acetate of sesquioxide of iron), the whole of the phosphoric acid precipitates as *hyperbasic phosphate of sesquioxide of iron* (15 Fe_2O_3, PO_5 — *Rammelsberg*), in conjunction with the basic acetate of sesquioxide of iron. The hyperbasic phosphate of sesquioxide of iron is invariably obtained, mixed with free hydrated sesquioxide of iron, upon precipitating with ammonia, a solution containing phosphoric acid and sesquioxide of iron, the latter in excess. The precipitate is insoluble, or, more correctly speaking, most difficultly and sparingly soluble in water, and in ammonia. Sulphide of ammonium, added to the fluid filtered off from the precipitate, imparts to that fluid, after some time standing, a greenish tint. Upon washing the precipitate with cold water, the latter speedily runs off yellow; this coloration is still more marked when ammoniated water is used.

d. Phosphate of binoxide of tin is never obtained in the pure state in the analytical process, but contains always an admixture of hydrated binoxide of tin in excess, which, upon ignition, changes to anhydrous binoxide of tin. It has, generally speaking, the same properties as the pure binoxide of tin, or, previously to ignition, as the hydrates of the latter.

e. Tribasic phosphate of silver is a powder of a rich yellow color; it is insoluble in water, but readily soluble in nitric acid, and also in ammonia. In ammoniacal salts, it is difficultly soluble. It is unalterable in the air. Upon ignition, it acquires transiently a reddish brown color; at an intense red heat, it fuses without decomposition.

COMPOSITION.

3 AgO	= 4348·98 =	347·91 =	82·98
PO_5	= 892·04 =	71·36 =	17·02
	5241·02 =	419·27 =	100·00

f. Pyrophosphate of silver is a white powder, unalterable and insoluble in water, even upon ebullition; but readily soluble in ammonia, and also in nitric acid. It is unalterable in the air. Exposed to a heat somewhat below redness, it fuses, without decomposition, to a dark brown colored liquid, which, upon cooling, solidifies to a white radiated mass.

COMPOSITION.

2 AgO	= 2899·32	= 231·94	= 76·47
b PO_5	= 892·04	= 71·36	= 23·53
	3791·36	= 303·30	= 100·00

g. Phosphate of suboxide of mercury. This combination is only had recourse to for the purpose of effecting the separation of phosphoric acid from many bases, after *H. Rose's* method.

Phosphate of suboxide of mercury presents the appearance of a white crystalline mass, or of a white powder. It is insoluble in water, but dissolves in nitric acid. The action of a red heat converts it into fused phosphate of oxide of mercury, with evolution of mercurial fumes. Fused in conjunction with alkaline carbonates, it yields alkaline phosphates and mercurial fumes, which escape.

h. Phospho-molybdate of ammonia. This combination also serves to effect the separation of phosphoric acid from other bodies; it is of the utmost importance in this respect.

Phospho-molybdate of ammonia forms a rich yellow, readily subsiding precipitate which, according to *Sonnenschein*, has the following composition.

Oxide of ammonium and water . .	11·18
Phosphoric acid	3·02
Molybdic acid	85·80
	100·00

In the pure state, it dissolves but sparingly in cold water; but it is soluble in hot water. It is readily soluble even in the cold, in the caustic, and in the carbonates and phosphates of the alkalies, in chloride of ammonium, and in oxalate of ammonia. It dissolves only sparingly in sulphate of ammonia, in nitrate of potassa, and in chloride of potassium; and very sparingly in nitrate of ammonia.

It is soluble in sulphate of potassa and sulphate of soda, chloride of sodium and chloride of magnesium, sulphuric, hydrochloric, and nitric acids (strong and dilute). Application of heat does not check the solvent action of these substances. Presence of molybdate of ammonia totally changes the deportment of the phospho-molybdate of ammonia with solvents: in

presence of that substance, the latter compound is almost insoluble in acids, even upon ebullition. The solution of the phospho-molybdate of ammonia in acids is probably attended, in all cases, with decomposition and with separation of the molybdic acid, which decomposition and separation the presence of molybdate of ammonia prevents. (*J. Craw*, Chem. Gaz. 1852. 216.)

5. BORACIC ACID.

Boracic acid is usually estimated in an *indirect* way. BORATE OF LEAD is the only form which interests us here.

Borate of lead, in the pure state, is a white powder, difficultly soluble in water. Upon exposure to heat it fuses, without decomposition, to a clear glass. The borate of lead obtained in the analytical process is never pure, but always contains an admixture of oxide of lead.

6. OXALIC ACID.

Oxalic acid is usually precipitated in the form of oxalate of lime; and its weight is generally inferred from the CARBONATE OF LIME produced from the oxalate by ignition. For the properties, &c., of carbonate of lime and of oxalate of lime, see § 52.

7. HYDROFLUORIC ACID.

The *direct* estimation of hydrofluoric acid is uniformly effected by weighing that acid in the form of FLUORIDE OF CALCIUM.

Fluoride of calcium forms a gelatinous precipitate which it is found difficult to wash. If digested with ammonia, previously to filtration, it is rendered denser and less gelatinous. It is wholly insoluble in water and also in aqueous solutions of the alkalies. It is very slightly soluble in dilute, but more readily in concentrated hydrochloric acid. When acted upon by sulphuric acid, it is decomposed, and, its elements transposing with those of the decomposing acid, sulphate of lime and hydrofluoric acid are formed. Fluoride of calcium is unalterable in the air, and at a red heat. Heated to very intense redness, it fuses. Mixed with chloride of ammonium, and exposed to a red heat, fluoride of calcium suffers a loss of weight; but the decomposition is incomplete.

COMPOSITION.

Ca	= 250·0	= 20	= 51·28
Fl	= 237·5	= 19	= 48·72
	487·5	= 39	= 100·00

8. CARBONIC ACID.

The *direct* estimation of carbonic acid is usually effected by weighing that acid in the form of CARBONATE OF LIME. For the properties of the latter substance, see § 52.

8. SILICIC ACID.

Silicic acid is uniformly weighed in its insoluble modification.

The insoluble modification of silicic acid, artificially prepared, is a white powder, insoluble in water and in acids, but soluble in solution of potassa and in solutions of the carbonates of the fixed alkalies. It is perfectly unalterable in the air, and at a red heat, and requires the very highest degrees of heat for its fusion. It does not affect vegetable colors.

Upon evaporating a solution of the soluble modification of silicic acid in water, or in any volatile acid (hydrofluoric acid excepted), we obtain the silicic acid at first as a gelatinous hydrate; this upon drying in the air, loses part of its water, and is converted into $3\,SiO_2$, HO; dried at 212°, it changes to $4\,SiO_2$, HO (*J. Fuchs*). This latter compound presents the appearance of a loose white powder; upon exposure to a red heat it loses the whole of its water; the escaping aqueous vapor is apt to carry up with it particles of the exceedingly fine powder.

Artificially prepared silicic acid, when exposed to a red heat, mixed with chloride of ammonium, loses at first in weight; but after a time, when the action of the heat has given greater density to the acid, this loss is completely checked.

COMPOSITION.

Si	= 185·18	= 14·81	= 48·08
2 O	= 200·00	= 16·00	= 51·92
	385·18	= 30·81	= 100·00

The gelatinous (but not the pulverulent) hydrate of silicic acid is slightly soluble in water, and in hydrochloric acid. One part of the gelatinous hydrate dissolves in 7700 parts of water; in 11000 parts of cold, and 5500 parts of boiling hydrochloric acid of 1·115 sp. gr. (*J. Fuchs.*)

ACIDS OF THE SECOND GROUP.

§ 73.

1. HYDROCHLORIC ACID.

Hydrochloric acid is almost uniformly determined in the form of CHLORIDE OF SILVER. For the properties of which compound, see § 61.

2. HYDROBROMIC ACID.

Hydrobromic acid is uniformly determined in the form of BROMIDE OF SILVER.

Bromide of silver, prepared in the humid way, forms a yellowish white precipitate. It is wholly insoluble in water, and in nitric acid, but tolerably soluble in ammonia; it dissolves in hot solution of chloride of ammonium, but very sparingly in solution of nitrate of ammonia. When

acted upon by chlorine, either in the dry, or in the humid way, it is decomposed, chloride of silver being formed, with separation of bromine. Exposed to the light, it gradually turns gray, and finally black. Under the influence of heat, it fuses to a reddish liquid, which, upon cooling, solidifies to a yellow horn-like mass. Brought into contact with zinc and water, bromide of silver is decomposed: a spongy mass of metallic silver subsides, and the solution contains bromide of zinc.

COMPOSITION.

Ag	= 1349·66	= 107·97	= 57·46
Br	= 999·62	= 79·97	= 42·54
	2349·28	= 187·94	= 100·00

3. HYDRIODIC ACID.

Hydriodic acid is usually determined in the form of IODIDE OF SILVER, and occasionally also in that of IODIDE OF PALLADIUM.

a. Iodide of silver, produced in the humid way, forms a bright yellow precipitate, insoluble in water and in dilute nitric acid, and very slightly soluble in ammonia. It is decomposed by chlorine, both in the dry and in the humid way. Hot concentrated nitric, and sulphuric acids convert it, but with some difficulty, into the corresponding nitrate and sulphate of silver, with expulsion of the iodine. Iodide of silver acquires a black color when exposed to the light. When heated, it fuses without decomposition to a reddish fluid which, upon cooling, solidifies to a yellow mass that may be cut with a knife. When brought into contact with zinc and water, it is decomposed: iodide of zinc is formed, and metallic silver separates.

COMPOSITION.

Ag	= 1349·66	= 107·97	= 45·98
I	= 1586·00	= 126·88	= 54·02
	2935·66	= 234·85	= 100·00

b. The protiodide of palladium, produced by precipitating a solution of the iodide of one of the fixed alkalies, with protochloride of palladium, is a deep brownish-black flocculent mass, insoluble in water, and in dilute hydrochloric acid, but slightly soluble in saline solutions (solution of chloride of sodium, chloride of magnesium, chloride of calcium, &c.) It is unalterable in the air. Dried simply in the air, it retains one equivalent of water=5·05 per cent. Dried long in vacuo, or at a high temperature (158° to 176°), it yields up the whole of this water, without the least loss of iodine. Dried at 212°, it loses a trace of iodine; at from 572° to 752°, the whole of the iodine is expelled. The precipitated iodide of palladium may be washed with hot water, without loss of iodine.

COMPOSITION.

Pd	= 665·48	= 53·24	= 29·57
I	= 1586·00	= 126·88	= 70·43
	2251·48	= 180·12	= 100·00

4. HYDROCYANIC ACID.

The *direct* estimation of hydrocyanic acid is uniformly effected by weighing that acid in the form of cyanide of silver—for the properties of which compound, see § 61.

5. HYDROSULPHURIC ACID.

Sulphuretted hydrogen.

The forms into which sulphuretted hydrogen, or the sulphur in metallic sulphides is converted for the purpose of quantitative estimation, are TERSULPHIDE OF ARSENIC, and SULPHATE OF BARYTA.

a. *Tersulphide of arsenic*—see § 71.

b. *Sulphate of baryta*—see § 50.

ACIDS OF THE THIRD GROUP.

§ 74.

1. NITRIC ACID; and 2. CHLORIC ACID.

These two acids are estimated invariably in an *indirect* way. We have, in the preceding paragraphs, had occasion already to treat of those compounds which serve for the indirect quantitative estimation of nitric acid and of chloric acid.

SECTION IV.

In the preceding section, we have examined the composition and properties of the various appropriate forms and combinations in which substances are separated from others, or in which their weight is estimated. We have now to consider the means of converting substances into such forms and combinations.

For the sake of greater clearness and simplicity, we will divide this part of the work into two sections, confining ourselves, in the first, to the exposition of the various methods applied to effect the *quantitative estimation of substances*, and deferring to the next section the consideration of the means best adapted for the *separation of substances from one another*.

QUANTITATIVE DETERMINATION OF SUBSTANCES.

§ 75.

We have to deal here exclusively with compounds consisting of *one base and one acid*, or of *one metal and one metalloid*.

In the quantitative estimation of substances, we have to study two points, viz., first, the most appropriate manner of dissolving the analysed substance, either in its isolated state, or in its various combinations,—ITS SOLUTION; and secondly, the methods best adapted to convert the analysed substance into a ponderable form,—THE DETERMINATION OF ITS WEIGHT.

With regard to the latter point, we have to turn our attention, 1, to the *practical performance* of the several processes and operations constituting the special method, or methods applied in every individual case; and 2, to the greater, or less degree of *accuracy* attained respectively by the several methods applied.

It happens very rarely in quantitative analyses that the amount of a substance, as determined by the analytical process, corresponds exactly with the amount theoretically calculated.

The cause of this almost invariably occurring discrepancy between the proportion calculated and that actually found, is to be ascribed either exclusively to *certain unavoidable defects inherent in the execution of the necessary processes and operations*, or it lies partly in the *method itself*.

With regard to the *execution* of the analytical processes and operations, this can never be *absolutely* accurate, even though the greatest care and attention be bestowed on the most trifling minutiæ. To account for this, we need only bear in mind that our weights and measures are never *absolutely* correct, nor our balances *absolutely* accurate, nor our reagents *absolutely* pure, and moreover, that we do not weigh *in vacuo;* and that, even if we deduce the weight we might expect to obtain by weighing *in vacuo*, from the weight we *actually* obtain by weighing in the air, we can only *approximate*, but never *attain* absolutely accurate figures;—that the hygroscopic state of the air is liable to vary between the moment of weighing the crucible whilst empty, and that of weighing the crucible after having introduced into it the substance to be analysed;—that we know the weight of the ashes of our filters only *approximately;*—that, upon the evaporation of many fluids, traces of salts will volatilize, which, in their solid state, are considered perfectly fixed;—that absolute perfection cannot be attained in the operation of washing and rinsing;—that we can never succeed in sheltering the contents of dishes and crucibles, &c., *absolutely* from dust, &c., &c.

With regard to the *methods*, many of them are not entirely free from certain unavoidable *sources of error;*—precipitates are not *absolutely* in-

soluble, compounds which require ignition are not *absolutely* fixed, others which require drying, have a slight tendency to volatilize, &c., &c.

Strictly speaking, no method can be pronounced quite free from defect; it should be borne in mind, for example, that even *sulphate of baryta* is not *absolutely* insoluble in water.

We have, therefore, in our analytical processes, invariably to contend against certain sources of inaccuracy which it is impossible to overcome entirely, even though our operations be conducted with the most scrupulous care and with the utmost attention to established rules. It will be readily understood that several defects and sources of error may, in some cases, *combine* to vitiate the results, whereas, in other cases, they may *compensate* one another, and thus enable us to attain a higher degree of accuracy. The *comparative* accuracy of the results attainable by an analytical method, oscillates between two points, or limits, fixed respectively on either side of the point of *absolute* accuracy. In the case of methods relatively free from defects and sources of error, these limits will closely approximate the medium point of absolute accuracy; thus, for instance, in the quantitative estimations of chlorine, a careful operator will always be able to obtain between 99·9 and 100·1, for the 100 parts of chlorine theoretically calculated.

Less perfect methods will, of course, exhibit far greater discrepancies; thus, in the estimation of strontia, the most attentive and skilful operator may not be able to obtain more than 99·0 (and even less) for the 100 parts of strontia theoretically calculated. I may here incidentally state, that the numbers occasionally given in this manner in the further course of the present work to denote the respective and relative accuracy of certain methods, refer invariably to the substance estimated (chlorine, nitrogen, baryta), and not to the forms and combinations in which that substance may happen to be weighed (chloride of silver, bichloride of platinum and chloride of ammonium, sulphate of baryta).

The occasional attainment of results *exactly* corresponding with the numbers calculated, does not always justify the assumption, on the part of the analyst, that his operations, to have led to such a result, must have been conducted with the utmost precision and accuracy. It may sometimes happen, in the course of the analytical process, that one error serves to compensate another; thus, for instance, the analyst may, at the commencement of his operations, spill a minute portion of the substance to be analyzed; whilst, at a later stage of the process, he may recover the loss by an imperfect washing of the precipitates. As a general rule, results showing a trifling deficiency of substance, may be looked upon as better proof of accurate performance of the analytical process, than results exhibiting an excess of substance.

As not the least effective means of guarding against error and inaccuracies, I would most strongly recommend the student *always carefully to*

mark the appearance and properties of the weighed substance, and to compare them with those which that substance ought to exhibit, and which have been amply described in the preceding section.

In my own laboratory I insist upon all substances that are weighed in the course of an analysis, being kept between watch-glasses, until the whole process is concluded. This affords always a chance of testing them once more for some admixture, or impurity, of which the presence may become suspected in the after-course of the process.

I. QUANTITATIVE ESTIMATION OF BASES IN COMPOUNDS CONTAINING ONLY ONE BASE AND ONE ACID, OR ONE METAL AND ONE METALLOID.

FIRST GROUP.

POTASSA—SODA—OXIDE OF AMMONIUM (AMMONIA).

§ 76.

1. POTASSA.

a. Solution.

Potassa and its salts with those inorganic acids which we have to consider here, are dissolved in water, in which menstruum they dissolve readily, or at all events, pretty readily.

Potassa salts with organic acids, are first converted into carbonate of potassa by continued ignition in covered crucibles.

b. Quantitative estimation.

Potassa is weighed either as *sulphate of potassa*, or *nitrate of potassa*, or as *chloride of potassium*, or *bichloride of platinum and chloride of potassium* (see § 47).

We may convert into

1. SULPHATE OF POTASSA.

Salts of potassa with strong volatile acids; *e. g.* chloride of potassium, bromide of potassium, nitrate of potassa, &c.

2. NITRATE OF POTASSA.

Caustic potassa, and compounds of potassa with weak volatile acids, that are not decomposed by nitric acid; *e. g.* carbonate of potassa (salts of potassa with organic acids).

3. CHLORIDE OF POTASSIUM.

In general, salts of potassa with weak volatile acids, that are decomposed by nitric acid; *e. g.* sulphide of potassium.

Also, and more especially, sulphate, chromate, chlorate, and silicate of potassa.

4. BICHLORIDE OF PLATINUM AND CHLORIDE OF POTASSIUM.

Salts of potassa with non-volatile acids soluble in alcohol; *e. g.* phosphate of potassa, and borate of potassa.

The potassa in the borate of that alkali may be determined also as sul-

phate (§ 107); and the potassa in the phosphate, as chloride of potassium (§ 106).

The form of bichloride of platinum and chloride of potassium may also be resorted to in general, for the quantitative estimation of the potassa in all salts of that alkali with acids soluble in alcohol. This form is, moreover, of especial importance here, as that in which the separation of potassa from soda, &c., is effected.

1. *Determination as sulphate of potassa.*

Evaporate the aqueous solution of the sulphate of potassa to dryness, ignite the residue in a platinum crucible, or a platinum dish, and weigh (§ 25). The residue must be thoroughly dried first, before you proceed to ignite it; the heat applied for the latter purpose must be moderate at first, and very gradually increased to the requisite degree; the crucible or dish must be kept well covered—neglect of these precautionary rules involves always a loss of substance from decrepitation. If free sulphuric acid happens to be present, we obtain, upon evaporation, bisulphate of potassa; in such cases the excess of sulphuric acid is to be removed by addition of carbonate of ammonia.—See § 47.

For properties of the residue, see § 47.—Observe more particularly that the residue must dissolve to a clear fluid, and that the solution must be neutral. Should traces of platinum remain behind, these must be carefully weighed, and their weight subtracted from that of the ignited residue.

With proper care and attention this method gives accurate results.

To convert the salts above mentioned, chloride of potassium, &c., into sulphate of potassa, add to their aqueous solution a quantity of pure sulphuric acid more than sufficient to saturate the whole of the potassa, evaporate the solution, and ignite the residue.

As the expulsion of a large quantity of hydrated sulphuric acid is a very disagreeable process, you had better avoid adding too great an excess of it. Should you have used too little of the acid, which you will learn from the cessation of the disengagement of hydrated sulphuric acid fumes towards the end of the process of ignition, you need simply moisten the residue with dilute sulphuric acid, evaporate, and ignite again. If you have to deal with a small quantity only of chloride of potassium, &c., you may at once proceed to treat the dry salt, cautiously, with dilute sulphuric acid in the platinum crucible, provided always the latter be capacious enough; in the case of bromide of potassium, and iodide of potassium, the use of platinum vessels must be avoided.

2. *Determination as nitrate of potassa.*

General method the same as described sub 1. Nitrate of potassa must be heated very gently to the fusing point, otherwise some loss is likely to arise from evolution of oxygen.

For properties of the residue, see § 47.—The method is easy, the results are accurate.

In the conversion of carbonate of potassa into the nitrate, § 21 must be consulted.

3. *Determination as chloride of potassium.*

General method the same as described sub 1. The residue of chloride of potassium must be thoroughly dried, before you proceed to ignite it. The operation must be conducted in a well covered crucible, and with the application of a moderate red heat otherwise loss is likely to arise from volatilization. No particular regard need be had to the presence of free acid. For properties of the residue, see § 47. This method if properly and carefully executed, gives acccurate results. The potassa in the carbonate of that alkali, is, as stated above, generally determined in the form of nitrate of potassa. However, as the residue of carbonate of potassa which remains in the crucible upon the ignition of potassa salts with organic acids, is apt to effervesce in the process of its conversion into nitrate, which effervescence it is often desirable to avoid, the carbonate of potassa may be determined in the form of chloride of potassium, instead of that of nitrate of potassa. The conversion of the carbonate into chloride of potassium is effected by treating the former with solution of chloride of ammonium, slightly in excess, evaporating the mixture, and igniting the residue, when carbonate of ammonia and the excess of chloride of ammonium will escape, leaving chloride of potassium behind.

The methods of converting into chloride of potassium, the potassa compounds specified sub 3, will be found in Part II. of this section, under the respective heads of the acids with which they are formed.

Determination as bichloride of platinum and chloride of potassium.

a. Salts of potassa with volatile acids (nitric acid, acetic acid, &c.).

Mix the solution with hydrochloric acid, add bichloride of platinum in excess, and evaporate in a porcelain dish, in the water bath, nearly to dryness. Add to the residue spirits of wine of about 80 per cent.; let it stand for some time, and then put the bichloride of platinum and chloride of potassium, which remains undissolved, upon a weighed filter (which may be readily done by means of a washing bottle filled with spirits of wine). Wash with spirits of wine, dry at 212°, and weigh (§ 33).

β. Potassa salts with non-volatile acids, phosphoric acid, boracic acid, &c.

Make a concentrated solution of the salt in water, add hydrochloric acid and bichloride of platinum in excess, mix with a considerable portion of the strongest alcohol, let the mixture stand 24 hours; after which filter, and proceed as directed sub *a*. For properties of the precipitate, see § 47. The method, if properly and carefully executed, yields satisfactory results.* Still there is generally a trifling loss of sub-

* The atmosphere of a laboratory is very apt to be more or less strongly ammoniacal. This is a circumstance of some importance, and which must not be lost sight of in this process,

stance, bichloride of platinum and chloride of potassium not being absolutely insoluble even in strong alcohol. In accurate analysis, therefore, the rinsings must be evaporated in the water bath, and the residue treated once more with rectified spirits of wine. A trifling additional amount of bichloride of platinum and chloride of potassium is thus obtained, which is to be collected on a separate small filter,* and determined as platinum, in the manner here subjoined.

Dry the salt on the filter, and then put the latter, with the salt wrapped up in it, into a platinum crucible. Cover the crucible, and let the filter slowly char; remove the cover now, burn the carbon of the filter, and let the crucible get cold. Put now a very minute portion of pure oxalic acid into the crucible, cover, and ignite gently at first, finally to a strong red heat. The addition of the oxalic acid greatly promotes the complete decomposition of the bichloride of platinum and chloride of potassium, which cannot well be effected by simple ignition. Treat now the contents of the crucible with water, and wash the residuary platinum, until the last rinsings remain clear upon addition of solution of nitrate of silver.† Dry the residuary platinum, ignite, and weigh. One equivalent of platinum represents one equivalent of potassium.

§ 77.

2. SODA.

a. Solution.

See § 76, *a.*—Solution of potassa—all the directions given in that place applying equally to the solution of soda and its salts.

b. Determination of weight.

Soda is determined either as *sulphate of soda*, or *nitrate of soda*, or as *chloride of sodium*, or as *carbonate of soda* (§ 48).

We may convert into

1. SULPHATE OF SODA; 2. NITRATE OF SODA; 3. CHLORIDE OF SODIUM.

In general the salts of soda, corresponding to the salts of potassa, specified under the same heads in § 76.

4. CARBONATE OF SODA.

Caustic soda, bicarbonate of soda, and salts of soda with organic acids.

since, if the influence of an atmosphere of this kind be not properly guarded against, bichloride of platinum and chloride of ammonium may form, which would tend to make the weight of the bichloride of platinum and chloride of potassium appear greater than it really is.

* As the collecting a precipitate upon a weighed filter is a rather tedious process, and besides, not over accurate, where we have to deal with minute quantities of substance, it is better to collect trifling portions (up to about 0·03 grm.) of bichloride of platinum and chloride of potassium, upon a very small *unweighed* filter.

† The washing of the residuary platinum may generally be effected by simple affusion and decantation.

In the borate of soda the alkali is estimated as sulphate of soda (§ 107); in the phosphate as chloride of sodium (§ 106).

Salts of soda with organic acids are determined either, like the corresponding potassa compounds, as chloride of sodium, or as nitrate of soda, or finally, and in preference, as carbonate of soda, which latter method is not well adapted to salts of potassa.

1. *Determination as sulphate of soda.*

Evaporate the aqueous solution of the sulphate to dryness, ignite the residue in a covered platinum crucible, and weigh (§ 25). The process does not involve any risk of loss from decrepitation, as in the case of sulphate of potassa. If free sulphuric acid happens to be present, this is removed by means of carbonate of ammonia, in the same way as in the case of sulphate of potassa (§ 48 and 76).

With regard to the conversion of chloride of sodium, &c., into sulphate of soda, see § 76, *b*. 1.—For properties of the residue, see § 48. The method is easy and gives accurate results.

2. *Determination as nitrate of soda.*

Same method as described sub 1. The rules given and the observations made in § 76, *b*. 2, apply equally here. For properties of the residue—see § 48.

3. *Determination as chloride of sodium.*

Same method as described sub 1. The rules given and the observations made in § 76, *b*. 3, apply equally here. For properties of the residue, see § 48.

The methods of converting the sulphate, chromate, chlorate, and silicate of soda, into chloride of sodium, will be found in Part II. of this section, under the respective heads of the acids with which these salts are formed.

4. *Determination as carbonate of soda.*

Evaporate the aqueous solution, ignite the residue, and weigh. The results are perfectly accurate. For properties of the residue—see § 48.

Caustic soda is converted into the carbonate by adding to its aqueous solution carbonate of ammonia in excess, evaporating at a gentle heat, and igniting the residue.

The bicarbonate of soda, if in the dry state, is converted into the simple carbonate, by ignition. The heat must be very gradually increased, and the crucible kept well covered; if in aqueous solution, the latter is evaporated to dryness in a capacious silver or platinum dish, and the residue ignited.

Salts of soda with organic acids are converted into the carbonate by ignition in a covered platinum crucible, from which the lid is removed after a time. The heat must be increased very gradually. When the mass has ceased to swell, the crucible is placed obliquely, with the lid leaning against it (see § 35, Fig. 37), and a dull red heat is applied until

the carbon is consumed as far as practicable. The contents of the crucible are then heated with water, and the fluid is filtered off from the residuary carbon which is carefully washed. The filtrate and rinsings are evaporated to dryness; the residue is ignited and weighed. If the quantity of carbon happens to be very trifling (a few milligrammes), the crucible may be weighed at once with its contents after the process of ignition, the weight of the carbon being subsequently deducted from the resulting numbers. For this purpose the carbon is collected on a small weighed filter, carefully dried with the latter and weighed. Both methods give accurate results, provided, of course, they be properly and carefully executed. The direct experiment (No. 55), performed after the latter method, gave 99·7 instead of 100 parts of soda. If, however, the quantity of carbon exceeds from 10 to 20 milligrammes, the former method is preferable, being less liable to errors in weighing.

§ 78.

3. OXIDE OF AMMONIUM (*Ammonia*).

a. Solution.

Ammonia is soluble in water, and so are all its salts, with those acids which claim our attention here. It is not always requisite, however, to dissolve the ammoniacal salts for the purpose of determining the amount of ammonia contained in them.

b. Determination of weight.

Ammonia is weighed either in the form of *chloride of ammonium*, or in that of *bichloride of platinum and chloride of ammonium*. Into these forms it may be converted either *directly* or *indirectly*, *i. e.*, after previous expulsion as ammonia, and re-combination with an acid. Ammonia is also frequently determined by analysis by measure, or its quantity is inferred, though rarely, from the volume of nitrogen (§ 49).

We convert directly into

1. CHLORIDE OF AMMONIUM.

Caustic ammonia and ammonia in aqueous solution, and also ammoniacal salts with weak volatile acids (carbonate of ammonia, sulphide of ammonium, &c.).

2. BICHLORIDE OF PLATINUM AND CHLORIDE OF AMMONIUM.

Ammoniacal salts with acids soluble in alcohol, such as sulphate of ammonia, phosphate of ammonia, &c.

3. The methods based on the EXPULSION OF THE AMMONIA from its compounds, and also that of inferring the amount of ammonia from the volume of nitrogen, are equally applicable to all ammoniacal salts.

The expulsion of ammonia in the dry way, by ignition in conjunction

with soda-lime, and the estimation of that alkali from the volume of nitrogen, being effected exactly in the same manner as the estimation of the nitrogen in organic compounds, I refer the student on this subject to the section on organic elementary analysis. Here I shall only give the method based upon the expulsion of ammonia in the humid way.

1. *Determination as chloride of ammonium.*

Evaporate the aqueous solution in the water-bath, and dry the residue at 212°, until the weight remains constant (§ 25). The results are accurate. The supposed volatilization of the chloride is very trifling indeed. A direct experiment (No. 14), gave 99·94 for 100 parts of ammonia. The presence of free hydrochloric acid makes no difference; the conversion of caustic ammonia into chloride of ammonium may accordingly be effected by simple supersaturation with hydrochloric acid. The same applies to the conversion of the carbonate, with this addition only, that the process of supersaturation, and also that of heating to expulsion, must be conducted in an obliquely-placed flask or retort. In the analysis of sulphide of ammonium we proceed in the same way, taking care simply, to filter off the sulphur which may have separated after the expulsion of the sulphuretted hydrogen, and before proceeding to evaporate.

2. *Determination as bichloride of platinum and chloride of ammonium.*

a. Direct determination.

a a. Ammoniacal salts with volatile acids.

Same method as described in § 76, *b.* 4. *α* (Bichloride of platinum and chloride of potassium).

b b. Ammoniacal salts with non-volatile acids.

Same method as described § 76, *b.* 4. *β* (Bichloride of platinum and chloride of potassium). The results obtained by these methods are accurate.

If you wish to control the accuracy of your results,* you may ignite the double chloride, wrapped up in the filter, in a covered crucible, and calculate the amount of ammonia from that of the residuary platinum. The heat must be increased very gradually.† Want of due caution in this respect is apt to lead to loss, from particles of the double salt being carried away along with the chloride of ammonium. Very small quantities of bichloride of platinum and chloride of ammonium are collected on an unweighed filter, dried, and at once reduced to platinum by ignition.

3. *Estimation by expulsion of the ammonia in the humid way.*

This method, which is applicable in all cases, but more particularly in such where ammoniacal salts are mixed with organic matters, or also with

* If the bichloride of platinum and chloride of ammonium is pure, this control may be dispensed with.

† The best way is to continue the application of a moderate heat for a long time, then to remove the lid, place the crucible obliquely with the lid leaning against it, and burn the charred filter at a gradually increased heat (*H. Rose*).

other salts, is divided into two parts, viz., *the expulsion* of the ammonia, and the *determination of its weight*.

The expulsion of the ammonia may be effected, either by mixing the substance under examination with lime water, or solution of soda, boiling the mixture continuously in a retort or flask, and conducting the vapors, through a cooling apparatus of glass, into a tubulated receiver, containing some hydrochloric, or dilute sulphuric acid, and from the tubulature of which a limbed tube leads to a small flask, containing some dilute hydrochloric, or dilute sulphuric acid; or also after the following method, recently recommended by *Schlösing*, and the accuracy of which that chemist has tested by repeated experiments. It is based upon the fact that an aqueous solution containing free ammonia gives off the latter completely and in a comparatively short time, upon exposure to air.

The fluid containing the ammoniacal salt, and the volume of which must not exceed 35 cubic centimeters, is introduced into a shallow vessel with low rim, and from 10 to 12 centimeters in diameter; this vessel is put on a plate filled with mercury. A triangle, made of a massive glass rod, is placed into the vessel which contains the solution of the ammoniacal salt, and a saucer or shallow basin with dilute sulphuric acid put on it. A beaker-glass is now inverted over the whole arrangement. This glass is lifted up on one side as far as is required, and a sufficient quantity of lime water is allowed to pass out from a *pipette* (which should not be drawn out at the lower end). The beaker-glass is then rapidly pressed down, and weighted with a stone slab. After forty-eight hours the glass is lifted up, and a slip of moist reddened litmus paper held in it; if no change of color is observable, this is a sign that the expulsion of the ammonia is complete; in the contrary case the glass must be replaced. To judge from *Schlösing's* experiments, forty-eight hours are always sufficient to expel 0·1 to 1 gramme of ammonia from 25 to 35 cubic centimeters of solution.

The expelled ammonia may be determined in the form of bichloride of platinum and chloride of ammonium (*vide supra*), more particularly where the expelled ammonia has been received in hydrochloric acid. Or the estimation may be effected by the following method, recommended first by *Peligot*, and subsequently applied also by *Schlösing*. The principle of the method is very simple: the ammonia is fixed by means of a definite quantity (either weighed or measured) of dilute sulphuric acid of known strength, and the amount of free acid remaining is then ascertained by adding an alkaline solution (of soda, for instance) of known strength, until the free acid is neutralised. From the amount of alkali so required to effect the neutralization of the free acid, we learn the quantity of acid saturated by the ammonia, and accordingly, also, the quantity of the latter.

To prepare the test acid, add about 28 grammes of hydrated sulphuric acid to 200 grammes of water, and determine the strength of the dilute

acid by measuring off, successively, two portions of it, of 10 cubic centimeters each, precipitating them with the aid of a small pipette, after addition of water, with chloride of barium, and weighing the sulphate of baryta obtained (compare § 105). If the two analyses give sufficiently corresponding results, the mean may be taken as the actual proportion of sulphuric acid contained in the test fluid. Suppose you have found in this way that 10 cubic centimeters of the dilute acid contain 1·01 grm. of sulphuric acid: these 10 centimeters are saturated by exactly 0·429 grm. of ammonia (NH_3) Accordingly one cubic centimeter of the dilute acid (test acid), corresponds to 0·0429 grm. of ammonia (NH_3).

The test acid is kept in a well closed bottle.

As alkaline test solution, dilute solution of pure soda may be used. Prepare a solution of about 1·02 sp. gr., and which accordingly contains about 1·5 per cent of soda, and determine the amount of it required to saturate 10 cubic centimeters of the test acid. To this end, pour 10 cubic centimeters of the acid into a beaker-glass, add a few drops of litmus tincture, or of decoction of logwood (*Mitchel*), and let the soda solution drop into it from a graduated *pipette*, or *burette*, filled to the 0 point, until the red fluid (where litmus tincture has been used), turns blue, or the yellowish brown fluid (where decoction of logwood has been used), black blue. Supposing the attainment of these results to have required 53 cubic centimeters of the solution of soda, you know now that 53 cubic centimeters of your alkaline test fluid contain exactly the amount of soda required to saturate 1·01 grm. of sulphuric acid.

Besides the actual test acid, another ten times more dilute test acid must be prepared, by mixing 10 cubic centimeters of the former with 90 cubic centimeters of water.

To determine the ammonia by this method, measure off 10 or 20 cubic centimeters (according to the greater or less amount of the ammoniacal salt), of the *strong* test acid, and bring that quantity into contact with the expelled ammonia. When the operation is completed, neutralise the free acid remaining most carefully with your alkaline test fluid. Should you happen somewhat to exceed the neutralisation point, you need simply add of the *dilute* test acid until the exact point is reached. Suppose you have used 10 cubic centimeters of the strong test acid, 20 cubic centimeters of the alkaline test fluid, and subsequently still 0·5 c. c. of the dilute test acid, your calculation will stand thus :

Total amount of strong test acid used 10 + 0·05 c. c. = 10·05 c. c.	
53 cubic centimeters of the alkaline test fluid corresponding to 10 c. c. of the test acid, 20 c. c. of the former correspond to	3·77 c. c.
(53 : 10 :: 20 : x = 3·77.)	
Amount of test acid combined with ammonia	6·28 c. c.

Now, as one cubic centimeter of test acid corresponds to 0·0429 grm. of ammonia (NH_3), 6·28 cubic centimeters correspond to 0·2694 grm. of ammonia.

The calculation may be simplified still more, by preparing the test acid so that 10 c. c. of it correspond exactly to 0·5 grm. of NH_3; and the alkaline test fluid so that 50 cubic centimeters saturate exactly 10 cubic centimeters of the test acid, in which case we have simply to deduct from the amount of ammonia expressible in round numbers, as many centigrammes as we have used cubic centimeters of the alkaline test fluid. However, as the preparation of so accurately mixed test fluids always involves a chance of some slight errors, I would recommend the former way; at all events, in cases where the attainment of perfectly accurate results is desirable.

SECOND GROUP.

BARYTA, STRONTIA, LIME, MAGNESIA.

§ 79.

1. BARYTA.

a. Solution.

Caustic baryta is soluble in water, and so are many of the salts of that alkaline earth. The salts of baryta, which are insoluble in water, are, with the exception of the sulphate, readily dissolved by dilute hydrochloric acid. The solution of the sulphate is effected by fluxing with a mixture of carbonate of soda and potassa, &c. See § 105.

b. Determination of weight.

Baryta is weighed either as *sulphate*, or as *carbonate* (§ 50). It is rarely converted into *silico-fluoride of barium*, and only for the purpose of separating it from strontia—(see § 122).

We may convert into

1. SULPHATE OF BARYTA.

a. By precipitation.

All compounds of baryta, without exception.

b. By evaporation.

All compounds of baryta with volatile acids, if no other non-volatile body is present.

2. CARBONATE OF BARYTA.

α. All salts of baryta soluble in water.

β. Salts of baryta with organic acids.

The method of precipitating baryta in the form of sulphate is the most frequently employed, being the best adapted also for the separation of baryta from other bases. The method of evaporating (1. *b.*) yields accurate results, and is very convenient in cases where we have to deal

with small portions of fluid only. The conversion into the carbonate in the humid way, is resorted to only in cases where the conversion into the sulphate is inadmissible or unadvisable.

1. *Determination as sulphate of baryta.*

a. By precipitation.

Dissolve the baryta compound in water or in hydrochloric acid, as the case may be, in a beaker-glass, taking care to make the solution moderately dilute; heat the fluid to 212°, and add to it dilute sulphuric acid, as long as a precipitate continues to form; stir the mixture with a glass rod, and rinse off the fluid adhering to the rod with a little water into the beaker-glass; cover the glass, and let it stand at rest until the precipitated sulphate of baryta has completely subsided, and the supernatant fluid become perfectly clear (which will require about twelve hours). Pour the fluid gently and cautiously, so as to leave the precipitate undisturbed, on a proper filter. As soon as the fluid has run off, stir up the precipitate in the beaker-glass with a little hot water (or, if the filtering paper happens to be very porous, with a little moderately diluted hot solution of chloride of ammonium), and transfer it also gradually to the filter, with the aid of a small glass rod, taking care, after the addition of every fresh portion of the precipitate, to wait until the fluid has completely drained off, before you proceed further, and to add each time a fresh amount of hot water, or of hot solution of chloride of ammonium, to the precipitate remaining in the beaker-glass. Small particles of the precipitate adhering more firmly to the glass, are removed with the beard of a feather. If the filtering paper is of tolerably good quality, this way of proceeding will always effect the complete separation of the precipitate from the menstruum; deviations from the rules laid down here, will generally give rise to the passing of a turbid fluid through the filter. Wash the precipitate with hot water, until the last washings remain clear upon addition of chloride of barium. Dry the precipitate, and proceed in the way indicated in § 35.

It is sometimes desirable to precipitate baryta with sulphuric acid, in a more rapid and expeditious way than the one just now described. This may be effected by heating the baryta solution in a porcelain dish, or in an appropriate glass-vessel, to incipient ebullition, adding a sufficient quantity of dilute sulphuric acid, and keeping the mixture for a few minutes in gentle ebullition,—when the precipitated sulphate of baryta will at once completely subside. The supernatant clear fluid is then passed through the filter, the precipitate is treated with water, or also, as the case may require, with dilute hydrochloric acid, and the mixture heated once more. The precipitate is then finally transferred to the filter. With this way of proceeding the filtrate is rarely turbid.

b. By evaporation.

Add to the solution, in a weighed platinum dish, pure sulphuric acid

very slightly in excess, and evaporate in the water-bath; expel the excess of sulphuric acid by cautious application of heat, and ignite the residue.

For the properties of sulphate of baryta, see § 50.

Both methods, if properly and carefully executed, give almost absolutely accurate results.

2. *Determination as carbonate of baryta.*

a. In solutions.

Mix the moderately dilute solution of the baryta salt in a beaker-glass with ammonia, add carbonate of ammonia in moderate excess, and let the mixture stand several hours in a warm place. Filter, wash the precipitate with water mixed with a little ammonia, dry, and ignite (§ 36).

For the properties of the precipitate, see § 50. This method involves a trifling loss of substance, as the carbonate of baryta is not absolutely insoluble in water. It is, however, more expeditious and convenient than the precipitation with sulphuric acid. The direct experiment, No. 56, gave 99·79 instead of 100 parts of baryta.

If the solution happens to contain a notable quantity of ammoniacal salts, the loss incurred is much more considerable, since the presence of such salts greatly increases the solubility of the carbonate of baryta.

b. In salts of baryta with organic acids.

Heat the salt slowly in a covered platinum crucible, until no more fumes are evolved; place the crucible obliquely, with the lid leaning against it, and heat to redness, until the whole of the carbon is consumed, and the residue presents a perfectly white appearance; moisten the residue with a concentrated solution of carbonate of ammonia, evaporate, ignite the residue gently, and weigh. The results obtained by this method are quite satisfactory. The direct experiment, No. 57, gave 99·61 instead of 100 parts of baryta. The loss of substance which almost invariably attends this method, is owing to particles of the salt being carried off along with the fumes evolved upon ignition, and is accordingly the less considerable, the more slowly and gradually the heat is increased. Omission of the moistening the residue with carbonate of ammonia would involve a further loss of substance, as the ignition of carbonate of baryta in contact with carbon, is attended with formation of some caustic baryta, and evolution of carbonic oxide gas.

§ 80.

2. STRONTIA.

a. Solution.

See the preceding paragraph (§ 79, *a.*—Solution of baryta), the directions given there applying equally here.

b. Determination of weight.

Strontia is weighed either as *sulphate* or as *carbonate of strontia* (§ 51).

We may convert into

1. SULPHATE OF STRONTIA.

a. By precipitation.

All compounds of strontia, without exception.

b. By evaporation.

All salts of strontia with volatile acids, if no other non-volatile body is present.

2. CARBONATE OF STRONTIA.

α. All compounds of strontia soluble in water.

β. Salts of strontia with organic acids.

The method based on the precipitation of strontia with sulphuric acid, yields accurate results only in cases where the fluid from which the strontia is to be precipitated, may be mixed, without detriment, with alcohol. Where this cannot be done, and where the method based on the evaporation of the solution of strontia with sulphuric acid, is equally inadmissible, the conversion into the carbonate ought to be resorted to in preference, in the case of soluble compounds of strontia and of salts of strontia with organic acids.

1. *Determination as sulphate of strontia.*

a. By precipitation.

Mix the solution of the salt of strontia (which must not be too dilute), with dilute sulphuric acid in excess, in a beaker-glass, and add a volume of alcohol, at least equal to that of the fluid present; let the mixture stand a few hours, and filter; wash the precipitate with dilute spirits of wine, dry, and ignite, and weigh the residue (§ 35).

If the circumstances of the case contra-indicate the use of alcohol, the fluid must be precipitated in a tolerably concentrated state, allowed to stand in the cold for at least twenty-four hours, filtered, and the precipitate washed with cold water, until the last rinsings manifest no longer an acid reaction, and leave no perceptible residue upon evaporation. If traces of free sulphuric acid remain adhering to the filter, the latter turns black, on drying, and crumbles to pieces; too long protracted washing of the precipitate, on the other hand, tends to increase the loss of substance inseparable from the application of this method in cases where the use of alcohol is inadmissible.

Care must be taken that the precipitate be thoroughly dry, before proceeding to ignite it; otherwise it will be apt to throw off fine particles during the latter process. The filter, which is to be consumed on the lid of the crucible, must be scraped as clean as possible, or else some loss of substance will be incurred; as may be clearly seen from the depth of the carmine tint of the flame with which the filter burns if the precipitate has not been properly removed from it.

For the properties of the precipitate, see § 51. This method gives very accurate results in cases where the addition of alcohol to the solution is admissible; but where we have to deal with a simple aqueous solution, a rather considerable loss is unavoidable, as sulphate of strontia is not absolutely insoluble in water. The direct experiments, noted sub No. 58, gave only 98·12 and 98·02 instead of 100 parts of strontia. However, the error may, in a great measure, be rectified, by calculating the amount of sulphate of strontia dissolved in the filtrate and the rinsing water, basing the calculation upon the known degree of solubility of sulphate of strontia in pure water and in acidified water. See Experiment No. 59, which gave 99·77 instead of 100 parts of strontia.

b. By evaporation.

The same method as described § 79, 1 *b*.

2. *Determination as carbonate of strontia.*

a. In solutions.

The same method as described § 79, 2 *a*. For the properties of the precipitate, see § 51. The method gives very accurate results, as carbonate of strontia is nearly absolutely insoluble in water containing ammonia and carbonate of ammonia. The direct experiment No. 60, gave 99·82 instead of 100 parts of strontia. Presence of ammoniacal salts exercises here a less adverse influence, than in the precipitation of carbonate of baryta.

b. In salts with organic acids.

The same method as described § 79, 2 *b*.

§ 81.

3. LIME.

a. Solution.

See § 79 *a*.—Solution of baryta. Fluoride of calcium is, by means of sulphuric acid, converted into sulphate of lime, and the latter again, if necessary, decomposed by fluxing with an alkaline carbonate.

b. Determination of weight.

Lime is weighed either as *sulphate* or as *carbonate of lime* (§ 52).

We may convert into

1. SULPHATE OF LIME.

a. By precipitation.

All salts of lime with acids soluble in alcohol, provided no other substance insoluble in alcohol, be present.

b. By evaporation.

All salts of lime with volatile acids, provided no non-volatile body be present.

2. CARBONATE OF LIME.

a. By precipitation with carbonate of ammonia.

All salts of lime soluble in water.

b. By precipitation with oxalate of ammonia.

All salts of lime soluble in water, or in hydrochloric acid.

c. By ignition.

Salts of lime with organic acids.

Of these several methods, that sub. 2 *b*. (precipitation with oxalate of ammonia) is the one most frequently resorted to. This, and the method 1 *b*, give the most accurate results. The method 1 *a*, is usually resorted to only to effect the separation of lime from other bases; 2 *a*, generally only to effect the separation of lime in conjunction with other alkaline earths from the alkalies.

1. *Determination as sulphate of lime.*

a. By precipitation.

Mix the solution of lime in a beaker-glass, with dilute sulphuric acid in excess, and add twice its volume of alcohol; let the mixture stand twelve hours, filter, and thoroughly wash the precipitate with spirits of wine, dry and ignite moderately (§ 36). For the properties of the precipitate, see § 52. The results are very accurate. The direct experiment, No. 61, gave 99·64 instead of 100 parts of lime.

b. By evaporation.

The same method as described § 79, 1 *b*.

2. *Determination as carbonate of lime.*

a. By precipitation with carbonate of ammonia.

The same method as described § 79, 2 *a*. The precipitate must be exposed only to a very gentle red heat, but this must be continued for some time. For the properties of the precipitate, see § 52.

This method gives very accurate results, the loss of substance incurred being hardly worth mentioning.

If the solution happens to contain chloride of ammonium, or similar ammoniacal salts in considerable proportion, the loss of substance incurred is greater. The same is the case if the precipitate is washed with ammoniacal water instead of pure water. The direct experiment, No. 62, in which ammoniacal water was used, gave 99·17 instead of 100 parts of lime.

b. By precipitation with oxalate of ammonia.

α. The lime salt is soluble in water.

Dissolve the salt in hot water, in a beaker-glass; add oxalate of ammonia in moderate excess, and then ammonia sufficient to impart an ammoniacal smell to the fluid; cover the glass, and let it stand in a warm place until the precipitate has completely subsided, which will require twelve hours, at least. Transfer the precipitate now to the filter, with the aid of hot water, in the manner described § 79, 1 *a*. (sulphate of baryta). Small particles of the precipitate that may happen to remain adhering to the glass so firmly that they cannot be removed by mechanical means, had best be dissolved in a small vessel, in a few drops of highly dilute hydro-

chloric acid, ammonia added to the solution, and the precipitate formed added to the first. After having washed the precipitate, dry it on the filter in the funnel, and transfer the dry precipitate to a platinum crucible, taking care to scrape the filter as clean as may be practicable; burn the filter on the lid, and then put the latter inverted on the crucible, to prevent the filter ashes mixing with the precipitate; apply now a gentle heat, and increase this gradually until the bottom of the crucible exhibits a faint red appearance. Keep it at that temperature from ten to fifteen minutes, then let it cool, and weigh. After this, moisten the contents of the crucible, which must be perfectly white, or, at all events, show only the least tinge of gray, with a little water, and test this after a time with a very small slip of turmeric paper. If the color of the test paper remains unaltered, the process may be considered at an end, and the result taken as correct; but should the paper turn brown—a sign that the heat applied was too intense—rinse off the fluid adhering to the paper with a little water into a crucible, throw in a small lump of pure carbonate of ammonia, evaporate to dryness (best in the water-bath), heat to faint redness, and weigh the residue. If the weight shows an increase over that of the first residue, which is almost invariably the case under these circumstances, you had always better ascertain by renewed gentle ignition and subsequent weighing, whether this increase of weight was really owing to absorption of carbonic acid, or to imperfect expulsion of the water. This method, if properly and carefully performed, gives nearly absolutely accurate results, and if the application of heat is properly managed, there is no need of the tedious supplementary operation recommended here—evaporation with carbonate of ammonia. The direct experiment, No. 63, gave 99·99 instead of 100 parts of lime.

For the properties of the precipitate and residue see § 52.

If the quantity of oxalate of lime obtained is only very trifling I prefer to convert that salt into the sulphate. To this end, the residue is strongly ignited together with the filter, in a platinum crucible; some water is then added, and a little hydrochloric acid, until the residue is dissolved; the solution is mixed with pure dilute sulphuric acid as slightly in excess as possible. The mixture is then evaporated, first in the water-bath, afterwards cautiously over the lamp; the residue is finally heated to a moderate degree of redness.

Many chemists prefer collecting the oxalate of lime upon a weighed filter, to dry at 212°, and to weigh the dry precipitate. This precipitate is not, as is often erroneously supposed, CaO, C_2O_3, but, $CaO, C_2O_3 + aq.$, and must therefore be calculated as such.

This method gives less accurate results than that based on the conversion of the oxalate into the carbonate. The direct experiment, No. 64, gave 100·45 instead of 100 parts of lime.

β. The salt is insoluble in water.

Dissolve the salt in dilute hydrochloric acid. If the acid combined with the lime, is of a nature to escape in this operation (carbonic acid for instance), or to admit of its separation by evaporation (silicic acid for instance), proceed, after the removal of the acid, as directed, sub *a*. But if the acid is of more stable nature (phosphoric acid, for instance), neutralize the free acid present with ammonia until a precipitate commences to form, re-dissolve this again with a drop of hydrochloric acid, add oxalate of ammonia in excess, and finally acetate of soda; allow the precipitate to deposit, and proceed for the remainder of the operation as directed, sub *a*. In this process the free hydrochloric acid present combines with the ammonia and soda of the oxalate and acetate, liberating a corresponding quantity of oxalic acid and acetic acid, in which acids oxalate of lime is nearly insoluble. The method yields pretty accurate results. The direct Experiment, No. 65, gave 99·78 instead of 100 parts of lime.

c. By ignition.

The same method as described § 79, 2 *b* (baryta). The residue remaining upon evaporation with carbonate of ammonia (which operation it is advisable to perform twice), must be ignited very gently.

§ 82.

4. MAGNESIA.

a. Solution.

Many of the compounds of magnesia are soluble in water; those which are insoluble in that menstruum, dissolve in hydrochloric acid, with the exception of some silicates.

b. Determination of weight.

Magnesia is weighed either as *sulphate of magnesia*, as *pyrophosphate*, or as *pure magnesia*.

We may convert into

1. SULPHATE OF MAGNESIA.

a. Directly.

All compounds of magnesia with volatile acids, provided no other non-volatile substance be present.

b. Indirectly.

All compounds of magnesia soluble in water, and likewise those which, insoluble in that menstruum, dissolve in hydrochloric acid, with separation of their acid (in case no ammoniacal salts are present).

2. PYROPHOSPHATE OF MAGNESIA.

All compounds of magnesia without exception

3. PURE MAGNESIA.

a. Salts of magnesia with organic acids, or with readily volatile inorganic oxygen acids.

b. Chloride of magnesium, and the compounds of magnesia convertible into that salt.

The direct determination as sulphate of magnesia is to be highly recommended in all cases where it is applicable. The indirect conversion into the sulphate, serves only to separate magnesia from certain bases, and is hardly ever had recourse to where it can possibly be avoided. The method based on the conversion of the magnesia compound into the pyrophosphate is most generally resorted to; especially also to effect the separation of magnesia from other bases. The method based on the conversion of chloride of magnesium into pure magnesia is usually resorted to only to effect the separation of magnesia from the fixed alkalies. Compounds of magnesia with phosphoric acid are analysed as § 106 directs.

1. *Determination as sulphate of magnesia.*

a. *Direct determination.*

Add to the solution of magnesia a more than sufficient amount of dilute pure sulphuric acid to combine with the whole of the magnesia present, evaporate the mixture to dryness, in a weighed platinum dish, in the water-bath; put the lid on, and heat cautiously until the excess of sulphuric acid is completely expelled; heat the residue now over the lamp for some time to gentle redness; let it cool, and weigh. Should no sulphuric acid fumes escape, upon heating, this may be looked upon as a sure sign that the sulphuric acid has not been added in sufficient quantity, in which case the mixture is allowed to cool, and a fresh portion of sulphuric acid added to it. The method yields very accurate results. Care must be taken not to use an over large quantity of sulphuric acid, since this would tend to protract the process unnecessarily; the residue must be exposed to a moderate red heat only, and weighed as soon as it is cold. For the properties of the residue, see § 53.

b. *Indirect determination.*

The solution of magnesia is heated in a flask to 212°, and clear saturated water of baryta is added in excess; the temperature is maintained for some time near the boiling point; the fluid is then filtered off from the precipitate, and the latter carefully washed with boiling water, and subsequently dissolved upon the filter with somewhat dilute hot hydrochloric acid; the filter is carefully washed, and the further operation conducted as directed sub *a*. Should a precipitate of sulphate of baryta form, upon the addition of the sulphuric acid, this may be considered a sign that the carbonic acid of the air had not been sufficiently excluded from contact with the water of baryta during the operation. In that case, we may either

allow this precipitate to subside, filter off from it, and evaporate the filtrate, or we may evaporate at once, weigh the residue, wash it with water, filter the solution off from the undissolved sulphate of baryta, ascertain the weight of the latter (§ 79, 1 *a*.), and subtract this from the original residue.

The results obtained by this method fall somewhat short of 100, since hydrated magnesia is not quite insoluble in water. The method is, moreover, rather too complicated to yield perfectly accurate results. (Compare § 121, *a*).

2. *Determination as pyrophosphate of magnesia.*

The solution of the salt of magnesia, which it is intended to convert into the pyrophosphate, is mixed, in a beaker-glass, with chloride of ammonium and ammonia added in slight excess. Should a precipitate form upon the addition of ammonia, this may be considered a sign that a sufficient amount of chloride of ammonium has not been used; a fresh amount of that salt must consequently be added, sufficient to effect the re-solution of the precipitate formed. The fluid is then mixed with a solution of phosphate of soda in excess, and the mixture stirred with a glass rod, taking care to avoid touching the sides of the beaker-glass with the stirring-rod otherwise particles of the precipitate will be apt to adhere so firmly to the rubbed parts of the glass, that it will be found difficult to remove them; the glass is then well covered, and allowed to stand at rest for twelve hours, in a moderately warm place; after the lapse of that time, the fluid is filtered off from the precipitate, taking care to collect every particle of the latter upon the filter; when the fluid has completely drained off, water mixed with one-fifth of solution of ammonia is poured upon the precipitate on the filter, and allowed to drain off; this operation is repeated until the fluid running through the filter ceases to leave a residue when evaporated upon a platinum knife.

The precipitate is now completely dried, and then transferred to a platinum crucible (§ 36); the latter, with the lid leaning against it, is then exposed for some time to a very gentle heat, which is finally increased to intense redness. The filter is incinerated upon the lid of the crucible, an operation requiring some patience, since the filter is difficult of combustion. The lid is now put on inverted, and the crucible once more exposed to a red heat; the crucible is then allowed to cool, and the weight of the residue ascertained.

For the properties of the precipitate and residue, see § 53.

This method, if properly executed, yields most accurate results.

The direct experiments, No. 66 *a* and *b*, gave respectively 100·09 and 99·97, instead of 100 parts of magnesia.

3. *Determination as pure magnesia.*

a. In salts of magnesia with organic acids.

The salt of magnesia, which it is intended to reduce to the state of pure magnesia, is gently heated in a covered platinum crucible, increasing the

temperature gradually, until the evolution of empyreumatic products ceases; the lid is then removed from the crucible, and the latter placed in an oblique position, with the lid leaning against it. A red heat is now applied, until the residue presents a perfectly white appearance. For the properties of the residue, see § 53. The method yields pretty accurate results, provided the application of heat be managed slowly and gradually. Some loss of substance is usually sustained, owing to traces of the salt being carried off along with the empyreumatic products. Salts of magnesia with readily volatile oxygen acids, may be reduced to magnesia in a similar way, by simple ignition.

b. Conversion of chloride of magnesium into pure magnesia.

The concentrated solution of chloride of magnesium is mixed in a porcelain crucible, with pure oxide of mercury, reduced to the very finest powder, by trituration with water, and elutriation, and added in proportion more than sufficient to convert by its oxygen the whole of the magnesium present into magnesia. The mixture is evaporated in the water-bath, and the residue thoroughly dried; the crucible is now covered, and exposed to a red heat, until the chloride of mercury formed is expelled, together with the excess of oxide of mercury. The operator should carefully guard against inhaling the fumes evolved. The residue is either weighed at once in the crucible, or, if the operation had for its end the separation of magnesia from the alkalies, it is collected upon a filter, washed with hot water, dried, and ignited (§ 35.)

THIRD GROUP OF THE BASES.

ALUMINA—SESQUIOXIDE OF CHROMIUM.

§ 83.

1. ALUMINA.

a. Solution.

Those of the compounds of alumina which are insoluble in water, dissolve, almost without exception, in hydrochloric acid. Native crystallized alumina (sapphire, ruby, &c.), and many native alumina compounds, and also alumina artificially produced after intense ignition, require fluxing with carbonate of soda, caustic potassa, or hydrate of baryta, as a preliminary step to their solution in hydrochloric acid. Many of the alumina compounds are fluxed more advantageously with bisulphate of potassa. (Compare § 22.)

b. Determination of weight.

Alumina is invariably weighed in the pure state (§ 54). The several compounds of alumina are converted into pure alumina, either by precipitation as hydrate of alumina, and subsequent ignition, or by simple ignition.

We may convert into

PURE ALUMINA.

a. By precipitation.

All compounds of alumina soluble in water, and those which insoluble in that menstruum, dissolve in hydrochloric acid, with separation of their acid.

b. By ignition.

α. All salts of alumina, with readily volatile acids (sesquichloride of aluminium, nitrate of alumina, &c.)

β. All salts of alumina with organic acids.

The methods *b*, *α* and *β*, are applicable only in cases where no other fixed substances are present. The method of estimating alumina in its combinations with phosphoric acid, boracic acid, silicic acid, and chromic acid, will be found in Part II. of this section, under the respective heads of these several acids.

Determination as pure alumina.

a. By precipitation.

Mix the moderately dilute solution of alumina in a beaker-glass, with a considerable quantity of chloride of ammonium, add ammonia *slightly* in excess, expose the mixture for some time to a temperature approaching boiling heat, filter, wash the precipitate with hot water, dry it thoroughly, ignite (§ 35), and weigh. The heat applied must be very gentle at first, and the crucible kept well covered, to guard against the risk of loss of substance from spirting, which is always to be apprehended if the precipitate is not *thoroughly* dry. In the case of sulphate of alumina, the washed precipitate must be redissolved in hydrochloric acid, and reprecipitated with ammonia,* before we can proceed to ignite and weigh it. If this supplementary process is not attended to, the precipitate will always, and despite of the most intense ignition, retain sulphuric acid. For the properties of the precipitate and residue, see § 54. The method, if properly executed, gives very accurate results. But if a considerable excess of ammonia is used, more particularly when no ammoniacal salts are present, and when the addition of chloride of ammonium has been omitted, a very considerable loss is likely to be incurred; this loss is the greater the more dilute the solution, and the shorter the time which elapses between the precipitation and filtration (§ 54).

b. By direct ignition.

α. Compounds of alumina with volatile acids.

aa. In the solid state.

Expose the salt (in the case of sesquichloride of aluminium, after previous addition of water) in a platinum crucible to a red heat, gentle at first, but increased gradually to the very highest degree of intensity, until the weight remains constant. For the properties of the residue, see § 54. The

* Some chemists prefer using carbonate of ammonia in the second precipitation.

purity of the residue must be carefully tested. This method gives accurate results.

bb. In solution.

Evaporate the solution to dryness in the water-bath, and proceed with the residue as directed sub *aa*.

β. Compounds of alumina with organic acids.

The same method as described § 82, 3. *a* (Magnesia).

§ 84.

2. SESQUIOXIDE OF CHROMIUM.

a. Solution.

Many of the compounds of sesquioxide of chromium are soluble in water. Hydrated sesquioxide of chromium, and most of the salts of sesquioxide of chromium insoluble in water, dissolve in hydrochloric acid. Ignition renders sesquioxide of chromium, and many of its salts, insoluble in acids; this insoluble modification must be prepared for solution in hydrochloric acid, by fluxing with carbonate of soda (§ 22 *a*). A small quantity of sesquioxide of chromium is converted, in the process of fluxing, into chromic acid, by the action of the air; this is, however, reduced again to sesquioxide, upon heating with hydrochloric acid. Addition of alcohol greatly promotes this reduction.

b. Determination.

Sesquioxide of chromium may be weighed in the *pure state*, or it may be converted into *chromic acid*, and its weight calculated from the amount of the latter (see § 104). The several compounds of sesquioxide of chromium are reduced to the sesquioxide either by precipitation as hydrated sesquioxide, and subsequent ignition, or by simple ignition.

We may convert into

1. PURE SESQUIOXIDE OF CHROMIUM.

a. By precipitation.

All compounds of sesquioxide of chromium soluble in water, and also those which insoluble in that menstruum, dissolve in hydrochloric acid, with separation of their acid.

b. By ignition.

α. All salts of sesquioxide of chromium with volatile oxygen acids, provided no non-volatile substances be present.

β. Salts of sesquioxide of chromium with organic acids.

2. CHROMIC ACID, or more correctly speaking, ALKALINE CHROMATE.

Sesquioxide of chromium and all its compounds.

The methods of estimating the sesquioxide of chromium in its combinations with chromic acid, phosphoric acid, boracic acid, and silicic acid, will be found in Part II. of this section, under the respective heads of these several acids.

1. *Determination as sesquioxide of chromium.*

a. By precipitation.

The salt is dissolved in a beaker-glass, and the solution, which must not be too highly concentrated, heated to 212°. Ammonia is then added slightly in excess, and the mixture exposed for half an hour to a temperature approaching boiling heat. After this the fluid is filtered off from the precipitate, and the latter well washed with hot water, thoroughly dried, and ignited (§ 35). The heat must be increased gradually, and the crucible kept covered, otherwise some loss of substance is likely to arise from spirting, upon the incandescence of the sesquioxide of chromium which marks the passing of the soluble into the insoluble modification. Care must be taken, also, not to filter until the liquid is *perfectly colorless*. If the fluid be passed through the filter whilst it looks still reddish, a perceptible loss of substance will be incurred. For the properties of the precipitate and residue, see § 55. This method, if properly executed, gives very accurate results.

b. By direct ignition.

a. Salts of sesquioxide of chromium with volatile acids.

The same method as described, § 83, *b. a* (Alumina).

b. Salts of sesquioxide of chromium with organic acids.

The same method as described, § 82, 3. *a* (Magnesia).

2. CONVERSION OF SESQUIOXIDE OF CHROMIUM INTO ALKALINE CHROMATE.

(For the estimation of chromic acid, see § 104.)

The two following methods have been proposed to effect the conversion of sesquioxide of chromium into alkaline chromate.

a. The solution of the salt of sesquioxide of chromium is mixed with solution of potassa, or soda in excess, until the hydrated sesquioxide, which forms at first, is redissolved. Chlorine gas is then conducted into the cold fluid until it acquires a yellowish red tint; it is then mixed with potassa or soda in excess, and the mixture evaporated to dryness; the residue is ignited in a platinum crucible. The whole of the chlorate of potassa (or soda) formed is thereby decomposed, and the residue consists, accordingly, now of an alkaline chromate and chloride of potassium (or sodium).—(*Vohl.*)

b. Hydrate of potassa is heated in a silver crucible to calm fusion; the heat is then somewhat moderated, and the perfectly dry compound of sesquioxide of chromium put into the crucible. When the sesquioxide of chromium is thoroughly moistened with the hydrated potassa, small lumps of fused chlorate of potassa are added. A lively effervescence ensues from the escape of oxygen; at the same time the mass acquires a more and more yellow color, and becomes, finally, clear and transparent. Loss of substance must be carefully guarded against.—(*H. Schwarz.*)

Titanic Acid fused with KHO
Ti 61.2
O2 38.8
3rd Edition

FOURTH GROUP OF THE BASES.

OXIDE OF ZINC—PROTOXIDE OF MANGANESE—PROTOXIDE OF NICKEL—PROTOXIDE OF COBALT—PROTOXIDE OF IRON—SESQUIOXIDE OF IRON.

§ 85.

1. OXIDE OF ZINC.

a. Solution.

Many of the salts of zinc are soluble in water. Metallic zinc, oxide of zinc, and the salts of zinc, which are insoluble in water, dissolve in hydrochloric acid.

b. Determination.

Oxide of zinc is invariably weighed as such (§ 56). The conversion of the salts of zinc into the oxide is effected either by precipitation as carbonate or sulphide of zinc, or by direct ignition.

We may convert into

OXIDE OF ZINC.

a. By precipitation as carbonate of zinc.

All the salts of zinc which are soluble in water, and all those with organic volatile acids; likewise those salts of zinc which, insoluble in water, dissolve in hydrochloric acid, with separation of their acid.

b. By precipitation as sulphide of zinc.

All compounds of zinc without exception.

c. By direct ignition.

Salts of zinc with inorganic volatile oxygen acids.

The last method is to be recommended only for carbonate of zinc and nitrate of zinc. Sulphide of zinc and sulphate of zinc require a white heat for their complete conversion into the oxide (the former with access of air). The method *b.* is only resorted to in cases where *a.* is inadmissible. It serves more especially to separate oxide of zinc from other bases. Salts of zinc with organic acids must not be converted into the oxide by ignition, since this process would cause the reduction of a small portion of the oxide to the metallic state, and its dissipation in vapor. If the acids are volatile, the zinc may be determined at once according to method *a.*; if, on the contrary, the acids are non-volatile, the zinc may either be precipitated as sulphide, or the salt under examination may be heated to gentle redness, the residue extracted with nitric acid, and the solution treated according to *a.* or *c.* The methods of estimating the oxide of zinc in its combinations with chromic acid, phosphoric acid,

boracic acid, and silicic acid, will be found in Part II. of this section, under the respective heads of these several acids.

Determination as oxide of zinc.

a. By precipitation as carbonate of zinc.

Heat the moderately dilute solution of the salt of zinc under examination nearly to ebullition, in a high and capacious flask; add, drop by drop, carbonate of soda in excess; place the flask obliquely, and boil the contents a few minutes; filter off the fluid, wash the precipitate with hot water, dry and ignite it, as directed § 36, taking care, more particularly, to scrape the filter as clean as may be practicable, before proceeding to incinerate it. Should the solution contain ammoniacal salts, the ebullition must be continued until, upon a fresh addition of the carbonate of soda, the escaping vapor no longer imparts a brown tint to turmeric paper. If the quantity of ammoniacal salts present is considerable, the fluid must be evaporated *boiling* to dryness, the flask being kept all the while in an oblique position. It is, therefore, in such cases almost more convenient to precipitate the zinc as sulphide (see *b.*).

The presence of a great excess of acid in the solution of zinc must be as much as possible guarded against, that the effervescence from the escaping carbonic acid gas may not be too impetuous. The filtrate must be tested with sulphide of ammonium, to ascertain whether the whole of the zinc has been precipitated; a *slight* precipitate will indeed *invariably* form upon the application of this test; but, if the process has been properly conducted, this is so insignificant that it may be altogether disregarded, being limited to some exceedingly slight and imponderable flakes, which moreover make their appearance only after many hours' standing (comp. § 56). If the precipitate is more considerable, however, it must be treated as directed sub *b.*, and the weight of the oxide of zinc obtained added to that of the first process. For the properties of the precipitate and residue, see § 56. This method yields pretty accurate results, though the numbers found in most cases are a little below those given by theoretical calculation, as the precipitation is never *absolutely* complete, and as particles of the precipitate will always and unavoidably adhere to the filter, which exposes them to the chance of reduction and volatilization during the process of ignition. On the other hand, the results show sometimes also an *excess* over the numbers theoretically calculated; this is owing to defective washing of the precipitate, as may be seen from the alkaline reaction which the residue manifests in such cases.

b. By precipitation as sulphide of zinc.

Mix the solution of zinc with ammonia until the precipitate which forms at first is redissolved; add sulphide of ammonium in excess, let the precipitate subside, decant the supernatant fluid off on the filter, transfer

the precipitate to the latter, and wash it with water containing sulphide of ammonium; put the moist filter with the precipitate in a beaker-glass, and treat it with concentrated hydrochloric acid slightly in excess. Put the glass now in a moderately warm place, until the solution smells no longer of sulphuretted hydrogen; dilute the fluid with a little water, filter, wash the original filter with hot water, and proceed with the solution of chloride of zinc obtained, as directed sub *a*.

From a solution of acetate of zinc the metal may be precipitated completely, or nearly so, with sulphuretted hydrogen gas, even if an excess of acetic acid happens to be present, provided always no other acid be present. The precipitated sulphide of zinc is washed with water impregnated with sulphuretted hydrogen, and, for the rest, treated exactly like the sulphide of zinc obtained by precipitation with sulphide of ammonium. (Compare the Experiments, sub No. 67.)

Small quantities of sulphide of zinc may be converted directly into the oxide, by intense ignition, with free access of air.

c. By direct ignition.

Expose the salt in a covered platinum crucible to a gentle heat at first, which is gradually increased to the highest degree of intensity, until the weight of the residue remains constant.

§ 86.

2. PROTOXIDE OF MANGANESE.

a. Solution.

Many of the salts of protoxide of manganese are soluble in water. The pure protoxide, and those of its salts which are insoluble in that menstruum, dissolve in hydrochloric acid, which dissolves also the higher oxides of manganese. The solution of the higher oxides is attended with evolution of chlorine, and the fluid, after previous application of heat, is found to contain protochloride of manganese.

b. Determination.

Manganese is weighed either as *sulphate of protoxide of manganese*, or as *protosesquioxide of manganese* (§ 57). Into the latter form it is converted either by precipitation as hydrated protoxide, or as carbonate of the protoxide (sometimes preceded, in the latter case, by precipitation as sulphide of manganese), and subsequent ignition, or by direct ignition.

We may convert into

1. PROTOSESQUIOXIDE OF MANGANESE.

a. By precipitation as carbonate of protoxide of manganese.

All the soluble salts of manganese with inorganic acids, and all its salts with volatile organic acids;

b. By precipitation as hydrated protoxide of manganese.

All the compounds of manganese, with the exception of its salts with non-volatile organic acids.

likewise those of its salts which, insoluble in water, dissolve in hydrochloric acid, with separation of their acid.

c. By precipitation as sulphide of manganese.

All compounds of manganese without exception.

d. By direct ignition.

All oxygen compounds of manganese; salts of manganese with readily volatile acids, and with organic acids.

2. SULPHATE OF PROTOXIDE OF MANGANESE.

All the oxides of manganese, and likewise all its salts with volatile acids, provided no non-volatile substance be present.

The method 1 *d.* is the most simple and accurate, and is therefore preferred to all others, wherever it is admissible. The method 2, is convenient and expeditious, but its results are not absolutely accurate. The method 1 *c.* is resorted to only in cases where the application of none of the other methods is admissible. 1 *a.* is generally preferred to 1 *b.* in cases where the choice is permitted. If the solution of manganese contains sugar or some similar non-volatile organic substance, neither 1 *a.* nor 1 *b.* is applicable, and recourse must be had to 1 *c.* The phosphate and borate of protoxide of manganese, are treated either according to the directions of 1 *b.* or to those of 1 *c.* The proportion of manganese in the silicate of the protoxide, is determined after the separation of the silicic acid (§ 111), according to the directions of 1 *a.* For the analysis of chromate of protoxide of manganese, see § 104 (chromic acid).

1. *Determination as protosesquioxide of manganese.*

a. By precipitation as carbonate of protoxide of manganese.

The solution of the salt under examination is heated to 212°, and is then mixed with carbonate of soda in excess, the application of heat being continued for some time longer—actual ebullition not being necessary; the fluid is then filtered off from the precipitate formed, and the latter is washed, dried, and ignited, as directed § 35. The lid is removed from the crucible, and the heat maintained at a high degree of intensity, until the weight of the residue remains constant. If the solution contains ammoniacal salts, it must be precipitated in a flask, and the process conducted exactly as directed for the precipitation of zinc as carbonate under similar circumstances (see § 85 *a*). For the properties of the precipitate and residue, see § 57. This method, if properly executed, gives accurate results.

b. By precipitation as hydrated protoxide of manganese.

Precipitate the solution of the salt under examination by solution of soda or potassa, and proceed in all other respects as directed sub *a.*

If phosphoric acid is present, or boracic acid, the solution must be precipitated in a flask, and the precipitated fluid kept boiling for some time with an excess of soda or potassa, which will effect the complete decomposition of the phosphate or borate of protoxide of manganese.—For the properties of the precipitate see § 57. The method gives accurate results.

c. By precipitation as sulphide of manganese.

Mix the manganese solution with chloride of ammonium, and then with ammonia, until the alkali predominates; add yellow sulphide of ammonium in moderate excess; let the precipitate formed subside; decant the supernatant fluid on the filter, transfer the precipitate to the latter, and wash it thoroughly, and without interruption, with water mixed with a little yellow sulphide of ammonium. Put the moist filter with the precipitate into a beaker-glass, and treat it with dilute hydrochloric acid; apply heat until the mixture smells no longer of sulphuretted hydrogen, wash the residuary paper carefully, and proceed with the filtrate as directed sub *a*.

d. By direct ignition.

The manganese compound under examination is introduced into a platinum crucible, which is kept closely covered at first, and exposed to a gentle heat; after a time, the lid is taken off, and replaced loosely on the crucible, and the heat is increased to the highest degree of intensity, until the weight of the residue remains constant. The conversion of the higher oxides of manganese into protosesquioxide of manganese requires a more intense heat and a more protracted application of it than the conversion of the protoxide and sesquioxide. In the case of salts of manganese with organic acids, care must always be taken to ascertain whether the whole of the carbon has been consumed; and should the contrary turn out to be the case, the residue must either be redissolved in hydrochloric acid, and the solution precipitated, &c., as directed sub *a*, or it must be repeatedly evaporated with nitric acid, until the whole of the carbon is oxidized. The method, if properly executed, gives accurate results. In the ignition of salts of manganese with organic acids, minute particles of the salt are generally carried off along with the empyreumatic products evolved in the process, which, of course, tends to reduce the weight.

2. *Determination as sulphate of protoxide of manganese.*

The same method as described § 82, 1. *a*. For the properties of the residue, see § 57. Care must be taken, more particularly, to expose the residue to a faint red heat only, as a stronger degree of heat is liable to cause the expulsion of a minute quantity of sulphuric acid, which, of course, would tend to reduce the resulting number.

§ 87.

3. PROTOXIDE OF NICKEL.

a. Solution.

Many of the salts of protoxide of nickel are soluble in water. The pure protoxide, and those of its salts which are insoluble in that menstruum, dissolve, without exception, in hydrochloric acid. Metallic nickel dissolves slowly, with evolution of hydrogen gas, when heated with dilute hydrochloric or sulphuric acid; in nitric acid it dissolves with great readiness. Sulphide of nickel is but sparingly soluble in hydrochloric acid, but it dissolves readily in nitrohydrochloric acid. Peroxide of nickel dissolves in hydrochloric acid, upon the application of heat, to protochloride, the solution being attended with evolution of chlorine.

b. Determination.

Protoxide of nickel is always weighed as such (§ 58). The compounds of nickel are converted into the pure protoxide, either by precipitation as hydrated protoxide, preceded, in some instances, by precipitation as sulphide of nickel, or by ignition.

We may convert into

PROTOXIDE OF NICKEL.

a. By precipitation as hydrated protoxide of nickel.

All the salts of nickel with inorganic acids which are soluble in water, and all its salts with volatile organic acids; likewise all salts of nickel which, insoluble in water, dissolve in the stronger acids, with separation of their acid.

b. By precipitation as sulphide of nickel.

All compounds of nickel without exception.

c. By ignition.

The salts of nickel with organic acids, and with readily volatile oxygen acids, or with such oxygen acids as are decomposed at a high temperature (carbonic acid, nitric acid).

The method *c*, wherever it is applicable, is preferable to the other methods, more especially in the case of salts of nickel with the inorganic acids pointed out sub *c*. The method *a* is most frequently resorted to. If sugar or other non-volatile organic substances happen to be present, they must either be destroyed by ignition before proceeding to the solution and precipitation of the compound under examination, or the method *b*, of which the application otherwise is almost exclusively confined to effect the separation of the protoxide of nickel from other bases, must be resorted to. The methods of estimating the protoxide of nickel in its

combinations with chromic acid, phosphoric acid, boracic acid, and silicic acid, will be found in Part II. of this section, under the respective heads of these several acids.

Determination as protoxide of nickel.

a. By precipitation as hydrated protoxide of nickel.

Mix the solution of nickel in a beaker-glass with pure solution of potassa or soda in excess, heat for some time to near ebullition, filter, wash the precipitate thoroughly with hot water, dry and ignite (§ 35). Presence of ammoniacal salts, or of free ammonia, does not interfere with the precipitation. For the properties of the precipitate and residue, see § 58. This method, if properly executed, gives very accurate results.

b. By precipitation as sulphide of nickel.

The moderately diluted solution of nickel is, if necessary, neutralized with ammonia (still the reaction should be rather slightly acid than alkaline): perfectly saturated colorless hydrosulphate of sulphide of ammonium is then added, as long as a precipitate continues to form, care being taken, however, not to add the reagent in too considerable excess. The mixture is now well stirred, passed through a moistened filter, and the precipitate thoroughly washed with a continuous stream of distilled water, to which one or two drops of perfectly saturated colorless hydrosulphate of sulphide of ammonium have been added. The filtrate and the rinsing water must be perfectly colorless. The precipitate is then dried in the funnel (§ 33), and subsequently removed as completely as possible from the filter, and transferred to a beaker-glass; the filter is incinerated upon the lid of a platinum or porcelain crucible, and the ashes are added to the dry precipitate. The precipitate is now treated with concentrated nitrohydrochloric acid, and the mixture digested at a gentle heat, until the whole of the sulphide of nickel is dissolved, and the undissolved sulphur appears of a pure yellow; the fluid is then diluted, filtered, and the filtrate precipitated, &c., as directed sub *a*. For the properties of the precipitate, see § 58. The method, if properly executed, gives accurate results.

If the solution contains ammonia, or if the yellow hydrosulphate of sulphide of ammonium is substituted as precipitant for the colorless hydrosulphate, the fluid filtered off from the sulphide of nickel, possesses always a more or less brownish tint, and contains sulphide of nickel, which it is found a difficult task to remove completely from it by mere exposure to the air. If the filter were not incinerated, but treated at once, together with the precipitate, with nitrohydrochloric acid, the solution of the sulphide of nickel would contain an admixture of organic substances, and the soda or potassa would accordingly afterwards fail to effect the complete precipitation of the nickel from it.

c. By direct ignition.

The same method as described § 86, 1. *d*. (Manganese.)

§ 88.

4. PROTOXIDE OF COBALT.

a. Solution.

Protoxide of cobalt and its compounds deport themselves with solvents like the corresponding compounds of nickel; metallic cobalt like metallic nickel.

b. Determination.

The accurate estimation of cobalt presents considerable difficulties, since, as *Fremy* has lately shown, the hydrated protoxide thrown down by alkalies is not pure, as was formerly supposed, but invariably retains traces of the acid, and a not inconsiderable admixture of the precipitant alkali, which washing fails to remove. I thought the metal reduced from the oxide by hydrogen gas, might be freed from all foreign admixtures by boiling with water; but I found that it could not be accomplished: the metallic powder, though repeatedly boiled with water, still continues to impart a brown tint to turmeric paper, if left in contact with it for some time. The old method of estimating cobalt, by precipitating that metal with alkalies, in the form of hydrated protoxide, must, accordingly, be altogether discarded, where accurate results are required.

The best forms into which to convert the protoxide of cobalt for quantitative estimation, are, *metallic cobalt*, *protosesquioxide of cobalt*, and *sulphate of protoxide of cobalt*; the conversion into the latter form is frequently preceded by precipitation as sulphide of cobalt.

We may convert into

1. METALLIC COBALT.

All salts of cobalt that may be reduced directly by hydrogen gas (sesquichloride of cobalt, nitrate of protoxide of cobalt, carbonate of protoxide of cobalt, &c).

2. PROTOSESQUIOXIDE OF COBALT. (Co_2O_3, CoO).

Sesquioxide of cobalt and nitrate of protoxide of cobalt.

3. SULPHATE OF PROTOXIDE OF COBALT.

All compounds of cobalt without exception.

1. *Determination as metallic cobalt.*

Evaporate the solution of sesquichloride of cobalt, or of nitrate of protoxide of cobalt, and which must be free from sulphuric acid and alkali, in a weighed platinum crucible, to dryness; cover the crucible with a lid having a small aperture in the middle, conduct through this a moderate current of pure dry hydrogen gas, and then apply to the crucible a gentle heat, which increase gradually to intense redness. When the reduction is considered complete, let the reduced metal cool in the current of hydrogen gas, weigh and ignite again in the same way, and repeat the process until

the weight of the reduced metal remains constant. The results are accurate. For the properties of cobalt, see § 59, *b*.

Fig. 40 shows the arrangement of the reducing apparatus.

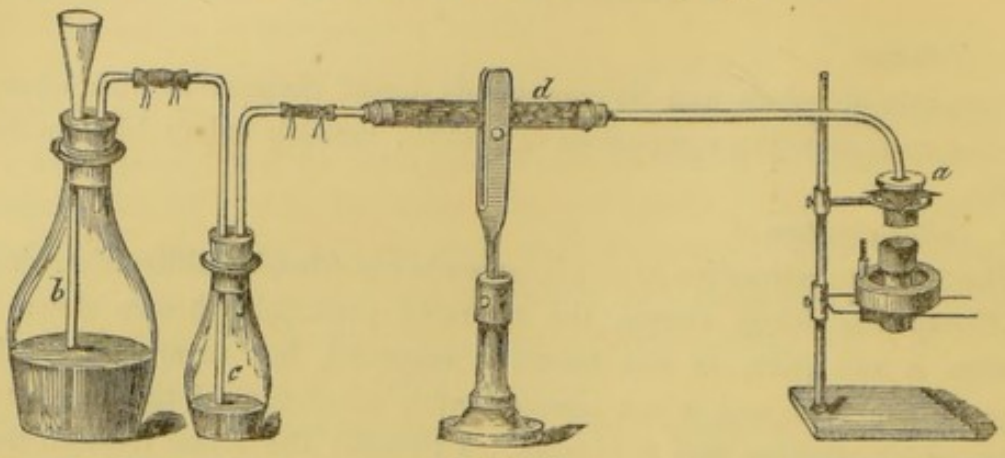


Fig. 40.

a is the crucible with the compound of cobalt, *b* the evolution flask; *c* contains sulphuric acid, *d* chloride of calcium.

2. *Determination as protosesquioxide of cobalt.*

Heat the nitrate of protoxide of cobalt, or the pure sesquioxide, to intense ignition, and repeat the process until the weight remains constant. For the properties of the residue, see § 59. The results are accurate.

3. *Determination as sulphate of protoxide of cobalt.*

a. By direct conversion.

The solution of the compound of cobalt is evaporated to dryness, in a platinum dish or platinum crucible—(directly, if it contains sulphate of protoxide of cobalt; but if it contains a volatile acid, after previous addition of sulphuric acid, slightly in excess)—and the residue cautiously heated, at a gradually increased temperature, which is finally raised to gentle redness; the application of heat is continued, until no more fumes escape, and the weight of the crucible remains constant.

After weighing, the salt is treated with hot water. If this fails to effect complete solution (a sign that the salt has become basic), it is dissolved in hydrochloric acid, and the amount of sulphuric acid is then estimated in the solution, as directed § 105; the quantity of the protoxide of cobalt being finally estimated from the difference. The results are accurate.

For the properties of the sulphate of protoxide of cobalt, see § 59.

b. Preceded by precipitation as sulphide of cobalt.

Mix the solution with a little chloride of ammonium, add ammonia in excess, and then sulphide of ammonium until the formation of a precipitate ceases; let the precipitate subside, filter it off, wash with water mixed with a little sulphide of ammonium, dry, and redissolve as directed § 87 *b*. (Sulphide of nickel.)

The solution obtained contains invariably sulphuric acid; the amount

of the cobalt in it is determined as directed in the preceding section (3. *a*). The results are accurate.

For the properties of the sulphide of cobalt, see § 59.

§ 89.

5. PROTOXIDE OF IRON.

a. Solution.

Many of the compounds of protoxide of iron are soluble in water. The pure protoxide, and those of its compounds which are insoluble in water, dissolve almost without exception in hydrochloric acid; the solutions, if not prepared with perfect exclusion of air, and with solvents absolutely free from air, contain invariably more or less sesquichloride. Some native compounds of iron require fluxing with carbonate of soda, as an indispensable preliminary to their solution in hydrochloric acid. The solutions so prepared contain almost exclusively sesquichloride, and but little protochloride, or none at all. Metallic iron dissolves in hydrochloric acid, and dilute sulphuric acid, with evolution of hydrogen, as protochloride or sulphate of protoxide; in hot nitric acid it dissolves as nitrate of sesquioxide, and in nitrohydrochloric acid, as sesquichloride.

b. Determination.

The amount of protoxide of iron in a compound, may be determined either by converting the protoxide into sesquioxide, and weighing the latter; or by analysis by measure. Both methods are applicable in all cases.

The estimation of protoxide of iron, from the quantity of gold, reduced by its means from the terchloride of that metal, will be treated of in the paragraph on the separation of the protoxide from the sesquioxide of iron, as it is only had recourse to for that purpose.

1. *Determination as sesquioxide of iron.*

The solution of the protoxide is converted into solution of sesquioxide, and afterwards treated as directed, § 90. In some cases (see § 90), and especially in the separation of the protoxide of iron from other oxides, the protoxide is first precipitated as sulphide of iron, in the manner described § 90.

The following is the best method of peroxidising a solution of protoxide of iron:—

Mix the solution of the protoxide of iron with a little hydrochloric acid, if it does not already contain that acid, add some nitric acid, and heat the mixture to incipient ebullition. The color of the fluid will show whether the nitric acid has been added in sufficient quantity. Though an excess of nitric acid does no harm, still it is better to avoid adding too much of it, on account of the subsequent precipitation. In concentrated solutions,

the addition of nitric acid produces a dark brown color, which disappears again upon heating. This color is owing to the nitric oxide formed dissolving in the still undecomposed portion of the solution of the protoxide.

The conversion of the protoxide into sesquioxide may likewise be effected by transmitting chlorine gas through the solution, or by adding to it chlorine water in excess, or by heating the hydrochloric acid solution with chlorate of potassa.

2. *Estimation by analysis by measure.*

a. Marguerite's method.

This method is based upon the following principle :—

If we add to a solution of protoxide of iron, containing an excess of acid permanganate of potassa, the former is peroxidised, at the expense of the latter, which suffers reduction [$10\,(FeO, SO_3) + 8\,SO_3 + KO, Mn_2O_7 = 5\,(Fe_2O_3, 3\,SO_3) + KO, SO_3 + 2\,(MnO, SO_3)$]. Now, if we have a solution of permanganate of potassa, of which we know the exact quantity required to convert one gramme of iron from the state of protoxide to that of sesquioxide, we can, by this means, readily determine an unknown quantity of iron ; we need simply, for this purpose, bring the iron into acid solution, in the form of protoxide, peroxidize the solution accurately, and see how many volumes of the solution of permanganate of potassa have been used to accomplish that end.

a a. Preparation of the solution of permanganate of potassa.

Mix 8 parts of finely pulverized binoxide of manganese with 7 parts of finely pulverized chlorate of potassa, add to the mixture a most highly concentrated solution of 10 parts of hydrate of potassa, and evaporate to dryness, taking care to stir the mass ; put the residue, before it has absorbed moisture, into a Hessian crucible, or, better still, into a platinum crucible, and heat gently (to faint redness at the most), until the chlorate of potassa is completely decomposed. Triturate the green mass, and boil it with water, until the green color of the manganate of potassa has changed to the violet tint of the permanganate, which change is attended with separation of hydrated binoxide of manganese. The decomposition may be expedited by the cautious addition of a little nitric acid. The solution is decanted off, or filtered through asbestos, and kept in a well stoppered bottle. The precipitate affords an excellent material for the preparation of a fresh quantity of solution.

b b. Determination of the strength of the solution.

Weigh off about one gramme of fine iron wire (pianaforte string wire), free from rust, coil it firmly together, put it in a flask of about 1000 cubic centimeters capacity, and add about 25 cubic centimeters of pure hydrochloric acid, and a little water ; close the flask with a perforated

cork, in which a glass tube is fitted, open at both ends; heat the contents of the flask until the iron wire is completely dissolved, and dilute the solution with about 500 cubic centimeters of cold water.

Now fill your *burette* with the solution of permanganate of potassa, and add this in small portions to the colorless solution of protochloride of iron, agitating all the while, until the latter just begins to exhibit a pale red tint, which the agitation of the fluid fails to dissipate. Read off now the number of volumes used, and dilute the test fluid to the extent, that 50 cubic centimeters=100°, *correspond exactly to one gramme of iron*. This is effected in the following way: suppose we had used 0·95 grm. of iron, and 80° of permanganate of potassa. The equation

$$0{\cdot}95 : 80 :: 1 : x = 84{\cdot}2$$

shows that we should have required 84·2° of the solution of permanganate of potassa, had we weighed off exactly 1 gramme of iron, a task difficult to accomplish.

$$100^\circ - 84{\cdot}2^\circ = 15{\cdot}8^\circ.$$

We have accordingly to add to every 84·2° of our solution of permanganate of potassa, 15·8° of water, to bring it to the proper degree of dilution. A portion of the concentrated fluid is kept, to remedy any eventual decomposition of the test solution.

The rules laid down here must be strictly attended to. For instance, if you do not dilute your iron solution, or use it whilst hot, chlorine will be evolved; if you do not make it sufficiently acid, or add the solution of permanganate of potassa too quickly, a brown precipitate (binoxide of manganese + sesquioxide of iron) will separate; this, however, is mostly redissolved, on shaking the fluid. The reddened solution invariably loses its color again after a time, as a dilute solution of free permanganic acid cannot keep long undecomposed.

For the analysis of very dilute solutions of iron, *e. g.*, ferruginous mineral waters, ten or a hundred times more dilute test fluids should be prepared; of which 100° will accordingly correspond respectively to 0·1 and to 0·01 grm. of iron.

As the test fluid suffers gradual decomposition, however carefully it may be kept, each fresh analysis, made after an interval of some time, must be preceded by a fresh determination of its strength, for which end a portion of the concentrated solution reserved is added to the test fluid. Care should be taken to dilute the iron solution used to determine the strength of the test fluid, to the same volume which it is intended to use of the iron solution to be examined. This is necessary, more particularly, in cases where we have to analyse very dilute solutions (ferruginous mineral waters, for instance), since in such cases we have to employ a very dilute test fluid, and of which several volumes are required to impart to

pure water a distinct color. Inequality of the quantities of water used respectively in determining the strength of the test fluid, and, subsequently, in the actual analysis, may accordingly lead to inaccuracy in the results.

The best way is to ascertain by experiment how many volumes or degrees of the dilute solution of permanganate of potassa are required to impart the requisite pale red coloration to a measure of pure water, equal to that of the iron solution employed to determine the strength of the test fluid, or of the solution of protoxide of iron, which it is intended to analyse; and to subtract the number of volumes so required from that of the volumes of the solution of permanganate of potassa used in those processes. If this is omitted, the degrees required to impart the proper color do not correspond with those required to effect the peroxidation of the protoxide in the solution to be analysed, which, of course, must tend to impair, more or less, the correctness of the results.

c c. Performance of the analytical process.

This has already been fully indicated in *b b*.

The solution of protoxide of iron is properly acidified and diluted, and the test fluid is then added, until the solution begins to exhibit a pale red tint.

If exactly one gramme has been dissolved of the substance to be analysed, the number of volumes or degrees used of the test fluid indicates directly the percentage amount of metallic iron present; if more or less than one gramme of substance has been used, the quantity of iron may be found by an easy calculation. For the method of determining the total amount of iron present in a solution containing both protoxide and sesquioxide of that metal, I refer to § 90; for that of determining the respective separate amounts of the sesquioxide and of the protoxide, to Section V.

b. Penny's method (recommended subsequently by *Schabus*).

If bichromate of potassa is added to an acid solution of protoxide of iron, the latter is converted into sesquioxide, whilst the chromic acid is reduced to sesquioxide of chromium ($6\,FeO + 2CrO_3 = 3\,Fe_2O_3 + Cr_2O_3$).

Now, it takes 0·8849 grm. of bichromate of potassa, to convert 1 gramme of iron from the state of protoxide to that of sesquioxide. If, therefore, 8·849 grammes of bichromate of potassa are dissolved in water, and the solution is diluted, until the fluid measures exactly 500 cubic centimeters, 50 cubic centimeters of it will correspond exactly to 1 gramme of metallic iron.

Care must be taken to use perfectly pure bichromate of potassa, and to dry it thoroughly at 212°, previously to weighing off the required quantity.

Besides the actual test fluid, another should be prepared, ten times more dilute, and a third, a hundred times more dilute.

It is always advisable to test the correctness of the quantitative compo-

sition of the solution of bichromate of potassa, by converting with it a known amount of pure iron from the state of protoxide to that of sesquioxide.

The actual analysis is performed as follows :—

The solution of protoxide of iron is sufficiently diluted, mixed with hydrochloric or dilute sulphuric acid, and the test fluid slowly added from the *burette*, the liquid being all the while stirred with a thin glass rod. The fluid, which is at first nearly colorless, acquires speedily a pale green tint, which changes gradually to dark chrome-green. A very small drop of the mixture is now from time to time taken out by means of the stirring-rod, and brought into contact with a drop of a solution of ferricyanide of potassium on a porcelain plate, on which a great many drops of that solution are sprinkled for the purpose. When the blue coloration thereupon ensuing begins to lose the intensity which it exhibited on the first trials, and to assume a paler tint, the addition of the solution of bichromate of potassa must be more carefully regulated than at first, and towards the end of the process, a fresh essay must be made, and with larger drops than at first, after each new addition of two drops, and finally of one drop. When no further blue coloration ensues, the oxidation is terminated. From the remarkable sensitiveness of the reaction, the exact point may be easily hit to a drop. To heighten the accuracy of the results, the dilute (ten times weaker) test fluid should, towards the end of the process, be substituted for the concentrated solution of bichromate of potassa.

If exactly one gramme has been dissolved of the substance to be analysed, the number of volumes or degrees used of the concentrated test fluid shows how many per cent that of the volumes used of the dilute test fluid, how many tenth per cent of pure iron the analysed substance contains in the form of protoxide. For the manner of proceeding in presence of sesquioxide of iron, I refer to § 90.

Of the two preceding methods of analysis by measure, the first presents the advantage that the termination of the process of oxidation is clearly indicated in it by the ensuing red coloration of the solution ; whilst the second, on the other hand, has this very essential point in its favor, that the solution of bichromate of potassa may be easily prepared, and kept unaltered.

§ 90.

6. SESQUIOXIDE OF IRON.

a. Solution.

Many of the compounds of sesquioxide of iron are soluble in water. Pure sesquioxide of iron, and most of those of its compounds which are insoluble in water, dissolve in hydrochloric acid, but many of them only slowly and with difficulty ; compounds of this nature are best dissolved in concentrated hydrochloric acid, in a flask, with the aid of heat ; which, however, should

not be allowed to reach ebullition; the compound must, moreover, be finely comminuted, and even then it will often take many hours to effect complete solution. Iron ores insoluble in hydrochloric acid are prepared for solution by fluxing with carbonate of soda.

b. Determination.

Sesquioxide of iron is invariably weighed as such (§ 60). It may, however, be estimated also indirectly, and also by analysis by measure, after previous reduction to protoxide. The conversion of compounds of iron into sesquioxide is effected either by precipitation as hydrated sesquioxide, preceded in some cases by precipitation as sulphide of iron, or as succinate of sesquioxide of iron; or by ignition.

We may convert into

SESQUIOXIDE OF IRON.

a. By precipitation as hydrated sesquioxide.

All salts of iron with inorganic or volatile organic acids, which are soluble in water; and likewise those which, insoluble in that menstruum, dissolve in hydrochloric acid, with separation of their acid.

b. By precipitation as sulphide of iron.

All compounds of iron without exception.

c. By precipitation as succinate of sesquioxide of iron.

The compounds enumerated sub. *a*.

d. By ignition.

All salts of sesquioxide of iron with volatile oxygen acids.

The method *d* is most expeditious and accurate, and is accordingly preferred in all cases where its application is admissible. The method *b* serves principally to effect the separation of the sesquioxide of iron from other bases; it is resorted to also in certain instances where *a* is inapplicable, especially in cases where sugar, or other non-volatile organic substances are present; and also to estimate the sesquioxide of iron in its compounds with phosphoric acid and boracic acid. The method *c* is used exclusively to effect the separation of the sesquioxide of iron from other bases. For the manner of determining the sesquioxide of iron in the chromate and silicate, I refer to §§ 104 and 111.

The indirect method, and that of analysis by measure are applicable in almost all cases.

1. *Determination as sesquioxide of iron.*

Dissolve the compound under examination in its appropriate menstruum in a dish or beaker-glass, and add to the solution, ammonia in excess; heat to ebullition; filter, wash the precipitate *carefully* with hot water, dry it *thoroughly*, and ignite in the manner directed in § 35; keeping the crucible covered at first, and exposed to a gentle heat only; removing the lid subsequently, and leaning it obliquely against the crucible, placed in the manner shown in Fig. 37, and then applying a more intense heat.

This method, if properly and carefully executed, yields very accurate results, and is free from sources of error. Should the operator have reason to fear that part of the sesquioxide has suffered reduction by the carbon of the filter, he need simply moisten the contents of the crucible with nitric acid, evaporate and ignite again; by this process he is sure to obtain all the iron present, in the form of sesquioxide.

For the properties of the precipitate and residue, see § 60. The precipitate must, under all circumstances, be *carefully* washed, since, should it retain any traces of chloride of ammonium, a portion of the iron would volatilize in the form of sesquichloride.

b. By precipitation, as sulphide of iron. The iron compound under examination is dissolved in its appropriate menstruum, in a beaker-glass, and ammonia added to complete neutralization of the free acid present. (In the absence of organic non-volatile substances, a little hydrated sesquioxide of iron precipitates; however, this is of no consequence.) Sulphide of ammonium is then added in excess, and a gentle heat applied. The operator generally obtains, in this manner, a black precipitate in a colorless or yellowish fluid, in which case he may at once proceed to filtration; but should the fluid exhibit a greenish color—which happens particularly with very dilute solutions, and is owing to extremely minute particles of sulphide of iron remaining mechanically suspended in the fluid—the beaker-glass, covered with a glass plate, must be kept standing at rest in a moderately warm place, until the greenish tint has changed to yellow, when the fluid may be filtered. In either case, the precipitate is washed uninteruptedly with water, mixed with a small amount of sulphide of ammonium, the funnel being kept covered all the while. Neglect of these precautions will occasion some loss of substance, the sulphide of iron gradually combining with the oxygen of the air, and passing thus into the filtrate as sulphate of protoxide of iron. As this sulphate is reprecipitated by the sulphide of ammonium present, the filtrate assumes, in such cases, a greenish color, and deposits gradually a black precipitate.

The washed precipitate of sulphide of iron is put, together with the filter, into a beaker-glass, some water added, and then hydrochloric acid, until the whole of the sulphide of iron present is redissolved. Heat is now applied, until the solution smells no longer of sulphuretted hydrogen; the solution is filtered into a flask, the filter carefully washed, and the filtrate peroxidized by heating with nitric acid (see § 89); the peroxidized solution is finally treated as sub *a*.

If a solution of potassio, sodio, or ammonio-tartrate of sesquioxide of iron contains a considerable excess of alkaline carbonate, the precipitation of the iron as sulphide is prevented more or less (*Blumenau*). In such cases the fluid must therefore be nearly neutralized with an acid, before the precipitation with the sulphide of ammonium can be effected.

c. By precipitation as succinate of sesquioxide of iron.

The salt of iron under examination is dissolved in the appropriate menstruum, in a flask, and very dilute solution of ammonia added drop by drop until a small portion of the iron precipitates in the form of hydrated sesquioxide; a gentle heat is then applied, to ascertain whether the precipitate will redissolve or not. If it redissolves, the addition of dilute ammonia is continued, until the application of heat fails to redissolve the precipitate formed. If, on the contrary, it remains undissolved, and the fluid continues to exhibit a brownish red color, all the preliminary conditions requisite for precipitation with succinate of ammonia are fulfilled. But should the fluid appear colorless, this is a sign that too much ammonia has been added; in which case, it will be necessary to add a small portion of hydrochloric acid, and then again some ammonia until the desired point is attained. To the fluid thus prepared, is now added a perfectly neutral solution of succinate of ammonia, as long as a precipitate continues to form; a gentle heat is then applied, and the fluid is afterwards allowed to cool; when perfectly cold, it is filtered, and the precipitate washed first with cold water, finally with hot solution of ammonia—which operation, depriving the precipitate in a very great measure of its acid, imparts a darker tint to it. The washed precipitate is dried upon the filter in the funnel; the dry filter, together with its contents, is then put in a platinum crucible, and the latter exposed to the action of heat, first with the lid on, afterwards with the lid off, and with a current of air directed upon the filter and precipitate, until the former is thoroughly incinerated, and the latter converted into red oxide (sesquioxide). The object of washing the precipitate with ammonia is to remove part of the acid, since, were this neglected, and the precipitate simply washed with water, a portion of the sesquioxide of iron might suffer reduction upon the subsequent ignition of the succinate. For the properties of the precipitates, see § 60. The results are accurate.

d. By ignition.

Expose the compound, in a covered crucible, to a gentle heat at first; which increase gradually to the highest degree of intensity, until the weight of the residuary sesquioxide of iron remains constant.

2. *Indirect method of estimating iron*, recommended by *Fuchs*. (Journ. für prakt. Chem. 17, 160.)

Fuchs' method is based upon the circumstance that sesquichloride of iron in solution, when boiled with metallic copper, is reduced to protochloride, a corresponding amount of copper dissolving as subchloride. ($Fe_2Cl_3 + 2\,Cu = 2\,FeCl + Cu_2Cl$). Accordingly, if we know the quantity of copper dissolved, we may readily calculate from this the amount of the iron, every one equivalent of dissolved copper corresponding to one equivalent of iron, or to one-half equivalent of sesquioxide of iron.

The substance under examination is dissolved in a manner to convert the whole of the iron present into sesquichloride. The hydrochloric acid must strongly predominate, that the subchloride of copper formed in the process may be sure to continue in solution. Should a portion of the iron have dissolved as protochloride, chlorine water or chlorate of potassa is added, to convert this protochloride into sesquichloride, and the fluid is boiled (the flask being placed obliquely) until the whole of the free chlorine or of the inferior oxides of chlorine are expelled. Nitric acid must not be used to peroxidize the protoxide. An insoluble residue (alumina, silicic acid) will sometimes remain upon the solution of the substance; this, however, does not entail the necessity of filtration.

The solution is now diluted with hot water sufficient to fill the flask more than half, and strips, about 6 centimeters long, and 2 wide, of clean, rather stout sheet copper, are thrown into it (for 2 or 3 grammes of sesquioxide of iron in the solution, 15 to 20 grammes of copper are used); the flask being closed with a cork having a glass tube of moderate diameter fitted in it, is then placed obliquely, or, at all events, so that the copper is completely covered by the liquid, and the latter is rapidly heated to ebullition.

The fluid speedily changes color; at first it looks dark brown, becomes gradually lighter, and turns at last of a pale green. When there is no further change of color, the glass tube is closed with some wax, or with a little caoutchouc tube having one end stopped up with a small piece of glass-rod; the fluid is allowed to cool a little, and the flask is then filled up with hot water, the liquid is poured off, the flask filled again with hot water, the fluid poured off again, the copper taken out, carefully rinsed, first with a little dilute hydrochloric acid, afterwards with water, put on blotting paper, and turned about, but without rubbing it against the paper (the dark coating which it exhibits occasionally must not be meddled with); the copper is then dried in a warm place, and weighed.

The results are pretty accurate.

3. *Determination by analysis by measure.*

The sesquioxide of iron is reduced to the state of protoxide, and the solution of the latter is then again peroxidized by a sufficient quantity of an oxidizing agent of accurately known power. Here we have to occupy ourselves simply with the reduction of the sesquioxide, the remainder of the process having been fully discussed in § 89, 2.

a. Reduction by sulphuretted hydrogen.

Mix the warm hydrochloric acid solution, in a flask, with saturated sulphuretted hydrogen water in excess, or, if you have larger quantities of substance to deal with, conduct sulphuretted hydrogen gas into it, until the fluid smells strongly of that gas; place the flask obliquely, and heat to gentle ebullition, until the sulphuretted hydrogen is completely expelled. There is no need to filter off the precipitated sulphur.

b. Reduction by zinc.

Strips of pure sheet zinc, free from iron, are put into the hydrochloric acid solution. This leads to the evolution of some hydrogen gas, and, in presence of nitric acid, nitrous oxide gas. The color of the solution is paler in proportion as the sesquioxide changes to protoxide. If the solution happens to contain copper or arsenic, these metals separate in form of small scales, or as a metallic powder. When the reduction is fully effected, the fluid is filtered. In cases where zinc free from iron, cannot be procured, the quantity of iron contained in the zinc is determined by analysis by measure, the zinc strips are weighed before and after, and the amount of iron contained in the zinc dissolved is subtracted from the total quantity of iron found.

c. Reduction by sulphite of soda.

Mix the hydrochloric acid solution, in a flask, with a concentrated solution of sulphite of soda, and boil. If the first portion of sulphite of soda added proves insufficient to reduce the whole of the sesquioxide of iron, a fresh portion must be added. The ebullition must be continued, until the disengagement of sulphurous acid has absolutely ceased.

Of these three methods, I prefer *a;* in *c*, the reduction is effected more slowly, and other metals which may interfere with the reaction in the after process are not thrown down, but are left in the fluid; *b*, again, requires filtration and washing, and much additional trouble besides, if the zinc happens to contain an admixture of iron.

FIFTH GROUP.

OXIDE OF SILVER—OXIDE OF LEAD—SUBOXIDE OF MERCURY—OXIDE OF MERCURY—OXIDE OF COPPER—TEROXIDE OF BISMUTH—OXIDE OF CADMIUM.

§ 91.

1. OXIDE OF SILVER.

a. Solution.

Metallic silver, and those of its compounds which are insoluble in water, are best dissolved in nitric acid (that is, of course, if they are soluble in that acid). Dilute nitric acid suffices for most compounds; sulphide of silver, however, requires concentrated acid. The solution is effected best in a flask. Chloride, bromide, and iodide of silver are insoluble in water and in nitric acid. To get the silver contained in them in solution, it must first be reduced to the metallic state, which may be readily effected in the following way:—fuse the salt in a porcelain crucible (this operation, though not absolutely indispensable, had better not be omitted), pour water over it, lay a bit of clean zinc or iron upon it, and add some sul-

phuric or hydrochloric acid. Wash the reduced spongy silver, first with dilute sulphuric acid, and then with water, and dissolve it finally in nitric acid. However, as we shall see below, the quantitative analysis of the chloride, bromide, and iodide of silver does not necessarily require the solution of these salts.

b. Determination.

Silver may be weighed as *chloride of silver, sulphide of silver, cyanide of silver,* or in the *metallic* state. It is also frequently determined by analysis by measure.

We may convert into

1. CHLORIDE OF SILVER. 2. SULPHIDE OF SILVER. 3. CYANIDE OF SILVER.

All compounds of silver without exception.

4. METALLIC SILVER.

Oxide of silver, and several of its compounds with readily volatile acids; salts of silver with organic acids; chloride of silver.

The method 4 is the most convenient, and is preferred to the others in all cases where its application is admissible. The method 1 is that most generally resorted to. 2 and 3 serve mostly only to effect the separation of oxide of silver from other bases. In the workshops of the mint, the silver is usually determined by analysis by measure.

1. *Determination of silver as chloride.*

a. In the humid way.

The precipitated chloride of silver may be separated from the supernatant fluid either by decantation or by filtration; the former is generally preferred when we have a copious amount of precipitate before us, the latter answers better for small quantities.

α. Determination by decantation.

The moderately diluted solution of the compound under examination is introduced into a tall flask, with long neck and narrow mouth, and some nitric acid added to it; the fluid is heated to about 140°, and hydrochloric acid added to it, as long as a precipitate continues to form. The mouth of the flask is then closed with a perfectly smooth cork (or, better still, with a well-ground glass stopper), and the flask forcibly shaken until the precipitated chloride of silver has united into coherent lumps, and the supernatant fluid has become clear. The minute particles of chloride of silver, which may still adhere to the sides of the neck of the flask, are then rinsed down by means of a washing-bottle, and the stopper is loosely replaced. The flask is now put in the sand-bath, in a moderately warm place, until the precipitate has *completely* subsided, and the supernatant fluid has become *perfectly* clear and transparent, which generally requires several hours. The clear fluid is then slowly and cautiously decanted into a beaker-glass, so as to retain every particle of the chloride in the flask, whence it is carefully transferred to a porcelain crucible with

steep and smooth sides: the last particles of chloride of silver which remain adhering to the bottom and sides of the flask are rinsed into the neck of the latter with a little water (inverting the flask, and closing its mouth with the finger), and thence likewise transferred to the crucible.

When the chloride of silver has completely subsided in the crucible, which is greatly accelerated by exposing the latter to the heat of a water-bath, the clear supernatant fluid is carefully decanted along a glass rod into the same beaker-glass which contains the liquid of the first decantation. The chloride of silver in the crucible is moistened with a few drops of nitric acid, and then treated with hot distilled water; the chloride is again allowed to subside, the clear supernatant fluid again decanted, and the same operation repeated until a drop of the last decanted fluid occasions no longer the slightest turbidity in a solution of nitrate of silver. The last portions of supernatant fluid are then carefully and cautiously decanted or removed by means of a *pipette;* the chloride is thoroughly dried in the water-bath, and subsequently heated to incipient fusion over the lamp, taking care to apply a very gentle heat at first; as soon as the chloride begins to fuse round the border, the crucible is removed from the flame, allowed to cool, and finally weighed.

To remove the mass from the crucible, completely and without injury to the latter, a fragment of iron or zinc is placed upon the chloride, and highly dilute hydrochloric or sulphuric acid poured over it. The crucible is finally cleansed, dried, and weighed. Should the liquids successively decanted from the chloride of silver not be perfectly clear and transparent, they are kept standing in a warm place until the last particles of chloride have completely subsided, which frequently requires several hours; the clear supernatant fluid is then decanted, and the subsided chloride added to the bulk of the precipitate in the crucible; or—and this is a more expeditious way—the minute quantity of chloride is collected on a small filter, treated as directed in β, and the quantity found added to the principal amount.

β. Determination by filtration.

The chloride of silver is precipitated and allowed to subside as in α.; the supernatant fluid is then passed through a small filter, to which the precipitate likewise is subsequently transferred, with the aid of a little hot water acidulated with nitric acid; the precipitate collected on the filter is washed, first with water acidulated with nitric acid, afterwards with pure water; it is then thoroughly dried, ignited (§ 36), and weighed.

For the properties of the precipitate, see § 61. Both methods give very accurate results, though a trifling loss is incurred in β, owing to part of the minute portion of chloride of silver which, notwithstanding the most careful scraping, will always adhere to the filter, suffering reduction upon ignition, from the action of the carbonic oxide evolved by the combustion of the filter. This may be remedied, however, by putting the ashes of the filter

in the crucible with the chloride, adding a little dilute nitric acid, heating for some time, adding a few drops of hydrochloric acid, evaporating, drying, and igniting, as directed in *a*. Some chemists reckon the silver contained in the filter-ashes at once as metallic silver.

b. In the dry way.

This method serves more exclusively for the analysis of bromide and iodide of silver, although it is adapted also for the quantitative estimation of other salts of silver.

The process is conducted in the apparatus illustrated by Fig. 41.

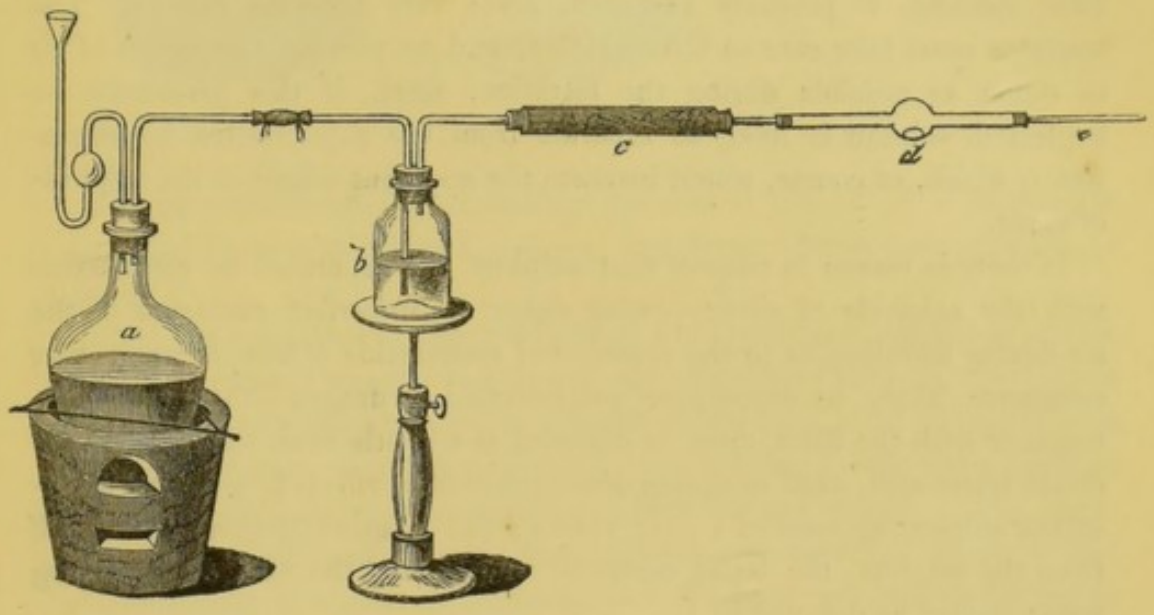


Fig. 41.

a is an apparatus for disengaging chlorine, *b* contains concentrated sulphuric acid, *c* chloride of calcium, *d* is intended for the reception of the iodide or bromide of silver, and *e* serves to conduct the chlorine gas out of the window. The operation is commenced by introducing the compound to be analysed into the bulb *d*, and applying heat to the latter until its contents are fused; when cold, the tube is weighed and connected with the apparatus. Chlorine gas is then evolved from *a*; when the evolution of the gas has proceeded for some time, the contents of *d* are heated to fusion, and kept in this state for about fifteen minutes, agitating now and then the fused mass in the bulb. The tube *d* is then removed from the apparatus, allowed to cool, and held in a slanting position to replace the chlorine by atmospheric air; it is subsequently weighed, and then again connected with the apparatus, and the former process repeated, keeping the contents of *d* in a state of fusion for a few minutes. The operation may be considered concluded if the weight of the tube suffers no variation by the repetition of the process. This method, if properly executed, gives exceedingly accurate results.

2. *Determination as sulphide of silver.*

Sulphuretted hydrogen precipitates silver completely from acid, neutral, and alkaline solutions; sulphide of ammonium precipitates it from neutral and alkaline solutions. Recently prepared perfectly clear solution of sulphuretted hydrogen may be employed to precipitate small portions of silver; to precipitate larger quantities, the solution of the salt of silver (which must not be too acid) is moderately diluted, and washed sulphuretted gas conducted into it. The precipitated fluid is then gently heated, the sulphide of silver collected on a weighed filter, washed, dried at 212°, and weighed. For the properties of the precipitate, see § 61. This method, if properly executed, gives very accurate results. The operator must take care to filter quickly, and to prevent the access of air as much as possible during the filtration, since, if this precaution be neglected, sulphur is likely to separate from the sulphuretted hydrogen-water, which, of course, would increase the apparent weight of the sulphide of silver.

If there is reason to suspect that sulphur has separated in conjunction with the sulphide of silver—owing either to imperfect exclusion of the air during filtration, or to the presence of sesquioxide of iron, or some other substance likely to decompose sulphuretted hydrogen—the precipitate, together with the filter, must be digested at a gentle heat, with moderately dilute nitric acid, until complete decomposition is effected, and the undissolved sulphur appears of a pure yellow; the solution is then filtered off from the sulphur, the latter carefully washed, and the filtrate and rinsing water treated as directed in 1.

3. *Determination as cyanide of silver.*

Mix the neutral or acid solution of silver with cyanide of potassium, until the precipitate which forms at first, is redissolved; add nitric acid in slight excess, and apply a gentle heat. After some time, collect the precipitated cyanide of silver on a weighed filter, wash, dry at 212°, and weigh. For the properties of the precipitate, see § 61. The results are accurate.

4. *Determination as metallic silver.*

Oxide of silver, carbonate of silver, &c., are easily reduced by simple ignition in a porcelain crucible. In the reduction of salts of silver with organic acids, the crucible is kept covered at first, and a moderate heat applied; after a time the lid is removed, and the heat increased, until the whole of the carbon is consumed. For the properties of the residue, see § 61. The results are absolutely accurate, except as regards salts of silver with organic acids; in the analysis of the latter, it happens not unfrequently that the reduced silver is contaminated with a minute portion of carbon, which increases the apparent weight of the silver; the difference, however, is only very trifling.

Chloride of silver is put into the bulb of a bulb-tube, fused in it, and weighed. The tube is then connected with an apparatus for the evolution of dry hydrogen gas. (See Fig. 42.)

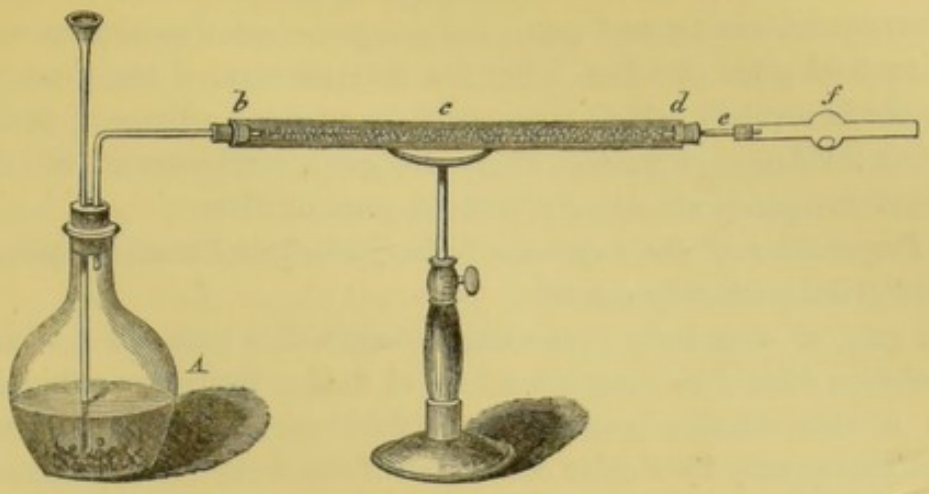


Fig. 42.

A is the evolution flask, containing granulated zinc, *b d*, a long glass tube, filled up to *c* with blotting paper, and from *c* to *d* with chloride of calcium.

When the apparatus is completely filled with hydrogen, and the evolution of the gas proceeds steadily and slowly, the chloride of silver in the bulb is heated to fusion, and maintained at a moderate red heat, until no more fumes of chloride of ammonium are generated upon holding a glass rod moistened with ammonia to the aperture through which the gas escapes. The apparatus is then allowed to cool, the bulb-tube is detached from it, and held some time in a slanting position, that the hydrogen still remaining in it may be replaced by atmospheric air; it is then finally weighed. The results are most accurate.

5. *Determination by analysis by measure.*

The determination of silver by analysis by measure is based upon the circumstance, that one equivalent of chloride of sodium throws down one equivalent of silver from solutions of that metal. We need accordingly simply prepare a solution of known strength of chloride of sodium, and ascertain how much of this is required to throw down the whole of the silver from a solution of the metal. This method, which *Gay-Lussac* substituted for the assay of silver by cupellation, may be found described at length in *Gay-Lussac's* "Instructions on the Method of Assaying Silver in the Humid Way," translated into German by *J. Liebig*, published by *Vieweg*, of Brunswick. I shall here give only so much of the process as is requisite for use in the chemical laboratory.

a. Preparation of the solution of chloride of sodium.

One grm. of pure silver combines with 0·32844 grm. of chlorine, to form chloride of silver. This quantity of chlorine is contained in 0·54142 grm. of chloride of sodium. If, therefore, we dissolve 5·4142 grms. of chemically pure chloride of sodium in water, and add water to the solution

until we have exactly one litre of fluid, 100 cubic centimeters of this fluid will correspond exactly to 1 grm., and every one cubic centimeter accordingly to 0·01 grm. of silver. Besides this solution, a ten times more dilute one is required, which is prepared by mixing 1 volume of the solution with 9 volumes of water. Every one cubic centimeter of this dilute solution corresponds accordingly to 0·001 grm. of silver.

b. Preparation of the solution of silver, which is likewise required in the analytical method by measure.

One grm. of chemically pure silver is dissolved in pure nitric acid, and the solution diluted to exactly one litre of fluid. Every one cubic centimeter of this solution corresponds to 0·001 grm. of silver, which is precipitated exactly by 1 cubic centimeter of the dilute (tenth) solution of chloride of sodium.

c. Testing of the solutions.

One grm. of chemically pure silver is dissolved in 6 cubic centimeters of pure nitric acid, at a gentle heat; the solution is effected in a white flask with close fitting glass stopper. The nitrous acid fumes are blown out from the flask, with the aid of a bent glass tube. Exactly 100 cubic centimeters of the concentrated solution of chloride of sodium are then added, the moistened glass stopper is firmly screwed in, and the mixture is shaken until the chloride of silver formed has concreted into a lump, and the fluid become clear. One cubic centimeter of the dilute (tenth) solution of chloride of sodium is now added; if the solution has been correctly prepared, this must cause no turbidity in it. One cubic centimeter of the solution of silver is now added, and the fluid again shaken until it has recovered its clearness; another cubic centimeter of the solution of silver is then added, which again must cause no turbidity in the solution.

d. Performance of the analytical process.

It is, in the first place, necessary that the operator should have some *approximate* notion of the quantity of silver contained in the compound under examination (as is the case, for instance, in the assaying of coins, &c.) If he has not, he must have recourse to a preliminary assay; to this end, a portion of the substance under examination is weighed off, dissolved in nitric acid, and the concentrated solution of chloride of sodium added drop by drop from a *burette*, the mixture is shaken, and the addition of solution of chloride of sodium continued until no further precipitation takes places.

The quantity of silver in the salt or alloy having been thus approximately ascertained, a portion of it is weighed off, calculated to contain about one grm. of silver, and dissolved in pure nitric acid in the white flask mentioned in *c*. The nitrous acid fumes are blown out from the flask, and exactly 100 cubic centimetres of the concentrated solution of chloride of

sodium are added by means of a *pipette;* the moistened glass stopper is now firmly screwed in, and the mixture is vigorously shaken until the chloride of silver has concreted into a lump, and the fluid become clear. It remains now to be ascertained whether the fluid contains still silver or chloride of sodium. To this end, 1 cubic centimeter of the dilute (tenth) solution of chloride of sodium is added to it; if the fluid turns turbid, this is a sign that the quantity weighed off of the salt or alloy contained more than one grm. of silver. In that case, the fluid is shaken until the newly formed chloride has subsided, another cubic centimeter of the dilute solution of chloride of sodium is then added, and the same operation is repeated, until the cubic centimeter last added leaves the fluid clear. It is generally assumed that only one half of the cubic centimeter added before the last was required, and 1·5 c. c. are accordingly subtracted from the sum of the dilute solution of chloride of sodium used. The remaining number of cubic centimeters used gives the number of milligrammes of silver, contained in the weighed off sample, over and above one grm.

If the first cubic centimeter added, of the dilute solution of chloride of sodium leaves the fluid clear, 1 cubic centimeter of the test solution of silver is added, to throw down this chloride of sodium, the fluid is then shaken until the chloride of silver formed has subsided, and the fluid become clear again. Another cubic centimeter of the test solution of silver is now added in the same way, and the operation is repeated, until the cubic centimeter last added leaves the fluid clear. From the number of cubic centimeters used of the test solution of silver, we have to subtract 2·5, viz., the first and the last added, and the one half of the one added before the last. The remaining number gives the number of milligrammes of silver which the analysed sample contained less than one grm.

§ 92.

2. OXIDE OF LEAD.

a Solution.

Few of the salts of lead are soluble in water. Metallic lead, oxide of lead, and most of the insoluble salts of lead, dissolve in *dilute* nitric acid. Concentrated nitric acid effects neither complete decomposition nor complete solution, since, owing to the insolubility of nitrate of lead in concentrated nitric acid, the first portions of nitrate formed protect the yet undecomposed parts of the salts to be analysed from the action of the acid. For the solution of chloride and sulphate of lead, see § 62. As we shall see below, the analysis of these compounds may be effected without dissolving them. Iodide of lead does not dissolve in cold dilute nitric acid; but upon the application of heat it dissolves readily in it, with separation of iodine. Solution of potassa is the only menstruum in which chromate

of lead dissolves without decomposition; for the purpose of analysis, the chromate is best converted into the chloride.

b. Determination.

Lead may be weighed as *oxide, sulphate, chromate, sulphide, chloride,* or as *oxide of lead + lead;* it may be determined also by analysis by measure.

We may convert into

1. OXIDE OF LEAD.

a. By precipitation.

All salts of lead soluble in water, and those of its salts which, insoluble in that menstruum, dissolve in nitric acid, with separation of their acid.

b. By ignition.

α. Salts of oxide of lead with readily volatile or decomposable inorganic acids.

β. Salts of lead with organic acids.

2. SULPHATE OF LEAD.

a. By precipitation.

Those of the insoluble salts of lead, the acid of which cannot be removed from their solution in nitric acid.

b. By evaporation.

α. All the oxides of lead, and likewise the salts of oxide of lead with volatile acids; and also iodide and bromide of lead.

β. Many of the organic compounds of lead.

3. CHROMATE OF LEAD.

The compounds of lead soluble in water or in nitric acid.

4. CHLORIDE OF LEAD.

Chromate of lead, iodide, and bromide of lead.

5. OXIDE OF LEAD + LEAD.

Many of the organic compounds of lead.

6. SULPHIDE OF LEAD.

All salts of lead in solution. This method serves principally to separate lead from other substances.

The application of these several methods must not be understood to be rigorously confined to the compounds specially enumerated under their respective heads; on the contrary, the compounds enumerated, sub. 1, may likewise be determined as sulphate of lead; and those enumerated, sub. 1, 2, and 5, as sulphide of lead, &c. &c. Chloride of lead may either be determined according to 1. *a.*, or it may be reduced to the metallic state, in a current of hydrogen gas, in the manner described, § 91, 4 (reduc-

tion of chloride of silver); the heat applied should not be too intense, since this might cause some of the chloride of lead to volatilize.

The higher oxides of lead are reduced by ignition to the state of simple oxide, and may thus be readily dissolved, and analysed. Should the operator wish to avoid having recourse to ignition, the most simple mode of dissolving the higher oxides of lead, is to act upon them with dilute nitric acid, mixed with a small quantity of alcohol. For the methods of analysing sulphate, chromate, iodide, and bromide of lead, I refer to the paragraphs treating of the corresponding acids, in the second part of this section.

1. *Determination of lead as oxide.*

a. By precipitation.

α. By precipitation as carbonate of lead.

Mix the moderately dilute solution of the compound to be analysed, with carbonate of ammonia slightly in excess, add some ammonia, apply a gentle heat, and, after some time, filter. Wash the precipitate with pure water, dry, and ignite in a porcelain crucible, having previously incinerated the filter on the lid. For the properties of the precipitate and residue, see § 62. The results are satisfactory, although generally a trifle too low, owing to carbonate of lead not being absolutely insoluble, particularly in fluids rich in ammoniacal salts. (Experiment No. 43.) A small and thin filter should be used, and care taken to scrape it as clean as practicable, before proceeding to incinerate it; otherwise additional loss of substance might be incurred, from reduction of the adhering particles of the carbonate to metallic lead, by the charcoal of the filter.

β. By precipitation as oxalate of lead.

The solution of the compound under examination is mixed with oxalate of ammonia in excess, and ammonia added until it begins to predominate; the precipitated oxalate is then allowed to subside, the fluid filtered off from it, and the further process conducted as directed in *a.*; the porcelain crucible is left uncovered during the ignition of the precipitate. Results as in *a.*

b. By ignition.

Compounds like carbonate or nitrate of lead are carefully ignited in a porcelain crucible, until the weight remains constant. For the manner of reducing salts of lead with organic acids, to the state of oxide, see 5.

2. *Determination as sulphate of lead.*

a. By precipitation.

α. Mix the solution (which should not be over dilute) with moderately dilute pure sulphuric acid slightly in excess, and add to the mixture double its volume of spirits of wine; wait a few hours, to allow the precipitate formed to subside; filter, wash the precipitate with spirits of wine, dry, and ignite, after the method described in § 36. Though a careful operator

may use a platinum crucible, still a thin porcelain crucible is preferable. A small and thin filter should be employed, and the adhering sulphate of lead carefully scraped off, before proceeding to incineration. (See 1 *a.*, *α.*)

β. In cases where the addition of spirits of wine is inadmissible, a greater excess of sulphuric acid must be used, and the precipitate, which is allowed some time to subside, washed first with water acidulated with a few drops of sulphuric acid, finally with spirits of wine. The remainder of the process is conducted as in *α.*

For the properties of the precipitate, see § 62. The method *α* gives very accurate results; those obtained by *β* are nearly equally accurate, provided the proper excess of sulphuric acid be used, and the washing water be properly acidulated with that acid. Neglect of the former injunction will, in the presence, for instance, of ammoniacal salts, nitric acid, &c., cause a portion of the lead to remain in solution; neglect of the latter will lead to the solution of perceptible traces of the precipitate in the washing water.

b. By evaporation.

Put the weighed substance into a weighed dish, dissolve it in dilute nitric acid, add moderately dilute pure sulphuric acid slightly in excess, and evaporate, at a gentle heat, at last high over the lamp, until the excess of sulphuric acid is completely expelled. In the absence of organic substances, the evaporation may be effected in a platinum dish; but if organic substances are present, a light porcelain dish is preferable. The results are perfectly accurate.

β. Organic compounds of lead are converted into the sulphate by treating them, in a porcelain crucible, with pure concentrated sulphuric acid in excess, evaporating cautiously in the covered crucible, until the excess of sulphuric acid is completely expelled, and igniting the residue. Should the latter not look perfectly white, the process must be repeated. The method gives accurate results; a trifling loss is, however, usually incurred, the escaping sulphurous and carbonic acid gas being liable to carry away traces of the salt.

3. *Determination as chromate of lead.*

Mix the neutral or slightly acid solution with neutral chromate of potassa in excess, and, if free nitric acid has been present, add acetate of soda in sufficient quantity to replace the free nitric acid by free acetic acid; let the precipitate formed subside, at a gentle heat, pass the fluid through a weighed filter dried at 212°, wash the precipitate with water, dry at 212°, and weigh. For the properties of the precipitate, see § 72. The results are accurate.

H. Schwarz (Annal. d. Chem. u. Pharm. 84, 92) recommends to determine by analysis by measure, the chromic acid in the chromate of lead, instead of weighing the latter. To this end, the washed precipitate together with the filter, is treated with a hydrochloric acid solution of a

weighed quantity of iron, in excess, and heat applied. In this way we obtain chloride of lead, sesquichloride of chromium, and sesquichloride of iron, by the side of the excess of protochloride of iron; as every one equivalent of chromic acid converts three equivalents of iron from the state of protoxide or protochloride, to that of sesquioxide or sesquichloride [$2(PbO, CrO_3)+6\ FeCl+8\ HCl = 3Fe_2Cl_3+2PbCl+Cr_2Cl_3+8\ HO$]. We need now simply determine, with solution of permanganate of potassa, or bichromate of potassa (§ 89, 2.), the quantity of iron still remaining in the state of protoxide, to learn the quantity that has been oxidized; and from this we may then readily calculate the quantity of the chromic acid and of the lead.

Every three equivalents of iron (1050 parts), converted from the state of protoxide to that of sesquioxide, correspond to one equivalent of lead (1294·6 parts). The precipitation is effected in a porcelain dish, the fluid having been previously gently heated in the water-bath. The particles of the precipitate which stick to the dish need not be transferred to the filter, as the latter has under all circumstances to be returned to the dish, to be treated with the solution of protochloride of iron. The excess of hydrochloric acid in the latter should not be too slight. The dark-green solution is filtered while hot, and the filters are carefully washed. As the green tint of the solution renders the immediate detection of the red coloration —where solution of permanganate of potassa is used—a task of some difficulty, *Schwarz* advises not to count the last drop added.

It is evident that this method of determining chromate of lead by analysis by measure, can be considered advantageous only in cases where we have to make a whole series of analyses. In cases of this kind the solution of protochloride of iron is prepared in sufficient quantity to do for the whole series, the amount of protoxide in it is determined, and measured quantities of it are added respectively to the several samples.

4. *Determination as chloride of lead.*

Mix the solution with hydrochloric acid in excess, concentrate strongly in the water-bath, treat the residue with absolute alcohol, mixed with some ether, let the precipitate subside, filter the fluid off, wash the precipitate with alcohol mixed with some ether, dry it, and expose it to a gentle heat; were you to heat it to redness, some of the chloride of lead would volatilize. In other respects the operation is conducted as directed in 1. *a*, *a*. This method is had recourse to in certain separations of lead from other substances.

5. *Determination as oxide of lead+lead.*

Heat from one to two grms. of the organic compound of lead in a small weighed porcelain dish very gently, taking care to make the heat act first upon the brim of the dish, so that the ensuing decomposition may begin on one side, and proceed slowly. When the whole mass is perfectly de-

composed, increase the heat a little, and continue, until no more glowing particles are perceptible, and the residue forms a mixture of oxide of lead with globules of metallic lead, and is *perfectly* free from carbon. Weigh the residue, and heat it with acetic acid, until the oxide is completely dissolved; decant the solution now from the metallic lead, and wash the latter by repeated decantation; remove the last traces of water finally by heat, and weigh the residuary metallic lead. By subtracting the weight of the metal from that of the original residue, you will find the quantity of oxide of lead which was present in that residue; and by calculating the proportion of metal contained in the oxide, and adding the resulting number to the weight of the metallic lead, you will obtain the total amount of that metal originally present in the analysed compound. This method is very convenient, and, if properly and carefully executed, yields very accurate results. The operator must take care to conduct the decomposition of the organic compound very slowly, since the *rapid* combustion of its carbon and hydrogen at the expense of the oxygen of the oxide of lead, would produce so high a temperature as to volatilize a portion of the lead in visible fumes. If the residue is not perfectly free from carbon—(which will always be detected in the heating of it with acetic acid)—this will tend to give a higher number.

This method was originally introduced by *Berzelius*. *Dulk* has recently recommended the following modification of it:—The compound to be analysed is gently heated, in a covered porcelain crucible, until the organic substance is completely carbonized; the lid is then removed, and the mass stirred with a piece of iron wire. Upon this, the mass begins to ignite, and a mixture of oxide of lead with metallic lead results, which may still contain unconsumed carbon. A few crystals of dry nitrate of ammonia are now thrown into the crucible, which has previously been removed from the flame, and the lid is then again put on. The salt fuses, oxidizes the lead, and converts it partly into nitrate. The crucible is now exposed to a red heat, until no more fumes of hyponitric acid escape. The residuary oxide is then weighed. This modification of *Berzelius*' method gives very accurate results. It possesses this great advantage, that it ensures the complete combustion of the whole of the carbon; it saves also some trouble in weighing and calculating.

6. *Determination as sulphide of lead.*

a. The same method which serves for the determination of silver as sulphide (§ 91, 2.), may also be resorted to for lead; with this exception, however, that the precipitation of the sulphide of lead from acid solutions must be effected without the application of heat; otherwise, a portion of the precipitate will redissolve. For properties of the precipitate, see § 62.

β. If the precipitate contains some admixture of sulphur, it must be converted into sulphate of lead. To that end, the precipitate is

dried on the filter, and put into a beaker-glass, into which the filter is then likewise thrown; pure fuming nitric acid is now added, drop by drop, the glass being kept covered with a glass plate. When the oxidation is effected, a gentle heat is applied for some time, and the contents of the beaker-glass are then transferred to a small porcelain dish, the last particles being carefully rinsed into the latter; a few drops of pure sulphuric acid are now added, the mixture is cautiously evaporated, and the residue finally ignited. The results are accurate. The use of the *fuming* nitric acid is indispensable, the application of an acid of a lower degree of concentration involving always a separation of sulphur, which oxidizes in the subsequent process only with extreme slowness.

7. *Determination of lead by analysis by measure.*

Besides *Schwarz'* method (see 3), the following two methods are also recommended:—

a. Flores Domonte's method.

Add to the solution of lead, solution of potassa or soda in excess, and heat to boiling, until the basic salt, which precipitates at first, is redissolved. Add now to the boiling solution, a dilute solution of accurately known strength of sulphide of sodium, as long as a precipitate continues to form. To hit the proper point in this, it is necessary to allow the fluid from time to time to get clear.

To prepare the solution of sulphide of sodium, saturate a measured quantity of solution of soda completely with sulphuretted hydrogen (which gives hydrosulphate of sulphide of sodium), and add an equal quantity of solution of soda. Dilute the mixture, until you have one litre of liquid to about 8 grms. of anhydrous sulphide of sodium. Thus, taking the specific gravity of your solution of soda to be 1·15 = 10 p. ct. of soda, you would have to saturate 28 cubic centimeters of the same with sulphuretted hydrogen, to add 28 cubic centimeters more, and then to dilute the mixture to 1000 cubic centimeters. 50 cubic centimeters = 100° of the solution so prepared, will precipitate about one grm. of lead. The exact strength of the solution is ascertained by applying it in the above-mentioned manner on a solution made for the purpose, and containing exactly one grm. of lead. As the solution of sulphide of sodium is liable to suffer alteration, the exact composition and strength of it must be accurately ascertained anew on the occasion of every fresh series of experiments. The decomposition on which this method is based is expressed by the equation

$$PbO + NaS = PbS + NaO$$

b. Marguerite's method.

Add to a boiling strongly alkaline solution of oxide of lead, solution of permanganate of potassa, until the whole of the lead is precipitated as binoxide. The permanganic acid is converted in this process to binoxide of manganese.

$$3\,PbO + Mn_2O_7 = 3\,PbO_2 + 2\,MnO_2$$

When the operation draws to its close, the liquid acquires a green tint, which it loses again upon protracted ebullition. When the green color at last remains, notwithstanding the long-continued boiling of the fluid, the oxidation of the lead is complete, and the operation at an end. The disagreeable spirting of the fluid, occasioned by the precipitates formed, makes this method rather inconvenient; besides, it is by no means easy to hit the exact point at which the peroxidation of the lead is achieved. For the preparation of the solution of permanganate of potassa, see § 89. The strength of the same is determined by means of a solution of lead of accurately known strength, which operation has to be gone through anew before every fresh series of experiments. I may here parenthetically remark, that if you use the solution of which 50 cubic centimeters correspond to 1 grm. of iron (§ 89, *bb.* 2 *a.*), the same quantity (50 cubic centimeters) will convert 1·11 grm. of lead from the state of oxide to that of binoxide.

§ 93.

3. SUBOXIDE OF MERCURY.

a. Solution.

Suboxide of mercury and its compounds had always best be oxidized to effect their solution, since it would be difficult to obtain a solution of suboxide entirely free from admixture of oxide. To this end, the suboxide or subsalt of mercury is heated for some time with nitric acid in excess; some hydrochloric acid is then added, and the application of heat continued until a perfectly clear solution is produced. All the compounds of suboxide of mercury, and also the metal itself, may be readily dissolved in this manner.

b. Determination.

It follows from the preceding remarks, that the determination of the suboxide is the same as that of the oxide of mercury, which will be found in the next paragraph. For the way of determining the suboxide in presence of oxide, I refer to § V.

§ 94.

4. OXIDE OF MERCURY.

a. Solution.

Oxide of mercury and those of its compounds which are insoluble in water, are dissolved, as the case may be, in hydrochloric acid or in nitric acid. Sulphide of mercury is heated with hydrochloric acid, and nitric acid added until complete solution ensues.

b. Determination.

Mercury may be weighed in the *metallic* state, or as *subchloride* or *sulphide*, or as *oxide*. In some cases the mercury is expelled from the analysed compound by ignition, and its amount inferred from the dimi-

nution of weight which the ignited compound has suffered. Mercury may be determined also by analysis by measure.

The methods of determining mercury as metal, subchloride, or sulphide, are applicable in all cases without exception; the latter, however, deserves the preference in most instances, on account of it accuracy, simplicity, and easiness. The method of determining mercury as oxide can be resorted to only in the case of compounds of suboxide or oxide of mercury with nitric acid. The analysis by measure presupposes that the solution contains no hydrochloric acid, nor any other compound of chlorine.

1. *Determination as metallic mercury.*

a. In the dry way.

The process is conducted in the apparatus illustrated by Fig. 43.

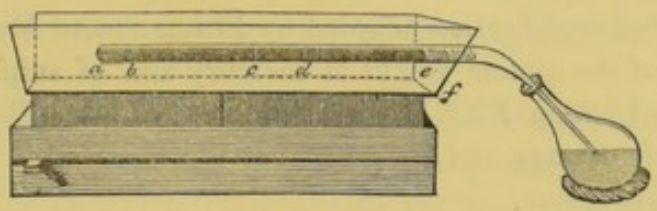


Fig. 43.

The principal part of the apparatus consists of a tube one and a half foot long, and between three and four lines wide, made of difficultly fusible glass, and closed at one end. Into this tube is put, in the first place, a layer, two inches long, of dry hydrate of lime, which is pushed down to the closed end, where it accordingly occupies the space from *a* to *b* (two inches). This is followed by an intimate mixture of the mercurial compound to be analysed, with an excess of soda-lime (§ 45. 4), and which occupies the space from *b* to *c*. The particles of the mixture adhering to the mortar are removed with the aid of some more soda-lime, which is then likewise put into the tube, where it occupies the space from *c* to *d*. This is followed by a layer of pure soda-lime, occupying the space from *d* to *e*, and this by a loose stopper of pure asbestos, from *e* to *f*. The anterior end of the tube is then drawn out, and bent at a somewhat obtuse angle. The manipulations in the processes of mixing and filling being the same as in organic elementary analysis, they will be found described in detail in the chapter on that subject.

A few gentle taps upon the table will suffice to shake the contents of the tube down sufficiently to leave a free passage above them throughout the whole length of the tube. The tube, so prepared and arranged, is now placed in a combustion furnace, the point being thrust into a receiving flask containing water, of which it must just touch the surface sufficiently to have the opening half closed by it.

The tube is now surrounded with live charcoal, in the same way as in organic analysis, and proceeding slowly from *e* to *a*, the last traces of mer-

curial vapor being finally expelled by heating the hydrate of lime in the end of the tube. Whilst the tube still remains in a state of intense ignition, the neck is cut off at *f*, and carefully and completely rinsed into the receiving flask, by means of a washing-bottle. The small globules of mercury which have distilled over into the flask, are united into a large one, by agitating the flask, and, after the lapse of some time, the perfectly clear water is decanted off and the mercury poured into a weighed porcelain crucible, where the greater portion of the waters till adhering to it is removed with blotting-paper. The mercury is then finally dried under a bell-jar, by the side of a vessel with concentrated sulphuric acid, until the weight remains constant. For the properties of this metal, see § 63. This method, if properly and carefully executed, gives accurate results. The most highly accurate results are, however, obtained by the application of the somewhat more complicated modification adopted by Erdmann and Marchand for the determination of the atomic weight of mercury and of sulphur. (Journal für praktische Chemie XXXI. page 385.—And also Pharmaceutisches Centralblatt, 1844, page 354.)

b. In the humid way.

The solution is, in the first place, freed from a possible admixture of nitric acid, by repeated evaporation with hydrochloric acid; it is then transferred to a flask, free hydrochloric acid added, and after this a clear solution of protochloride of tin in excess, which must likewise contain free hydrochloric acid; the mixture is now boiled for some time, and then allowed to cool. After a time, the perfectly clear supernatant fluid is decanted from the metallic mercury, which, if the process has fully succeeded, will be found united into one globule; if this is the case, the globule of mercury may be washed at once by decantation, first with water acidulated with hydrochloric acid, and finally with pure water, which is then partly removed by blotting-paper, and the mercury afterwards dried and weighed as in *a*.

If, on the other hand, the particles of the mercury have not united, their union into one globule may readily be effected by boiling them a short time with some moderately dilute hydrochloric acid (having, of course, previously removed by decantation the supernatant clear fluid). For the properties of metallic mercury, see § 63.

Phosphorous acid, sulphurous acid, and other reducing agents, may be substituted for the protochloride of tin.

This method gives accurate results, but it requires the *very greatest* care in the performance of the several operations. The resulting numbers are generally a little too low. (Compare experiment No. 68, made by one of the students in my laboratory.) This, however, is entirely owing to defective execution of the operations, and by no means to defects inherent in the method itself; and the generally received notion, which would impute

the deficiency to the volatilization of a portion of the mercury, in the processes of boiling and drying, is founded in error. (See Experiment No. 50.) In the case of solutions containing much nitric acid, it is always the best way to determine the mercury as sulphide.

2. *Determination as subchloride of mercury.*

Mix the solution with hydrochloric acid, if that acid is not already present, add solution of potassa until the excess of the acid is *nearly* neutralized, mix with a solution of formiate of soda in excess, and let the mixture stand four days, at a temperature of from 140° to 176°. Filter the fluid now off from the precipitated subchloride, and collect the latter on a weighed filter, dried at 212°. Let the filtrate stand twenty-four hours longer, at a temperature of from 140° to 176°, and, should a new precipitate form, add this to the first, and repeat the same process until the filtrate remains perfectly clear. Wash the collected precipitate, dry at 212°, and weigh.

This method is very tedious, and requires, besides, the strictest care and attention in the performance of the several operations; its application is therefore almost exclusively confined to the separation of mercury from certain metals. The operator must take particular care not to exceed a temperature of 176°, since otherwise metallic mercury might separate; should this be the case, the precipitate will exhibit a grayish appearance, and the experiment must, under such circumstance, be considered a failure.

3. *Determination as sulphide of mercury.*

a. The solution of the salt of mercury is free from nitric acid.

Acidify the solution slightly with hydrochloric acid, if that acid is not already present, transfer it to a flask with a ground stopper, and add a freshly prepared clear saturated solution of sulphuretted hydrogen in slight excess, just sufficient to make the odor of that gas clearly perceptible after shaking the flask; now put in the stopper, and let the precipitated sulphide subside.

b. The amount of mercury present is so considerable, that its precipitation would require a very large portion of sulphuretted hydrogen water.

Conduct into the moderately dilute solution washed sulphuretted hydrogen gas.

c. The solution contains nitric acid.

Add potassa to the solution until the acid is *nearly* neutralized; mix the fluid with a clear solution of cyanide of potassium in excess, and precipitate the mercury finally either with sulphuretted hydrogen water, or with colorless hydrosulphate of sulphide of ammonium, or by transmitting sulphuretted hydrogen gas through it. Let the precipitate subside, collect it on a weighed filter, wash it rapidly with cold water, dry at 212°, and weigh.

If the precipitate contains free sulphur (owing to the presence of sesquioxide of iron, chromic acid, &c., &c., or to some other cause),

transfer it, still moist, together with the filter, to a small flask, treat it with hydrochloric acid, apply heat, and add nitric acid, drop by drop, until the separated sulphur exhibits a pure yellow color; dilute the mixture now with water, filter, and precipitate again as sulphide, by addition of potassa, cyanide of potassium, and sulphuretted hydrogen gas, or sulphuretted hydrogen water, or colorless hydrosulphate of sulphide of ammonium, as above. For the properties of the precipitate, see § 63.

This method gives very accurate results, and is, in my opinion, preferable to all others.

4. *Determination as oxide.*

The mercury, in its salts with nitrogen acids, may be determined in the form of oxide. To this end, the salt is heated in a bulb-tube, of which the one end, drawn out to a point, dips under water, the other end being connected with a gasometer, by means of which dry air is transmitted through the tube, as long as the application of heat is continued. In this way complete decomposition of the salt is effected, whilst the oxide to which it is reduced, remains unaffected. (*Marignac*, in *Liebig* and *Kopp's* Annual Report, 1849, page 594.)

5. *Analysis by measure.* (*Liebig's* method—Annalen der Chemie und Pharmacie, 85, 307.)

This method is based upon the circumstance that phosphate of soda precipitates mercury from solutions of the nitrate, but not from solutions of the chloride, in the form of a flocculent white precipitate, which speedily turns crystalline; and that chloride of sodium accordingly readily redissolves this precipitate (as long as it has not yet acquired crystalline consistence), phosphate of soda and chloride of mercury being formed. Thus, if we know the quantity of chloride of sodium required to redissolve the precipitate, we learn from this also the quantity of the mercury, since every one equivalent of chloride of sodium dissolves one equivalent of oxide of mercury (in the form of phosphate): it requires, accordingly, 0·54103 grm. of chloride of sodium to dissolve 1 grm. of oxide of mercury.

a. Preparation of the solution of chloride of sodium.

Dissolve 10·8206 grms. of pure chloride of sodium in water, and dilute the solution until you have exactly one litre of fluid (*Liebig* uses 20 cubic centimeters of solution of chloride of sodium, saturated at the common temperature, to 566·8 cubic centimeters of water). Every cubic centimeter of the solution, prepared either way, corresponds to 0·020, grm. of oxide of mercury.

b. Preparation of the solution of oxide of mercury.

According to *Liebig*, this solution, which must, of course, be perfectly free from compounds of chlorine, and in which the whole of the mercury must be present in the state of oxide, should contain no more than about 0·2 grm. of oxide of mercury in 10 cubic centimeters of fluid. Accordingly,

if a preliminary experiment shows it to have a higher degree of concentration, dilution to the proper degree must be had recourse to. Neither must there be too much free acid present: the addition of from 3 to 4 cubic centimeters of a perfectly saturated solution of phosphate of soda to 10 cubic centimeters of the solution, must suffice to take off all acid reaction. If too much acid is present, carbonate of soda must be added, until the basic salt begins to precipitate, which latter is then redissolved by addition of one or two drops of nitric acid.

c. Performance of the analytical process.

There are two different methods recommended, which it is the best way to apply in combination, as the results obtained by the former are somewhat too high, those by the latter a little too low.

Method I.—Measure off 10 cubic centimeters of the solution of oxide of mercury in a beaker-glass, add 3 to 4 cubic centimeters of a saturated solution of phosphate of soda, and then immediately, before the precipitate has had time to acquire crystalline consistence, solution of chloride of sodium, until the precipitate is redissolved: the last portions of the solution of chloride of sodium must be added very cautiously, to avoid addition in excess.

Now, supposing you have used 12·5 cubic centimeters of solution of chloride of sodium, to effect the solution of the precipitate formed upon the addition of the solution of phosphate of soda, you must now—

(*Method II.*)—Measure off 12·5 of the same solution of chloride of sodium, add to this 3 to 4 cubic centimeters of solution of phosphate of soda, and then of your solution of oxide of mercury from a *burette*, until a permanent precipitate just begins to form. Supposing this has taken 10·25 cubic centimeters of solution of mercury, then 12·5 + 12·5 = 25 cubic centimeters of your solution of chloride of sodium having been consumed to 10 + 10·25 = 20·25 of your solution of oxide of mercury; and 1 cubic centimeter of your solution of chloride of sodium corresponding to 0·020 grm. of oxide of mercury, it follows that the 20·25 cubic centimeters of the analysed solution of oxide of mercury contained 0·5 grm. of oxide.

Liebig has proved by numerous experiments that this course of proceeding gives very nearly accurate results; he obtained 0·1878 grm. instead of 0·1870 grm., 0·174 grm. instead of 0·1748 grm., 0·1668 grm. instead of 0·1664 grm., &c.

§ 95.

5. OXIDE OF COPPER.

a. Solution.

Most of the compounds of oxide of copper dissolve in water. Metallic copper, oxide of copper, and those of its salts which are insoluble in water, are dissolved in dilute nitric acid. Sulphide of copper is heated with moderately dilute nitric acid, until the separated sulphur exhibits a pure

yellow tint; addition of a little hydrochloric acid greatly promotes this decomposition.

b. Determination.

Copper is usually weighed in the form of *oxide* (§ 64). Into this form it is converted either by *direct* precipitation as such, or by ignition, or after previous precipitation as *sulphide*. Copper may be determined also in an indirect way, and by analysis by measure.

We may determine as

1. OXIDE OF COPPER.

a. By precipitation as oxide.

α. By direct precipitation.

All salts of oxide of copper soluble in water, and also those of the insoluble salts, of which the acids may be removed upon their solution in nitric acid, provided no non-volatile organic substances be present.

β. By precipitation preceded by ignition of the compound.

Such of the salts enumerated sub *α* as contain a non-volatile organic substance, and thus more particularly salts of copper with non-volatile organic acids.

b. By precipitation as sulphide of copper.

All compounds of copper without exception.

c. By ignition.

Salts of copper with readily volatile oxygen acids, or with such oxygen acids as are readily decomposed at a high temperature. (Carbonate of copper, nitrate of copper.)

The indirect method, and the analysis by measure, which are applicable in almost all cases, are more particularly adapted for technico-chemical purposes.

1. *Determination as oxide of copper.*

a. By direct precipitation as oxide.

α. From neutral or acid solutions.

Heat the *rather dilute* solution, in a porcelain dish, to incipient ebullition, add a somewhat dilute pure solution of soda or potassa until the formation of a precipitate ceases, and keep the mixture a few minutes longer at a temperature near the boiling point.

After allowing some time for the subsidence of the precipitate, filter the fluid off, treat the precipitate with water, heat to boiling, let the precipitate subside, and repeat the operation just described. Collect the whole of the precipitate finally on the filter, wash it thoroughly with hot water, dry, and ignite in a platinum crucible, as directed § 36. After intense ignition, and having added the ashes of the filter to the contents of the crucible, put the latter under a bell-jar, by the side of a vessel containing concentrated sulphuric acid, place it on the balance whilst still a little warm to the touch, and weigh as quickly as possible.

It will sometimes happen, though mostly from want of proper attention

to the directions here given, that particles of the oxide of copper adhere so pertinaciously to the dish that mechanical appliances fail to remove them. In a case of this kind you need simply wash the dish thoroughly, dissolve the adhering particles with a few drops of nitric acid, and evaporate the solution over the principal mass of the precipitated oxide, before you proceed to ignite the latter. For the properties of the precipitate, see § 64.

With proper attention to the directions here given, most accurate results are attained by this method; deviations from these directions will, of course, impair more or less the accuracy of the results. Thus, if the solution be not sufficiently dilute, the precipitant will fail to throw down the whole of the oxide of copper present; or, if the precipitate be not thoroughly washed with hot water, it will retain a portion of the alkali; or, if the ignited precipitate be allowed to stand exposed to the air, before it is weighed, an increase of weight will be the consequence; and so, on the other hand, a diminution of weight, if the filter be ignited in contact with the oxide, since this will, of course, tend to reduce it more or less. Should a portion of the oxide have suffered reduction, it must be reoxidized by moistening with some nitric acid, evaporating cautiously to dryness, and exposing the residue to a gentle heat, increasing this gradually to a high degree of intensity.

Let it be an invariable rule with you to test the filtrate for copper with sulphuretted hydrogen water. If, notwithstanding the strictest compliance with the directions here given, the addition of this reagent produces a precipitate, or imparts a brown tinge to the fluid, this is to be attributed to the presence of organic matter; in that case, concentrate the filtrate and washing water by evaporation, precipitate with sulphuretted hydrogen water; treat the precipitated sulphide as directed in *c*, and add the oxide obtained to the first precipitate.

β. From alkaline solutions.

From ammoniacal solutions also, oxide of copper may be precipitated by potassa. In the main, the process is conducted as in *α*. After the precipitation the mixture is heated, until the fluid above the precipitate has become perfectly colorless; the fluid is then filtered off with the greatest possible expedition. If the fluid were allowed to cool with the precipitate in it, a small portion of the latter would redissolve.

b. By precipitation as oxide, preceded by ignition of the substance under examination.

α. Heat the substance in a porcelain crucible, until the organic matter present is totally destroyed; dissolve the residue in dilute nitric acid, filter, if necessary, and treat the clear solution as directed in *a. α*, or evaporate it, and treat the residue as in *d*.

β. In the case of salts of copper with organic acids, the quantitative estimation may be effected also by igniting the salt, moistening the residue

with nitric acid, evaporating, moistening once more with nitric acid, evaporating again, and finally igniting the residue cautiously. The application of this method involves generally a trifling loss of substance from particles of the salt being carried away in the process of ignition.

c. By precipitation as sulphide of copper.

Precipitate the solution—which may be alkaline, neutral, or slightly acid, but should not contain a great excess of nitric acid—according to the smaller or larger quantity of copper present, either with strong sulphuretted hydrogen water, or by conducting sulphuretted hydrogen gas into it. When the precipitate has fully subsided, filter off quickly, wash the precipitate without intermission with water impregnated with sulphuretted hydrogen, and dry it on the filter; transfer the dried precipitate to a beaker-glass, incinerate the filter in a small porcelain dish, add the ashes to the precipitate in the glass, treat with moderately dilute nitric acid, add some hydrochloric acid, and heat gently until the separated sulphur appears of a pure yellow color; dilute now with water, filter, and precipitate as directed in *a*.

d. By ignition.

The salt is put into a platinum, or porcelain crucible, and exposed to a very gentle heat, which is gradually increased to intense redness: the residue is then weighed.

As nitrate of copper spirts strongly when ignited, it is always advisable to put it into a small covered platinum crucible, and to place the latter in a large one, also covered. The results are accurate.

2. *Indirect determination by means of metallic copper.*

a. Levol's Method.—Put the solution of oxide of copper into a flask with a ground stopper, and add ammonia in excess, so as to obtain a clear azure blue solution; fill the flask almost to the top with water freed from atmospheric air by ebullition, put into it a perfectly clean, accurately weighed slip of copper, place the stopper in tightly, and let the flask stand at the common temperature until the fluid is perfectly colorless; withdraw the copper slip now, wash, dry, and weigh it. The diminution of weight which it has suffered indicates the amount of copper originally present in the solution. The results are accurate; but the method has this great disadvantage, that the experiment takes from three to four days, and often more. It is obvious that it is altogether inapplicable in cases where the solution contains, besides the copper, other metals precipitable by the latter.

[*Riegel* (Archiv. der Pharm. 56, 40) obtained satisfactory results with this method; but *Philipps* (Annalen der Chemie und Pharmacie, 81, 208) states that the results which he obtained by its application were from 15 to 20 per cent too high.]

b. Runge's Method.—In a solution of chloride of copper, free from

nitric acid (and from sesquioxide of iron), the amount of the metal may be estimated also in the following manner: mix the moderately dilute solution, in a long-necked flask, with free hydrochloric acid, put in a weighed slip of copper, and boil gently until the fluid has become colorless; take the slip of copper out, wash it carefully, dry, and weigh (compare § 90.) *Riegel* found the results satisfactory. This method is more expeditious than 2. *a*.

3. *Analysis by measure.*

a. *Pelouze's* Method.—If a solution of oxide of copper supersaturated with ammonia, is mixed, *at the common temperature*, with sulphide of sodium, a black precipitate of sulphide of copper (CuS) is formed, which *subsides slowly*, and *speedily absorbs oxygen*, upon exposure to the air. If, on the contrary, the precipitation is effected *at a temperature of from* 149° to 185°, a black precipitate is indeed formed, but this consists of a mixture of sulphide of copper with oxide of copper ($5CuS+CuO$), which *subsides readily*, and *absorbs oxygen slowly*. If the ammoniacal solution contains other metals besides copper, the former are not precipitated, as long as any portion of the latter remains in solution. If the application of heat is long continued, and the temperature raised above 185°, the mixture of sulphide and oxide of copper takes up an additional quantum of oxide; moreover a portion of the oxide is reduced to suboxide which remains in the ammoniacal solution, the liberated oxygen combining with the sulphur of the sulphide to form hyposulphurous acid. Therefore, if we know the amount of a solution of sulphide of sodium of known strength which is required at a temperature of about 167°, to throw down the whole of the metal from an ammoniacal solution of oxide of copper, we may infer from this the quantity of copper contained in he latter.

The solution of sulphide of sodium is prepared in the manner described in § 92. 7. *a*. The strength of the solution is ascertained as follows:—About 1 grm. of pure copper is dissolved in a flask, in the requisite amount of nitric acid,* and a quantity of about 30 cubic centimeters of strong solution of ammonia added; the clear azure blue fluid is then heated to gentle ebullition, by means of a small spirit-lamp with a short trimmed wick. When the liquid begins to boil, a thermometer plunged into it marks between 122° and 140°. The solution of sulphide of sodium is now gradually added, the application of heat being continued. (There is no fear that the temperature of the liquid will go beyond the limit of 185°, provided some ammonia be added from time to time, as that substance, in its evaporation, carries off a large amount of caloric.) As soon as the blue color of the fluid is no longer distinctly perceptible, the lamp is removed for a short time, the sides of the flask are rinsed with a little ammonia

* A solution of a corresponding quantity of pure sulphate of copper in water, may be substituted for the nitric acid solution.

injected by means of a washing bottle, and the precipitate is allowed to subside a little. If the fluid after this still presents a blue tint, the lamp is replaced, and a few more drops of sulphide of sodium are added; the lamp is then removed again, &c., and the same process continued until the fluid appears colorless after the subsidence of the precipitate.

In analytical investigations, the acid solution of a weighed quantity of the compound of copper which it is intended to analyse, is treated exactly in the manner just now described. It is always advisable to weigh off as much of the compound to be analysed as may be presumed to contain about 1 grm. of copper, which may be roughly ascertained by a preliminary experiment.

The strength of the solution of sulphide of sodium must be determined anew for every fresh series of experiments. The analytical process occupies about ten minutes. The results are satisfactory.

b. Schwarz's Method (Annal. der Chemie und Pharm. 84, 84.)—If we mix a solution of oxide of copper with a sufficient quantity of a tartrate of an alkali, and add solution of soda, we obtain a dark-blue fluid. If we heat this, and add a sufficient amount of grape-sugar, the whole of the copper precipitates, after a short time, in the form of suboxide. On heating this with sesquichloride of iron and hydrochloric acid, it dissolves, the following transposition taking place:

$$Cu_2O + Fe_2Cl_3 + HCl = 2CuCl + 2FeCl + HO.$$

Every 1 equivalent of copper reduces accordingly 1 equivalent of iron from the state of sesquichloride to that of protochloride. From the quantity obtained of the latter, we ascertain the amount of the copper.

The analytical process is conducted as follows:—Weigh the compound of copper under examination, dissolve it in water or nitric acid, in a capacious porcelain dish, mix it, in the cold, with a solution of neutral tartrate of potassa, and add solution of potassa or soda in excess. Mix the dark-blue fluid now with a sufficient quantity of an aqueous solution of grape-sugar, or of milk-sugar, and heat on the water-bath, until the fluid shows a brown tinge on the border, which is a sign that the whole of the copper is precipitated, and that the potassa begins to act upon the sugar, imparting a brown tint to it. When the precipitate has subsided, filter. The filtrate appears, in most cases, of a deep brown; upon the addition of the washing water a muddy yellowish layer forms on the top of it; however, this disappears immediately upon stirring the fluid—a proof that it does not proceed from any suboxide of copper having passed through the filter. Wash the precipitated suboxide of copper with hot water, until the washing water comes off perfectly colorless; particles of the suboxide, adhering firmly to the dish, are left in the latter. Put the filter with the suboxide on it, into the dish, add solution of pure sesquichloride of iron (free from nitric acid and from protochloride) in slight

excess, and a little hydrochloric acid, and heat gently, with stirring, which will suffice to redissolve the protochloride of copper which forms at first. Filter the green solution into a capacious flask, wash the remains of the first filter thoroughly with hot water, let the fluid cool down to about 86°, and estimate the amount of protochloride of iron formed, as directed in § 89, 2. Every 350 parts of iron, found in the state of protoxide or protochloride, correspond to 396 parts of copper. The results are satisfactory.

§ 96.

6. TEROXIDE OF BISMUTH.

a. Solution.

Metallic bismuth, the teroxide, and all other compounds of that metal, are dissolved best in more or less dilute nitric acid.

b. Determination.

Bismuth is always weighed in the form of *teroxide* (§ 65). Into this form the compounds of bismuth are converted either by ignition, or by precipitation as *carbonate of bismuth* (*carbonate of teroxide of bismuth*), preceded in some cases by precipitation as *tersulphide.*

We may convert into

TEROXIDE OF BISMUTH.

a. By precipitation as carbonate of bismuth.

All compounds of bismuth which dissolve in nitric acid to nitrate, no other acid remaining in the solution.

b. By ignition.

α. Salts of bismuth with readily volatile oxygen acids.

β. Salts of bismuth with organic acids.

c. By precipitation as tersulphide of bismuth.

This method is had recourse to in all cases where *a* or *b* is inadmissible.

Determination of bismuth as teroxide.

a. By precipitation as carbonate of teroxide of bismuth.

Mix the solution of bismuth with carbonate of ammonia in excess, and heat a short time nearly to boiling; filter, dry the precipitate, and ignite it in the manner described § 92 (ignition of carbonate of lead); the process of ignition serves to convert the carbonate into the pure teroxide of bismuth. Should the solution be too concentrated, dilute it with water, previously to the addition of the carbonate of ammonia; whether the dilution leads to the precipitation of basic nitrate of bismuth or not, is a matter of perfect indifference. For the properties of the precipitate and residue, see § 65.

The method gives accurate results, though generally a trifle too low,

owing to the circumstance that carbonate of teroxide of bismuth is not absolutely insoluble in carbonate of ammonia.

Were you to attempt to precipitate bismuth by means of carbonate of ammonia, from solutions containing sulphuric acid or hydrochloric acid, you would obtain incorrect results, since the teroxide would contain, in the former case, an admixture of basic sulphate, in the latter of basic terchloride of bismuth. Were you to filter off the precipitate, without previous application of heat, part of the basic carbonate would remain in solution, which would, of course, considerably reduce the resulting numbers. (Experiment No. 69.)

b. By ignition.

α. Compounds like the carbonate or nitrate of teroxide of bismuth are ignited in a porcelain crucible until their weight remains constant.

β. Compounds of teroxide of bismuth with organic acids, are treated like the corresponding compounds of oxide of copper (§ 95. 1. *b.* β.)

c. By precipitation as tersulphide of bismuth.

Dilute the solution with water slightly acidulated with acetic acid (to prevent the precipitation of a basic salt), and precipitate with sulphuretted hydrogen water or gas; filter, and wash the precipitate. Or mix with ammonia until the free acid is neutralized, and then add sulphide of ammonium in excess.

The tersulphide of bismuth may be weighed in that form, if the operator is convinced that no free sulphur has been thrown down in conjunction with it. But, as in the case of compounds of bismuth we have mostly to deal with very acid solutions, and which contain nitric acid, there is generally reason to apprehend a partial decomposition of the sulphuretted hydrogen, attended with separation of free sulphur, on which account it is always safest to convert the tersulphide into teroxide. To this end the filter, with the washed and still moist precipitate on it, is put into a beaker-glass, and heated with moderately strong nitric acid until complete decomposition is effected; the solution is then diluted with water, slightly acidulated with acetic or nitric acid, and filtered, the filter being washed with the acidulated water; the filtrate is then finally precipitated as directed in *a*.

§ 97.

7. OXIDE OF CADMIUM.

a. Solution.

Cadmium, its oxide, and all the other compounds of it which are insoluble in water, are dissolved in hydrochloric acid or in nitric acid.

b. Determination.

Cadmium is weighed either in the form of *oxide*, or in that of *sulphide* (§ 66).

We may convert into

1. OXIDE OF CADMIUM.

a. By precipitation.

The compounds of cadmium which are soluble in water; the insoluble compounds, the acid of which is removed upon their solution in hydrochloric acid; salts of cadmium with organic acids.

b. By ignition.

Salts of cadmium with readily volatile, or easily decomposable, inorganic oxygen acids.

2. SULPHIDE OF CADMIUM.

All compounds of cadmium without exception.

1. *Determination as oxide of cadmium.*

a. By precipitation.

Precipitate with carbonate of potassa, wash the precipitated carbonate of cadmium, and reduce it, by ignition, to the state of pure oxide. For the details of the method of proceeding, I refer the student to § 85. (Zinc.) For the properties of the precipitate and residue, see § 66.

b. By ignition.

See § 85 *c.* (Zinc.)

2. *Determination as sulphide of cadmium.*

Precipitate the solution—if neutral or acid, with sulphuretted hydrogen water or gas—if alkaline, with sulphide of ammonium, collect the precipitate upon a weighed filter, wash, dry at 212°, and weigh. For the properties of the precipitate, see § 66. The results are accurate.

Should the precipitated sulphide of cadmium contain an admixture of free sulphur, it must be converted into nitrate or chloride of cadmium, and subsequently precipitated as carbonate of cadmium, in the manner directed § 85. *b.* (Zinc.)

SIXTH GROUP OF THE BASES.

TEROXIDE OF GOLD—BINOXIDE OF PLATINUM—TEROXIDE OF ANTIMONY—BINOXIDE OF TIN—PROTOXIDE OF TIN—ARSENIOUS ACID AND ARSENIC ACID.

§ 98.

1. TEROXIDE OF GOLD.

a. Solution.

Metallic gold, and all compounds of gold insoluble in water, are heated with hydrochloric acid, and nitric acid is gradually added, until complete solution is effected; or they are repeatedly digested with strong chlorine water. The latter method is resorted to more especially in cases where we have to dissolve small quantities of gold, and wish to leave undissolved other oxides that may happen to be mixed with it.

b. Determination.

Gold is always weighed in the metallic state, to which its compounds are reduced by direct precipitation, or by ignition, preceded, in some cases, by precipitation as tersulphide of gold.

We may convert into

METALLIC GOLD.

a. By ignition.

All compounds of gold which contain no fixed acid.

b. By precipitation as metallic gold.

All compounds of gold, without exception, in cases where *a* is inapplicable.

c. By precipitation as tersulphide of gold.

This method serves to effect the separation of gold from certain other metals that happen to be mixed with it in a solution.

Determination as metallic gold.

a. By ignition.

Heat in a covered porcelain or platinum crucible, very gently at first, but finally to redness, and weigh the residuary pure gold. For properties of the residue, see § 67. The results are most accurate.

b. By precipitation as metallic gold.

α. The solution is free from nitric acid.

Mix the solution with a little hydrochloric acid, if it does not already contain some of that acid in the free state, and add a clear solution of sulphate of protoxide of iron in excess; heat gently for a few hours, until the precipitated fine gold powder has completely subsided; filter, wash, dry, and ignite. (§ 35.) A porcelain dish is a more appropriate vessel to effect the precipitation in than a beaker-glass, as the heavy fine gold powder is more readily rinsed out of the former than out of the latter. The results are accurate.

β. The solution of gold contains nitric acid.

Evaporate the solution on a water-bath, to the consistence of syrup, adding from time to time hydrochloric acid; dissolve the residue in water containing hydrochloric acid, and treat the solution as directed in *α*. It will sometimes happen that the residue does not completely dissolve, in consequence of a partial decomposition of the terchloride of gold into protochloride and metallic gold; however, this is a matter of perfect indifference.

γ. In cases where it is wished to avoid the presence of iron in the filtrate, the gold may be reduced by means of oxalic acid. To this end, the solution—freed previously, if necessary, from nitric acid, in the manner directed in *β*—is mixed in a beaker-glass, with oxalate of ammonia in excess, some hydrochloric acid is added (if that acid is not already present

in the free state), and the vessel, covered with a glass-plate, is kept standing for two days in a moderately warm place. At the end of that time, the whole of the gold will be found to have separated in small yellow scales; the supernatant fluid is then filtered off from the gold, and the latter washed, dried, and ignited.

c. By precipitation as tersulphide of gold.

Sulphuretted hydrogen gas is transmitted in excess through the dilute solution of the compound under examination; the precipitate formed is speedily filtered off, without heating, washed, dried, and ignited in a porcelain or platinum crucible. For the properties of the precipitate, see § 67. The results are accurate.

§ 99.

2. BINOXIDE OF PLATINUM.

a. Solution.

Metallic platinum, and the compounds of platinum which are insoluble in water, are dissolved by digesting them, at a gentle heat, with nitrohydrochloric acid.

b. Determination.

Platinum is invariably weighed in the pure metallic state, to which its compounds are reduced, either by precipitation as *bichloride of platinum and chloride of ammonium*, or as *bichloride of platinum and chloride of potassium*, or as *bisulphide of platinum*, or by ignition. All the compounds of platinum, without exception, may, in most cases, be reduced to the metallic state by either of these methods. Which is the most advantageous process to be pursued in special instances, depends entirely upon the circumstances of particular cases. The reduction of compounds of platinum to the metallic state by simple ignition, is preferable to the other methods, in all cases where its application is admissible. The precipitation as bisulphide of platinum is resorted to exclusively to effect the separation of platinum from other metals.

Determination as metallic platinum.

a. By precipitation as bichloride of platinum and chloride of ammonium.

Mix the solution in a beaker-glass, with ammonia, until the excess of acid (that is, supposing an excess of acid to be present), is *nearly* saturated; add chloride of ammonium in excess, and mix the fluid with a pretty large portion of absolute alcohol. Should your solution of platinum be very dilute, you must concentrate it previously to the addition of the alcohol.

Cover the vessel now with a glass-plate, and let it stand for twenty-four hours, after which filter (on an unweighed filter), wash the precipi-

tate thoroughly with spirits of wine, of about 80 per cent., and dry it carefully.

Put the dry precipitate, wrapped up in the filter, into a weighed platinum crucible, cover this, and apply a very gentle heat, until no more fumes of chloride of ammonium escape; now remove the lid, place the crucible obliquely (§ 35), and incinerate the filter, which latter operation you may aid by addition of a little dry nitrate of ammonia. Apply finally an intense heat for some time, and then weigh the residue. For the properties of the precipitate and residue, see § 68. The results are satisfactory, though generally a little too low, as the bichloride of platinum and chloride of ammonium are not altogether insoluble in spirits of wine (Experiment No. 15); and as the fumes of chloride of ammonium evolved during the first stage of the process of ignition are liable to carry along with them traces of the yet undecomposed double chloride, if the application of heat is not conducted with the greatest possible care and caution.

If the precipitated bichloride of platinum and chloride of ammonium were weighed in that form, the results would be inaccurate, since, as I have convinced myself of by direct experiments, it is impossible to free the double chloride by washing with spirits of wine, thoroughly from all traces of the chloride of ammonium thrown down in conjunction with it, without dissolving, at the same time, a considerable portion of the double chloride. As a general rule, however, the results obtained by weighing the bichloride of platinum and chloride of ammonium in that form are one or two per cent too high.

b. By precipitation as bichloride of platinum and chloride of potassium.

Mix the solution of the compound under examination in a beaker-glass, with potassa, until the greater part of the excess of acid (if there be any) is neutralized; add chloride of potassium slightly in excess, and finally a pretty large portion of absolute alcohol; should your solution of platinum be very dilute, you must concentrate it previously to the addition of the alcohol. Let the mixture stand for twenty-four hours, after which filter. Collect the precipitate upon a weighed filter, wash with spirits of wine of 70 per cent, dry thoroughly at 212°, and weigh. Now put a portion of the dried precipitate into a weighed bulb-tube, and clean the ends of the latter with the beard of a quill; then weigh the tube again, to ascertain the exact amount of bichloride of platinum and chloride of potassium which it contains. Connect the tube now with an apparatus evolving dry hydrogen gas (Fig. 40), and heat its contents to redness, until no more hydrochloric acid fumes are evolved, which you may readily ascertain by holding a glass rod moistened with ammonia to the opening of the tube. Let the contents of the bulb cool, remove the tube from the apparatus, fill it with water, decant the solution of chloride of potassium cautiously, wash the residuary platinum

carefully, dry the tube thoroughly, by heating it in a stream of hydrogen gas, and weigh. Subtract from the weight found the original weight of the empty tube, and calculate from the remainder (the weight of the residuary platinum in the tube) the amount of platinum contained in the precipitate of the bichloride of platinum and chloride of potassium.

For the properties of the precipitate and residue, see § 68.

The results are more accurate than those obtained by method *a*, since, on the one hand, the bichloride of platinum and chloride of potassium is more insoluble in spirits of wine than the corresponding ammonium salt; and, on the other hand, loss of substance is less likely to arise during the process of ignition than is the case in method *a*. The results would be less accurate were the ignition effected simply in a crucible, since in that case complete decomposition would not ensue, at all events not if the amount of substance acted upon is at all considerable. To weigh the bichloride of platinum and chloride of potassium in that form would not be practicable, as it is impossible to remove, by washing with spirits of wine, all traces of the chloride of potassium thrown down in conjunction with it, without, at the same time, dissolving a portion of the double chloride.

c. By precipitation as bisulphide of platinum.

Precipitate the solution, either with sulphuretted hydrogen water or gas, according to its greater or less dilution, heat the mixture to incipient ebullition, filter, wash the precipitate, dry, and ignite (§ 35). For the properties of the precipitate and residue, see § 68. The results are accurate.

d. By ignition.

Heat in a covered porcelain or platinum crucible, very gently at first, but finally to redness, and weigh the residuary pure platinum. For the properties of the residue, see § 68. The results are most accurate.

§ 100.

3. TEROXIDE OF ANTIMONY.

a. Solution.

Teroxide of antimony, and the compounds of that metal which are insoluble in water, or are decomposed by that agent, are dissolved in more or less concentrated hydrochloric acid. Metallic antimony is dissolved best in nitrohydrochloric acid. The ebullition of a hydrochloric acid solution of terchloride of antimony is attended with partial volatilization of the latter; the concentration of a solution of the kind by evaporation involves accordingly loss of substance. Solutions so highly dilute as to necessitate a recourse to evaporation, must therefore previously be supersaturated with potassa.

b. Determination.

Antimony is weighed either as *tersulphide*, or as *metallic antimony*, or as *antimonious acid* (SbO_4).

We may convert into

1. TERSULPHIDE OF ANTIMONY.

All compounds of antimony without exception.

2. ANTIMONIOUS ACID.

The oxides of antimony, and their salts with readily volatile or decomposable oxygen acids.

3. METALLIC ANTIMONY.

All compounds of teroxide of antimony without exception.

The method 3 is generally had recourse to only for the purpose of separating antimony from tin; a detailed description of it will be found in the proper place, in the fifth Section.

1. *Precipitation as tersulphide of antimony.*

*a. The operator is convinced that the solution contains teroxide of antimony or terchloride, and no other substance possessing the property of decomposing sulphuretted hydrogen.**

Mix the solution with some hydrochloric acid, if it does not already contain that acid, add tartaric acid, and dilute with water, if necessary. Conduct into the clear solution sulphuretted hydrogen gas, until it predominates strongly. Cover the beaker-glass now with a glass-plate, and let it stand half an houri na moderately warm place; then filter without interruption through a weighed filter, wash the precipitate thoroughly with water, dry at 212°, and weigh. For the properties of the precipitate, see § 69. The results are generally a trifle too high, owing to traces of free sulphur precipitating in conjunction with the tersulphide of antimony. As a precautionary measure, it is invariably advisable to dissolve a small portion of the weighed precipitate in hydrochloric acid, at a high temperature. If this leaves no appreciable trace of sulphur, the results may be considered accurate; but if a perceptible amount of sulphur remains, the precipitated tersulphide of antimony must be treated as directed in *b*.

b. The solution contains, besides teroxide of antimony, also antimonious acid, or antimonic acid, or some substance possessing the property of decomposing sulphuretted hydrogen.

The solution is treated as directed in *a*, with this difference, that, previously to filtration, the beaker-glass containing the precipitated fluid is covered with paper, and kept standing in a moderately warm spot until the odor of sulphuretted hydrogen has completely disappeared.

The precipitate is washed, dried, and weighed, as in *a*; it consists of an unknown sulphide of antimony mixed with free sulphur, or, in other terms, of antimony + x sulphur.

To determine the amount of the antimony present, it is necessary, there-

* This conviction the operator may safely entertain, in all cases where he has tersulphide of antimony, or a salt of the teroxide, dissolved in hydrochloric acid; but not if the solution contains also nitric acid.

fore, either to separate this metal from the sulphur, or to ascertain the proportion of sulphur present in the precipitate.

To separate the antimony from the sulphur, the precipitate may be heated in a bulb-tube in a stream of hydrogen gas, until the formation of sulphuretted hydrogen ceases completely. But since a slight loss of antimony can hardly be avoided in this process (the stream of hydrogen gas tending to carry off mechanically particles of the antimony), it is preferable to determine the amount of sulphur present in the precipitate, and to calculate from this the proportion of antimony.

For this purpose, the precipitate, dried on the filter at 212°, is weighed in a platinum crucible; as much of it as may be detached from the filter without difficulty is then cautiously transferred to a dry flask: the filter, with the still adhering portion of the precipitate, is now put back into the crucible, and the latter is then again weighed; the difference between the results of the two weighings expresses the quantity of the precipitate in the flask.

Red fuming nitric acid, perfectly free from sulphuric acid, is now gradually dropped upon the contents of the flask. When the action of the acid has a little abated in energy, a little more nitric acid, and some hydrochloric acid, are added, and heat applied; or chlorate of potassa is added to the sulphide of antimony in the flask, and then nitric acid (which need not be fuming) or strong hydrochloric acid, and, after a time, a moderate heat is applied. As soon as the whole mass is dissolved, or the sulphur which may have separated appears of a pure yellow color, a sufficient quantity of tartaric acid is added without delay, and the solution then diluted with water. Two cases are possible now, viz. :—

α. The solution is perfectly clear, and contains no trace of separated sulphur.

Solution of chloride of barium is added in slight excess, and the precipitated sulphate of baryta is then determined, as directed § 105, care being taken to wash it thoroughly, and to treat it after ignition once more with hydrochloric acid and water. The quantity of sulphur in the sulphate of baryta is now accurately calculated; this being equal to the quantity of sulphur which was present in the oxidized portion of the sulphide of antimony; and the proportion of the latter to the whole of the original precipitate being known, the amount of sulphur, and accordingly also the amount of antimony contained in the latter, may be found by a simple calculation. Or,

β. The solution is clear, but contains separated sulphur.

The solution is passed through a small weighed filter; the sulphur, collected on the latter, is dried at 212°, and weighed. The filtrate is treated as in α, and the weight of the free sulphur added to that calculated from the sulphate of baryta.

2. *Determination as antimonious acid.*

Evaporate the compound under examination cautiously with nitric acid, and ignite the residue, until the weight remains constant. The experiment may safely be made in a platinum crucible. In the case of antimonious acid, evaporation with nitric acid is not necessary. For the properties of the residue, see § 69. The results are accurate.

§ 101.

4. PROTOXIDE OF TIN, and 5. BINOXIDE OF TIN.

a. Solution.

In dissolving compounds of tin soluble in water, a little hydrochloric acid is added to ensure a clear solution. Nearly all the compounds of tin insoluble in water dissolve in hydrochloric acid, or in nitrohydrochloric acid. The insoluble modification of the binoxide, and its compounds, must be prepared for solution in hydrochloric acid, by reduction to the state of fine powder, and fusing with hydrate of potassa or soda in excess, in a silver crucible. Metallic tin is dissolved best in nitrohydrochloric acid; it is generally determined, however, by converting it into binoxide, without previous solution. Acid solutions of tin, which contain hydrochloric acid, or a chloride, cannot be concentrated by evaporation, not even after addition of nitric acid or sulphuric acid, without volatilization of bichloride of tin taking place.

b. Determination.

Tin is either weighed in the form of *binoxide*, or determined by analysis by measure. It is converted into binoxide either by the agency of nitric acid, or by precipitation as hydrated binoxide, or by precipitation as sulphide (protosulphide or bisulphide, as the case may be).

We may convert into

BINOXIDE OF TIN.

a. By the agency of nitric acid.

Metallic tin, and those compounds of tin which contain no fixed acid, provided no compounds of chlorine be present.

b. By precipitation as hydrated binoxide.

All compounds of tin containing volatile acids, provided no non-volatile organic substances, nor sesquioxide of iron, be present.

c. By precipitation as protosulphide or bisulphide.

All compounds of tin without exception.

In methods *a* and *c*, it is quite indifferent whether the tin is present in the state of protoxide or in that of binoxide. The method *b* requires the tin to be present in the state of binoxide; the methods of analysis by measure require it in the state of protoxide.

The methods of determining protoxide and binoxide of tin in presence of each other, will be found in Section V.

1. *Determination of tin as binoxide.*

a. By the action of nitric acid.

This method is resorted to principally to convert metallic tin into binoxide. For this purpose the finely divided metal is put into a capacious flask, and gradually treated with pretty strong pure nitric acid (about 1·3 sp. gr.); the flask is then covered with a watch glass. When the first impetuous action of the acid has somewhat abated, a gentle heat is applied until the binoxide formed appears of a pure white color, and further action of the acid is no longer perceptible. Water is then added, and the fluid filtered off; the binoxide is washed, dried, ignited, and weighed. The ignition is effected best in a small porcelain crucible, according to the directions giving in § 35; still a platinum crucible may also be used. Compounds of tin which contain no fixed substances, may be converted into binoxide also by treating them in a porcelain crucible with nitric acid, evaporating to dryness, and igniting the residue. If sulphuric acid be present, the expulsion of that acid may be promoted in the last stages of the process, by carbonate of ammonia, as in the case of bisulphate of potassa (§ 76, 1, and § 47). For the properties of the residue, see § 70. The results are accurate.

b. By precipitation as hydrate of binoxide.

The application of this method presupposes that the whole of the tin is present in the state of binoxide or bichloride. Therefore if a solution contains protoxide, this must first be converted into binoxide before the quantitative estimation can be proceeded with. For this purpose, mix the solution with chlorine water, conduct chlorine into it, or heat gently with chlorate of potassa, until the conversion of the protoxide into binoxide is effected. When this has been done, add ammonia, until a permanent precipitate just begins to form, and then hydrochloric acid, drop by drop, until this precipitate is redissolved; by this means a large excess of hydrochloric acid in the solution will be avoided. Add to the fluid so prepared, a concentrated solution of sulphate of soda (or of nitrate of potassa, or nitrate of soda, or nitrate of ammonia), and apply heat, whereupon the whole of the tin will precipitate as hydrate of binoxide. Filter, wash (§ 31), dry, and ignite. To make quite sure that the whole of the tin has separated, you need simply, before you proceed to filter, add a few drops of the clear supernatant fluid to a hot solution of sulphate of soda, when the formation or non-formation of a precipitate will be decisive.

This method, which we owe to *J. Löwenthal*, who has also repeatedly tested its merits in my own laboratory (Journal für prakt. Chem. 56, 366), is easy and convenient, and gives very accurate results. The decompo-

sition is expressed by the equation $SnCl_2 + 4\ (NaO, SO_3) + 4\ HO = SnO_2$, $2\ HO + 2\ NaCl + 2\ (NaO, SO_3) + 2\ (HO, SO_3)$.

c. By precipitation as protosulphide or bisulphide of tin.

Precipitate the dilute neutral or acid solution with sulphuretted hydrogen gas. If the tin was present in the solution in the form of protoxide, and the precipitate consists accordingly of the brown protosulphide, keep the solution, supersaturated with sulphuretted hydrogen, standing for half an hour in a moderately warm place, and then filter; if, on the other hand, the solution contains a salt of binoxide of tin, and the precipitate consists accordingly of the yellow bisulphide, put the fluid, loosely covered, in a warm place, until the odor of sulphuretted hydrogen has gone off, and then filter. Put the filter with the not quite dry precipitate, into a porcelain crucible, and apply a very gentle heat, with free access of air, until the odor of sulphurous acid is no longer perceptible. Increase the heat now gradually to a high degree of intensity, and treat the residue repeatedly with some carbonate of ammonia (see § 47 and 76,1), in order to insure the complete expulsion of the sulphuric acid which may be present. Were you to apply a very intense heat from the beginning, fumes of bisulphide of tin would escape, which would burn to binoxide (*H. Rose*). For the properties of the precipitates, see § 70. The results are accurate.

2. *Determination by analysis by measure.*

The various methods of estimating by analysis by measure the quantity of tin contained in a compound or mixture, are all based upon the conversion of the protoxide of that metal into the binoxide, by means of some oxidising agent. *Gaultier de Claubry* uses tincture of iodine as oxidising agent; *Mène*, sesquichloride of iron; *Penny*, bichromate of potassa; *Schwarz* (in absence of iron), permanganate of potassa.

In cases therefore, where we have the whole of the tin in solution in the form of protoxide, or where it is simply intended to determine the quantity of *protoxide* of tin contained in a solution, these methods are easy; but when the whole or part of the tin to be estimated in a solution, happens to exist in the form of binoxide, they present some difficulties.

The iodine method is the one best adapted to obviate or overcome these difficulties.

The facts on which this method is based, are the following:

1. One equivalent of iodine converts one equivalent of tin from the state of protoxide or protochloride to that of binoxide or bichloride.

2. The addition of iodine to a solution of protochloride of iron does not occasion the formation of sesquichloride of iron.

In the performance of the analytical process, attention must be paid to the following points:

a. The solution of the compound of tin is effected, if possible, by

means of hydrochloric acid alone; should this agent, however, fail to produce the desired result, nitric acid is added to it, but as little of it as possible.

b. The hydrochloric acid solution is boiled with an excess of small pieces of iron wire, to convert the bichloride of tin present into protochloride. When there is reason to believe that this object has been attained, the liquid cooled down is poured off into a measuring flask, and the undissolved iron is washed with water freed from air by ebullition, and acidulated with hydrochloric acid.

The fluid is now diluted to a certain definite volume, and uniformly intermixed; a small portion of it is poured into a boiling concentrated solution of sulphate of soda: if this produce no turbidity, the solution of tin is free from bichloride. A portion of it, containing about 0·1 grm. of tin is taken out by means of a graduated pipette, and diluted with some water freed from air by ebullition; a little very thin starch paste is added, and solution of iodine in iodide of potassium dropped into the mixture until the last drop produces a persistent blue coloration. Supposing the solution of iodine to have been prepared in *Bunsen's* way (5 grammes of iodine to 25 grammes of iodide of potassium and the requisite quantity of water to give a 1000 cubic centimeters of solution: see estimation of iodine), and to contain accordingly 0·005 grm. of iodine per cubic centimeter, every cubic centimeter used of the iodine solution corresponds to 0·002317 of tin, or 50 c. c.=100° correspond to 0·116 of tin.

c. Should the addition of the dilute fluid to the boiling concentrated solution of sulphate of soda (see *b*), have produced turbidity in the latter, the portion removed with the pipette, and intended for quantitative estimation, is poured into a small flask, hydrochloric acid and pieces of iron wire are added, the flask is placed obliquely, and the mixture in it is gently boiled for some time; the fluid is then decanted from the undissolved iron, the latter is washed as above, and the further operation conducted as in *b*.

In *Penny's* method the decomposition ensuing may be expressed as follows: $3\,SnCl + KO, 2\,CrO_3 + 7\,HCl = 3\,SnCl_2 + KCl + Cr_2Cl_3 + 7\,HO$.

One equivalent of bichromate of potassa=1858·26 corresponds accordingly to three equivalents of tin=2206; or 0·8424 grm. of bichromate of potassa correspond to 1·000 of tin. (According to *Penny* 0·832 KO, $2\,CrO_3$ correspond to one gramme of tin.)

If therefore we dissolve 8·424 grammes of chemically pure bichromate of potassa in the requisite quantity of water to give 500 c. c. of solution, 50 cubic centimetres=100° of this solution correspond to one gramme of tin, or, in other words, are just sufficient to convert one gramme of tin from the state of protoxide to that of binoxide.

To hit the exact point when the conversion of the protochloride into bichloride is terminated, the best way is to add to the highly dilute solu-

tion of tin some thin starch paste and a few drops of solution of iodide of potassium. As soon as the protochloride is completely converted into bichloride, the first drop of solution of bichromate of potassa added in excess changes the transparent green of the solution to an opaque violet blue color.

When it is intended to employ bichromate of potassa as the oxidising agent, iron cannot, of course, be used to effect the previous reduction of the bichloride present to protochloride; in cases of the kind zinc, free from iron, must be used for the purpose; the application of this agent is, however, often attended with separation of metallic tin, in which case the mixture must be heated with addition of hydrochloric acid, until the metallic deposit is redissolved.

§ 102.

6. ARSENIOUS ACID, and 7. ARSENIC ACID.

a. Solution.

The compounds of arsenious and arsenic acids which are not soluble in water, are dissolved in hydrochloric acid, or in nitrohydrochloric acid. Some native arseniates of metallic oxides require fluxing with carbonate of soda, as an indispensable preliminary to their solution. Metallic arsenic, and metallic arsenides are dissolved in nitrohydrochloric acid; those metallic arsenides which are insoluble in this menstruum are fused with carbonate of soda and nitrate of potassa, by which means they are converted into soluble arseniates of the alkalies and insoluble metallic oxides. All solutions of compounds of arsenic which have been effected by heating with nitrohydrochloric acid in excess contain arsenic acid. A solution of arsenious acid in hydrochloric acid cannot be concentrated by boiling, since chloride of arsenic would escape with the hydrochloric acid fumes. This occurs much less readily if the solution contains arsenic acid; it is advisable in all cases where a hydrochloric acid solution containing arsenic is to be concentrated, to make the same previously alkaline.

b. Determination.

Arsenic is weighed *as arseniate of lead*, or as *arseniate of magnesia and ammonia*, or as *arseniate of sesquioxide of iron*, or as *tersulphide of arsenic*; it may be estimated also in an *indirect* way, and also by *analysis by measure*.

We may convert into

1. ARSENIATE OF LEAD.

Arsenious and arsenic acid in aqueous or nitric acid solution. (Acids or metalloids forming fixed salts with oxide of lead or metallic lead, must not be present.

2. ARSENIATE OF MAGNESIA AND AMMONIA.

Arsenic acid in all solutions free from such acids or bases, as would be precipitated by magnesia or ammonia.

3. ARSENIATE OF SESQUIOXIDE OF IRON.

Arsenic acid in solutions free from such substances as fall down when to their solution is added sesquichloride of iron and then ammonia, or carbonate of baryta.

4. TERSULPHIDE OF ARSENIC.

All compounds of arsenic without exception.

The indirect method serves principally to effect the separation of arsenious acid from arsenic acid. (Compare Section V.)

1. *Determination as arseniate of lead.*

a. Arsenic acid in aqueous solution.

A weighed portion of the solution is put into a platinum or porcelain dish, and a weighed amount of recently ignited pure oxide of lead added (about five or six times as much as there is arsenic acid present); the mixture is cautiously evaporated to dryness, and the residue heated to gentle redness, and maintained some time at this temperature. The residue is arseniate of lead + oxide of lead. The quantity of arsenic acid is now readily found by subtracting from the weight of the residue that of the oxide of lead added.

For the properties of the arseniate of lead, see § 71. The results are perfectly accurate, provided the residue be not heated beyond gentle redness.

b. Arsenious acid in solution.

Mix the solution with nitric acid, add a weighed quantity of oxide of lead in excess, evaporate to dryness, and ignite the residue most cautiously in a covered crucible, until the whole of the nitrate of lead is decomposed. The residue consists here also of arsenic acid + oxide of lead. This method requires considerable care to guard against loss by decrepitation upon the ignition of the nitrate of lead.

2. *Estimation as arseniate of magnesia and ammonia.*

This method, which was first recommended by *Levol*, presupposes that the whole of the arsenic is contained in the solution in the form of arsenic acid. Where this is not the case, the solution is gently heated in a capacious flask with hydrochloric acid, and chlorate of potassa is added in small portions, until the fluid evolves a strong smell of chlorous acid; it is then allowed to stand at a gentle heat until the odor of this gas is nearly gone off.

The arsenic acid solution is now mixed with ammonia in excess, which must not produce turbidity, even after standing some time; a solution of sulphate of magnesia is then added, containing chloride of ammonium in sufficient quantity to prevent the fluid being rendered turbid by ammonia. (The best way is to keep a magnesia solution mixed with ammonia and chloride of ammonium ready prepared in the laboratory.) The fluid which

smells strongly of ammonia is allowed to stand twelve hours in the cold; and subsequently filtered through a weighed filter; the precipitate on the filter is washed with a mixture of three parts of water and one part of solution of ammonia, dried at 212°, and weighed. It has the formula $2\,MgO, NH_4O, AsO_5 + aq$. For the properties of the precipitate, see § 71. This method gives very satisfactory results (Journal f. prakt. Chem. 56, 32).

3. *Estimation as arseniate of sesquioxide of iron.*

(*Berthier* and *V. Kobell's* method.)

a. The solution contains no other fixed bases besides alkalies.

Add to the solution a measured quantity of solution of sesquioxide of iron of known strength, and precipitate with ammonia. The precipitate must be reddish-brown: if it is not of that color, it is a sign that sufficient of the solution of sesquioxide of iron has not been added. Let the precipitated liquid stand some time at a gentle heat; filter, wash, and dry the precipitate; expose the dry precipitate to a very gentle heat, to ensure the expulsion of the ammonia at a temperature at which it cannot exercise a reducing action upon the arsenic acid; increase the heat gradually, and at last to intense ignition; keep the residue in this state until the weight remains constant. The residue is basic arseniate of sesquioxide of iron + sesquioxide of iron, or, differently expressed, sesquioxide of iron + arsenic acid. Deduct from the weight of the residue the known weight of the sesquioxide of iron added; the remainder expresses the quantity of arsenic acid contained in the analysed solution. A solution of sesquioxide of iron of known strength may be obtained either by dissolving a weighed quantity of fine iron wire in nitric acid (100 of wire being assumed to give 142·6 of sesquioxide), or by precipitating a nitric acid solution of sesquioxide of iron of unknown strength with ammonia, washing, drying, and igniting (§ 90). The results are accurate. (Journal f. prakt. Chem. 56, 32.)

b. The solution contains other fixed bases.

The preceding method of *Berthier* is modified as follows, provided the bases present in the solution are not precipitated by carbonate of baryta in the cold. This solution is mixed with solution of sesquioxide of iron of known strength, as in *a*, but instead of ammonia, carbonate of baryta is added in excess (should the fluid contain a large excess of free acid, it is expedient to nearly neutralise this previously with carbonate of soda; the fluid must however still remain clear). The mixture is then allowed to stand several hours in the cold, and the precipitate, which contains the whole of the sesquioxide of iron, the whole of the arsenic acid, and some carbonate of baryta, is washed with cold water, first by decantation, then upon the filter, dried, gently ignited for some time, and weighed. The residue is dissolved in hydrochloric acid, the amount of baryta contained in it is determined by means of sulphuric acid, the sulphate of baryta ob-

tained calculated as carbonate, and the calculated weight, together with the known weight of the sesquioxide of iron, subtracted from the weight of the original residue: the remainder expresses the quantity of arsenic acid contained in the analysed solution. This method, which is recommended by *V. Kobell*, presupposes the absence of sulphuric acid. In cases therefore where that acid is present, it must be removed before the carbonate of baryta can be added; this removal is effected by precipitating with chloride of barium, and filtering off the precipitate.

4. *Determination as tersulphide of arsenic.*

a. Arsenious acid, or an arsenite, in solution free from arsenic acid.

Mix the solution into a glass-stoppered flask with hydrochloric acid, and precipitate, according to circumstances, either with sulphuretted hydrogen gas, or with sulphuretted hydrogen water. Put in the stopper, let the flask stand an hour, and then transmit washed carbonic acid through the mixture, until the odor of sulphuretted hydrogen has pretty nearly gone off. Let the mixture again stand some time, filter on a weighed filter, wash the precipitate, dry at 212°, and weigh. For the properties of the precipitate, see § 71. The results are accurate.

If the solution happens to contain a substance acting as a decomposing agent, upon sulphuretted hydrogen, such as sesquioxide of iron, chromic acid, &c., the free sulphur which precipitates with the tersulphide of arsenic, is estimated in the way recommended in § 100 (estimation of antimony as tersulphide), viz., as sulphur and sulphate of baryta, and the quantity found is deducted from the total weight of the precipitate; or the tersulphide of arsenic is filtered off on an unweighed filter, washed, put, together with the filter, into a large flask, and treated at a moderate heat with chlorate of potassa and nitric acid, until the whole of the arsenic is dissolved. The solution is then diluted, filtered, the undissolved part on the filter washed, and the arsenic acid in the filtrate is estimated (as arseniate of magnesia and ammonia, see 2). Another method which has been recommended, viz., to treat the mixed precipitate with ammonia, which is said to dissolve the tersulphide of arsenic, leaving the sulphur undissolved, gives only approximate results, as some of the sulphur dissolves in the ammoniacal solution of the tersulphide of arsenic.

b. Arsenic acid or an arseniate in solution, or a mixture of the two oxides of arsenic.

Mix the solution in a flask with a strong aqueous solution of sulphurous acid in excess, place the flask in a slanting position, and heat slowly to near ebullition; keep the mixture now at a temperature below the boiling point, until the fluid smells no longer of sulphurous acid, and treat the solution, which now contains only arsenious acid, as in *a*.

5. *Estimation by analysis by measure.*

a. Bunsen's method (Annal. d. Chem. u. Pharm. 86, 290).

This ingenious method is based upon the following facts :—

a. a. If bichromate of potassa is boiled with concentrated hydrochloric acid, three equivalents of chlorine are disengaged to every two equivalents of chromic acid ($2\ CrO_3 + 6\ HCl = Cr_2Cl_3 + 3\ Cl + 6\ HO$).

b. b. But if arsenious acid is present (not in excess) there is not the quantity of chlorine disengaged corresponding to the chromic acid, but so much less of that element, as is required to convert the arsenious into arsenic acid ($AsO_3 + 2\ Cl + 2\ HO = AsO_5 + 2\ HCl$). Consequently for every two equivalents of chlorine obtained less in proportion to the chromic acid, is to be reckoned one equivalent of arsenious acid.

c. c. The quantity of the chlorine is estimated by determining the quantity of iodine liberated by it from iodide of potassium.

These are the principles of *Bunsen's* method. For the manner of execution, I refer to § 104, 1. *d. β.*

b. P. Kotschoubey has applied to chromic acid *Räwsky's* method * of estimating phosphoric acid by analysis by measure (§ 106, I, f). The compound precipitated from the solution of the compound of arsenic acid in acetic acid (or in hydrochloric acid, after addition of ammonia to alkaline reaction, and then again of acetic acid to acid reaction), by acetate of sesquioxide of iron, or by a mixture of ammonia, iron, alum, and acetate of soda, has, according to *Kotschoubey*, the formula $Fe_2O_3,\ AsO_5 + 5\ HO$. For every two equivalents of iron (700) therefore is to be reckoned one equivalent of arsenic acid (1437·5) ; *Kotschoubey* effects the reduction with zinc, by which the arsenic is partly precipitated, and partly volatilised in the form of arsenietted hydrogen. This method is, in my opinion, open to the same objections as *Räwsky's* method of determining phosphoric acid.

II. QUANTITATIVE DETERMINATION OF THE ACIDS IN COMPOUNDS CONTAINING ONLY ONE ACID FREE OR COMBINED;—AND SEPARATION OF THE ACIDS FROM THE BASES.

FIRST GROUP.

ARSENIOUS ACID—ARSENIC ACID—CHROMIC ACID—SULPHURIC ACID—PHOSPHORIC ACID—BORACIC ACID—OXALIC ACID—HYDROFLUORIC ACID—CARBONIC ACID—SILICIC ACID.

§ 103.

1. ARSENIOUS AND ARSENIC ACIDS.

For the quantitative determination of these two acids, I refer to the preceding paragraph ;—the methods of separating them from the bases will be found in Section V.

* Journ. f. prakt. Chem. 49, 185.

§ 104.

2. CHROMIC ACID.

I. DETERMINATION.

Chromic acid is determined either in the form of *sesquioxide of chromium*, or in that of *chromate of lead*. But it may be estimated also from the quantity of carbonic acid disengaged by its action upon oxalic acid in excess, and also by analysis by measure.

a. Determination as sesquioxide of chromium.

α. The chromic acid is reduced to the state of sesquioxide, and the amount of the latter determined (§ 84). The reduction is effected either by heating the solution with hydrochloric acid and alcohol, or by mixing hydrochloric acid with the solution, and conducting sulphuretted hydrogen into the mixture; or by adding a strong solution of sulphurous acid, and applying a gentle heat. With concentrated solutions, the first method is generally resorted to, with dilute solutions, one of the two latter. With respect to the first method, I have to remark that the alcohol must be expelled again before the sesquioxide of chromium can be precipitated with ammonia; and with respect to the second, that the solution supersaturated with sulphuretted hydrogen must be allowed to stand in a moderately warm place, until the separated sulphur has completely subsided.

β. The neutral or slightly acid (by nitric acid) solution, is precipitated with nitrate of suboxide of mercury, the red precipitate of chromate of suboxide of mercury is filtered off, washed with a dilute solution of nitrate of suboxide of mercury, dried and ignited, and the residuary sesquioxide of chromium weighed (*H. Rose*).

b. Determination as chromate of oxide of lead.

The solution is mixed with acetate of soda in excess, and if necessary, acetic acid is added until the reaction is slightly acid; the solution is then precipitated with neutral acetate of oxide of lead. The washed precipitate is either collected on a weighed filter, dried in the water-bath, and weighed; or it is gently ignited as directed, § 36, and then weighed. For the properties of the precipitate, see § 72. The results are accurate.

c. Determination by means of oxalic acid (*Vohl's* method).

When chromic acid and oxalic acid are brought together, the former yields oxygen to the latter: sesquioxide of chromium is formed, and carbonic acid escapes ($2\ CrO_3 + 3\ C_2O_3 = Cr_2O_3 + 6\ CO_2$). Three equivalents of carbonic acid (825) correspond accordingly to one equivalent of chromic acid (634·7). The *modus operandi* is the same as that which will be given hereafter in the chapter on the examination of manganese ores. Every one part of chromic acid requires two and a quarter parts of oxalate of soda. If it is intended to determine in the residue the alkali which has been combined with the chromic acid, oxalate of ammonia is used.

d. Determination by analysis by measure.

a. Schwarz's method.

The principle of this method is identical with that upon which *Penny's* method of determining iron is based. The execution is simple: acidulate the solution of the chromic acid compound with sulphuric acid, add an excess of solution of protoxide of iron, of which you have previously ascertained the strength according to the directions of § 89, 2, a. or b., and then determine in the manner directed § 89, 2, a. or b., the quantity of protoxide of iron remaining. The difference shows the amount of iron that has been converted by the chromic acid from the state of protoxide to that of sesquioxide. One gramme of iron corresponds to 0·6045 of chromic acid (compare also § 92, 3).

β. Bunsen's method (Ann. der Chem. u. Pharm. 86, 279).

If a chromate is boiled with an excess of fuming hydrochloric acid, there are disengaged for every two equivalents of chromic acid three equivalents of chlorine; for instance, KO, 2 CrO_3 + 7 HCl = KCl + Cr_2Cl_3 + 7 HO + 3 Cl. If the escaping gas is conducted into solution of iodide of potassium in excess, the three equivalents of chlorine set free three equivalents of iodine. By determining the quantity of the latter element in the manner which will be found described in § 114, we find the quantity of the chromic acid; 4758 of iodine corresponding to 1269·4 of chromic acid.

The analytical process is conducted as follows :—put the weighed sample of the chromate into the little flask *a* (Fig. 44), (blown before the lamp, and holding only from 36 to 40 cubic centimeters,) fill the flask to two-thirds with fuming hydrochloric acid, and connect the evolution tube with the neck of the flask by means of a stout tight-closing india-rubber tube *b*. A loss of chlorine need not be apprehended in this operation, as the disengagement of that gas begins only upon the application of heat. Put the little glass bulb *c*, which is intended to serve as vent, with its end closed by fusion into the mouth of the evolution tube, and insert the latter into the neck of the retort *d d d*, which is filled with solution of iodide of potassium.* This retort holds about 160 c. c. The neck pre-

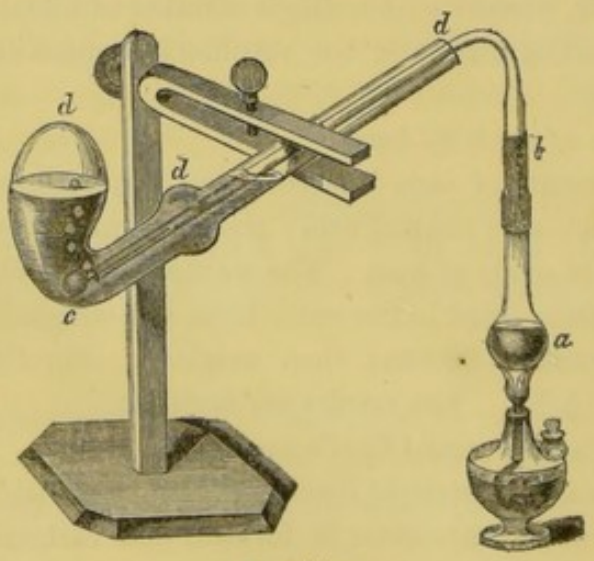


Fig. 44.

* One part of pure iodide of potassium, free from iodic acid, dissolved in ten parts of water. The fluid must show no brown tinge immediately after addition of hydrochloric acid.

sents a small expansion, and intended to receive the liquid which is forced up during the operation. Apply heat to the flask containing the chromate. After two or three minutes' ebullition, the whole of the chlorine has passed over, and is replaced by its equivalent of free iodine in the iodide of potassium solution. Transfer the contents of the retort to a beaker glass, and proceed as directed § 114, I., 3. *Bunsen* has shown that this method gives very satisfactory results.

II. SEPARATION OF CHROMIC ACID FROM THE BASES.

a. OF THE FIRST GROUP.

α. Reduce the chromic acid as directed in I., and separate the sesquioxide of chromium from the alkalies as directed in § 123.

β. Chromate of ammonia is reduced to sesquioxide of chromium by cautious ignition.

b. OF THE SECOND GROUP.

α. Fuse the compound under examination with four parts of carbonate of soda and potassa, and treat the fused mass with hot water, which dissolves the chromic acid in the form of an alkaline chromate. The residue contains the alkaline earths in the form of carbonates; but as it contains also an admixture of alkali; it cannot be weighed directly. The chromic acid in the solution is determined as in I.

β. Dissolve in hydrochloric acid, reduce the chromic acid according to the directions of I., *a*, and separate the sesquioxide of chromium and the alkaline earth according to § 124.

c. OF THE THIRD GROUP.

α. From alumina.

Precipitate the alumina by ammonia or carbonate of ammonia (§ 83), and determine the chromic acid in the filtrate according to the directions giving in I. (Compare also § 125.)

β. From sesquioxide of chromium.

α α. In solution.

Precipitate the chromic acid according to I., *a*, *β*, or I., *b*, and separate the sesquioxide of chromium and suboxide of mercury, or oxide of lead, as the case may be, as directed in § 130.

b b. The compound under examination is insoluble (neutral chromate of sesquioxide of chromium).

Ignite. The residue is sesquioxide, the loss oxygen, from which is calculated the amount of chromic acid originally present.

c c. Vohl's method.

Estimate first the amount of carbonic acid which the compound under examination liberates from oxalic acid; then treat the fluid, or, better still, another weighed sample of the compound, like a salt of sesquioxide (§ 84). The latter operation gives the total amount of chromium originally present in the examined compound, the former the amount which

existed in the form of chromic acid; the difference between the two shows the quantity which existed originally in the form of sesquioxide.

In a similar manner, the sesquioxide and the acid may also be estimated side by side,

d d. By analysis by measure.

d. OF THE FOURTH GROUP.

α. Proceed as directed in *b*, *α*. Upon treating the fused mass with hot water, the metals are left as oxides. In the case of manganese the fusion must be effected in a bulb-tube in a stream of carbonic acid gas.

β. Reduce the chromic acid as directed in I., *a*, and separate the sesquioxide of chromium from the metals of the fourth group, as directed in § 128.

e. OF THE FIFTH AND SIXTH GROUPS.

α. Mix the solution with free acid, and precipitate with sulphuretted hydrogen. The metals of the fifth and sixth groups precipitated in conjunction with free sulphur (§§ 91 to 102), the chromic acid is reduced. Filter, and determine the sesquioxide of chromium in the filtrate, as directed in I., *a*.

β. Chromate of lead is decomposed by heating with hydrochloric acid and some alcohol; the chloride of lead and protochloride of chromium formed, are subsequently separated by means of alcohol (compare § 130). The alcoholic solution ought always to be tested with sulphuric acid; should a precipitate of sulphate of lead form, this must be filtered off, weighed, and taken into account.

§ 105.

3. SULPHURIC ACID.

I. DETERMINATION.

The best way of determining sulphuric acid is to convert it into *sulphate of baryta*. With respect to a new method of analysis by measure, recommended by *Schwarz*, I refer to the original paper in the Annalen der Chemie und Pharm. 84, 99. The method is too complicated to be of practical utility; it requires three test fluids, and makes two filtrations with washing necessary.

1. Add to the solution, if necessary, some hydrochloric acid, to acid reaction, heat to near ebullition, add chloride of barium in slight excess, and proceed as directed § 79, 1, *a*. The washing is always best effected by decantation first. Should the analysed solution contain nitric acid, some nitrate of baryta is likely to precipitate in conjunction with the sulphate; the removal of this admixture of nitrate of bartya from the precipitate, requires long protracted washing with hot water. It is, under all circumstances, necessary to continue the washing of the precipitate until the last

rinsings remain perfectly clear upon testing with sulphuric acid. In cases where perfect accuracy is desirable, I would recommend the following proceeding; after igniting and weighing the precipitate according to the directions of § 36, moisten it with a very few drops of hydrochloric acid, add hot water, stir with a very thin glass rod or with a platinum wire, rinse the rod or wire, and heat gently for some time. Pour the almost clear fluid through a small filter, and test the filtrate with sulphuric acid. If this produces turbidity or a precipitate, which is a sign that the sulphate contains an admixture of another baryta salt, wash the residue again with hot water, until the rinsings are no longer rendered turbid by sulphuric acid. Dry now the precipitate in the crucible, together with the small filter, burn the latter on the lid, heat the crucible and its contents to redness, and weigh.

2. It is often desirable, for commercial purposes, to determine the sulphuric acid in an expeditious way by analysis by measure. The principle upon which an analysis of the kind may be based readily suggests itself; it consists simply in the addition of a solution of chloride of barium of known strength, as long as a precipitate is formed; the quantity used of the solution of chloride of barium indicates the amount of sulphuric acid present in the analysed solution. But the execution of the process presents some difficulty, as it is not easy to hit quickly the exact point at which the precipitation of the whole of the sulphuric acid is effected. The following method may be recomended as better adapted to the purpose:—

a. Dissolve 26·012 grammes of pure ignited chloride of barium in the requisite quantity of water to obtain exactly 500 c. c. solution. 50 c. c.= 100° of this solution precipitate exactly one gramme of sulphuric acid, and 1° accordingly, exactly 0·01 grm.

b. Mix one volume of the solution *a* with nine volumes of water; 1° of this dilute solution will precipitate exactly 0·001 grm. of sulphuric acid.

Put 45 c. c. of the solution of the sulphate under examination, which should approximately contain in 50 c. c. one gramme of sulphuric acid, into a glass flask, mix with some hydrochloric acid, heat to boiling, and add continuously of the concentrated chloride of barium solution (*a*), as long as a precipitate continues to form. The precipitate so formed speedily acquires density, and subsides readily. Stop the addition of the chloride of barium solution occasionally, to give the precitate time to subside. When further addition of the chloride of barium solution is no longer followed by the formation of a precipitate, add 5 c. c. more of the solution of the sulphate under examination, let the mixture boil some time, and then add, with the greatest caution, of the dilute test fluid (*b*), until further addition fails to produce renewed turbidity. Supposing you to have used in this way 43 c. c.=86° of the concentrated, and

11 c. c.=22° of the dilute test fluid, the analysed solution would contain 0·86+0·022=0·882 grm. of sulphuric acid. In cases where we have to deal with fluids free from chlorine, solution of acetate of lead may be advantageously substituted for solution of chloride of barium, as sulphate of lead subsides more readily than sulphate of baryta.

II. SEPARATION OF SULPHURIC ACID FROM THE BASES.

a. FROM THOSE BASES WITH WHICH THE ACID FORMS COMPOUNDS SOLUBLE IN WATER OR IN HYDROCHLORIC ACID.

Precipitate the sulphuric acid as in I. The filtrate contains besides the bases originally combined with the sulphuric acid also the excess of the chloride of barium used. The bases in the filtrate are determined by the methods given in the Fifth Section to effect the separation of these bases from baryta.

b. FROM THOSE BASES WITH WHICH THE ACID FORMS COMPOUNDS INSOLUBLE OR DIFFICULTLY SOLUBLE IN WATER OR IN HYDROCHLORIC ACID.

α. From baryta, strontia, and lime.

Fuse the compound under examination, first finely pulverised, in a platinum crucible, together with four parts of carbonate of soda and potassa. Put the crucible, with its contents, into a beaker glass, or into a platinum or porcelain basin, pour water over it, and apply heat until the alkaline sulphates and carbonates are completely dissolved; filter the solution still hot off from the residuary carbonates of the earths, and wash the latter thoroughly with hot water. Dissolve them now in hydrochloric acid, and determine them respectively by the methods given in §§ 79, 80, and 81. Precipitate the sulphuric acid from the filtrate, as in I. Finely pulverised sulphate of lime may be completely decomposed also by boiling with a solution of carbonate of soda or potassa.

β. From oxide of lead.

Ignite with carbonate of soda and potassa in a porcelain crucible, until the mass has completely agglutinated; digest with hot water until the alkaline sulphate formed and the excess of the alkaline carbonate used are dissolved; filter off the residuary oxide of lead, which always contains alkali, and wash it thoroughly. Acidulate the filtrate, which invariably contains a greater or less quantity of lead, according to the greater or less amount of water used in the process, slightly with nitric acid, taking care to do this cautiously, that no loss of substance may be incurred by spirting, and precipitate the sulphuric acid as in I., with nitrate of baryta; dissolve the washed oxide of lead in dilute nitric acid, add the solution, with the fluid filtered off from the sulphate of baryta, and precipitate the lead with sulphuretted hydrogen (§ 92).

§ 106.

4. PHOSPHORIC ACID.

I. DETERMINATION.

Tribasic phosphoric acid may be determined in a great variety of ways, but most appropriately as *phosphate of lead, pyrophosphate of magnesia, basic phosphate of sesquioxide of iron, phosphate of binoxide of tin, phosphate* or *pyrophosphate of silver*. The determination as pyrophosphate of magnesia is frequently preceded by precipitation as phosphate of sesquioxide of iron, phosphate of suboxide of mercury, or phospho-molybdate of ammonia. Methods of analysis by measure have also been recommended.

With regard to metaphosphoric acid and pyrophosphoric acid, I have simply to remark here that these acids cannot be determined by any of the methods given below. The best way to effect their quantitative analysis is to convert them into tribasic phosphoric acid; as follows:—

α. *In the dry way.* By protracted fusion with from four to six parts of carbonate of soda and potassa. This method is, however, applicable only in the case of metaphosphates and pyrophosphates of the alkalies, and of those metaphosphates or pyrophosphates of metallic oxides which are completely decomposed by fluxing with alkaline carbonates; it fails with compounds of metaphosphoric or pyrophosphoric acid with the alkaline earths, except magnesia.

β. *In the humid way.* The salt is heated for some time with a strong acid, best with concentrated sulphuric acid (*Weber, Pogg.* Annalen, 73, 137). This method leads only to the attainment of approximate results, in the case of all salts whose bases form soluble compounds with the acid added, since in these cases the metaphosphoric, or pyrophosphoric acid is never completely liberated; but the desired result may be fully attained by the use of any acid which forms insoluble compounds with the bases of the meta or pyrophosphates under examination. Respecting the partial conversion in the former case, I have found that it approaches the nearer to completeness the greater the quantity of free acid added,* and that the ebullition must be long continued (Compare experiment No. 35).

Bunce's statement that phosphoric acid volatilises when a phosphate is evaporated to dryness with hydrochloric or nitric acid, and the residue heated a little (*Sillim.* Journ. May, 1851, p. 405), is quite erroneous (compare my paper on the subject, in Annal. der Chem. und Pharm., 86, 216). But, on the other hand, it must be borne in mind that tribasic phosphoric acid under these circumstances changes, not indeed at 212°, but at a temperature below 302°, to pyrophosphoric acid; thus, for in-

* There are, however, certain considerations also which forbid to go too far in this respect.

stance, upon evaporating common phosphate of soda with hydrochloric acid in excess, and drying the residue at 302°, we obtain $NaCl + NaO, HO, PO_5$.

a. Determination as phosphate of lead.

Proceed as with arsenic acid, § 102, 1, *a*, (evaporate with a weighed quantity of oxide of lead, and ignite). This method presupposes that no other acid is present in the aqueous, or nitric acid solution; it has this great advantage that it gives accurate results, no matter whether the phosphoric acid present is mono, bi, or tribasic.

b. Determination as pyrophosphate of magnesia.

α. Direct determination.

Add to the solution a clear mixture of sulphate of magnesia, ammonia, and chloride of ammonium, as long as a precipitate continues to form; should the solution not yet evolve a strong ammoniacal odor, add some more ammonia; let the mixture stand twelve hours, without applying heat, filter, wash the precipitate with a mixture of three parts of water and one part of solution of ammonia, until the rinsings, after the addition of hydrochloric acid, are no longer rendered turbid in the least by chloride of barium, and proceed afterwards exactly as directed in § 82, 2. In the preparation of the mixture of sulphate of magnesia, ammonia, and chloride of ammonium, no more of the latter substance must be added than is just required to prevent the precipitation of the magnesia by the ammonia. The results are very accurate (Experiment No. 70). The loss sustained from the slight solubility of the basic phosphate of magnesia and ammonia, is very trifling (Experiment No. 31). For the properties of the precipitate and residue, see § 53. This method can be applied only in cases where it is quite certain that the whole of the phosphoric acid is present in the tribasic state. If the solution contains pyrophosphoric acid, the precipitate is flocculent, and dissolves in weak solution of ammonia (*Weber*).

β. Indirect determination, after previous precipitation as phosphomolybdate of ammonia (*Sonnenschein,* Journal für prakt. Chem. 53, 343).

Dissolve one part of molybdic acid in eight parts of solution of ammonia, mix this with twenty parts of nitric acid, and add of the mixture to the nitric acid solution of the phosphate sufficient to make the quantity of molybdic acid contained in the amount added thirty times that of the phosphoric acid contained in the phosphate. The large proportion of molybdic acid required sufficiently indicates the necessity of preparing a rather considerable quantity of solution. Digest the fluid with the yellow precipitate formed in it, several hours at a gentle heat, and wash the precipitate with the same solution of molybdic acid with which the precipitation has been effected. Let the filtrate stand some time in a warm place to see whether a further precipitate will form, and if so, add this precipitate to the first. (To make sure that the molybdic acid has been used in

excess, take a drop of the fluid, previously to filtration, and mix it with sulphuretted hydrogen water which must produce a brown precipitate of sulphide of molybdenum). Dissolve the precipitate on the filter in ammonia, and precipitate the phosphoric acid by solution of magnesia (compare *a*). The results are accurate (compare also *Craw*, Pharm. Centralblatt, 23, 669).

γ. Indirect determination, after previous precipitation as phosphate of suboxide of mercury (*H. Rose*, *Pogg.* Ann., 76, 218).

Dissolve the phosphate in neither too great nor too small a quantity of nitric acid, in a porcelain basin of proper size, add to the solution pure metallic mercury in sufficient quantity to leave a portion of it, even though only a small one, undissolved by the free acid. Evaporate on a water-bath to dryness. If the mass at a high temperature still evolves an odor of nitric acid, moisten it with water, and heat again on the water-bath, until it smells no longer of acid. Add now hot water, pass through a small filter, and wash until the rinsings leave no longer a fixed residue upon platinum. Dry the filter which, besides the phosphate, contains also basic nitrate of suboxide of mercury and free mercury, mix its contents in a platinum crucible with carbonate of soda and potassa in excess, roll the filter into the shape of a ball, place it into a hollow made into the mixture, and cover the whole with a layer of carbonate of soda and potassa. Expose the crucible under a chimney with good draught for about half an hour to a moderate heat, so that it does not get red hot. At this temperature the nitrate of suboxide of mercury and the metallic mercury volatilise. Heat now over the lamp to the most intense ignition, and treat the residue with hot water, which will dissolve it completely, if no sesquioxide of iron was present. Supersaturate the clear (if necessary, filtered) solution with hydrochloric acid, add ammonia and solution of magnesia, and proceed as in *a*.

c. Determination as basic phosphate of sesquioxide of iron.

a. Proceed exactly as in the determination of arsenic acid as arseniate of sesquioxide of iron, by *Berthier's* method (§ 102, 3, *a*). Avoid using a great excess of ammonia, as this would be liable to withdraw some phosphoric acid from the precipitate. The results are rather too low than too high (*H. Rose*).

β. Proceed exactly as in the determination of arsenic acid as arseniate of sesquioxide of iron, by *Kobell's* modification of *Berthier's* method (§ 102, 3, *b*). The results are accurate.

γ. Mix the acid solution containing the phosphoric acid, with an excess of solution of sesquichloride of iron of known strength, add, if necessary, sufficient alkali to neutralise the greater portion of the free acid, mix with acetate of soda in excess, and boil. If the quantity of solution of sesquichloride of iron added was sufficient, the precipitate must be

brownish-red. This precipitate consists of basic phosphate and basic acetate of sesquioxide of iron, and contains the whole of the phosphoric acid and of the sesquioxide of iron. Filter off boiling, wash with boiling water, dry carefully, and ignite in a platinum crucible with access of air. Burn the filter on the lid. Moisten the residue after its ignition with strong nitric acid, evaporate this at a gentle heat, and ignite again. Should this operation have increased the weight, which is not the case usually, it must be repeated, until the weight remains constant. Deduct from the weight of the residue that of the sesquioxide of iron contained in the solution added; the difference is the phosphoric acid.

This modification of *Schulze's* method was first recommended by *A. Müller* (Journ. f. prakt. Chem. 47, 341); it has been adopted also by *Way* and *Ogston* in their analyses of ashes (Journal of the Royal Agricultural Society, VIII. Part I). By the use of a solution of sesquichloride of iron of known strength, the estimation of the sesquioxide of iron in the residue (which would have to be effected in the manner described § 106, II. *h*) is dispensed with.

d. Determination as phosphate of binoxide of tin.

α. Reinoso's method (Journal f. prakt. Chem. 54, 261).

Heat a weighed amount of pure tin* with the phosphate and with nitric acid in excess, to ebullition, filter when the whole of the tin has been converted into binoxide, wash, dry, ignite cautiously, to guard against the reduction of any of the binoxide, and weigh promptly, as the residue is hygroscopic. What the residue weighs over the quantity of binoxide corresponding to the amount of tin used, is phosphoric acid (provided always that the analysed phosphate dissolves completely in nitric acid). This method has been repeatedly applied with success, for instance by *Girard* in the analysis of phosphate of uranium; by *Joy* in the examination of the tooth of the narwhal, &c.

β. Bennett's modification of *Reinoso's* method, in which the solution of the phosphate is mixed with an excess of a solution of bichloride of tin of known strength, and then with a solution of phosphate of soda, gave unsatisfactory results in experiments made in my laboratory.

e. Determination as phosphate of silver, see II. *a.* γ.

f. Determination by analysis by measure (*Räwsky*. Journal f. prakt. Chem. 41, 365).

Add to the acid solution (which, with the exception of sesquioxide of iron, must contain no bases forming with phosphoric acid compounds insoluble in acetic acid), ammonia, until the free acid is nearly neutralised,

* It is hardly necessary to remark that the tin must be used in excess. Commercial tin may be substituted for the pure article, provided the quantity of binoxide formed from it be known.

then acetate of sesquioxide of iron * in the least possible excess. The phosphate of sesquioxide of iron is deposited in the form of a faintly yellowish white precipitate. Filter, and wash carefully with cold water—an operation which in the case of larger quantities of substance consumes much time; dissolve the precipitate in hydrochloric acid, and determine the iron in the solution in the manner directed § 90, 3. *Räwsky* proceeds upon the assumption that the precipitate has the composition Fe_2O_3, PO_5, and calculates for every 700 of iron 900 (rigorously 892, the equivalent of phosphorus being 392) of phosphoric acid.

This method has been objected to by several chemists, on the ground that the phosphate of sesquioxide of iron is slightly soluble in solution of acetate of sesquioxide of iron, which is indeed the reason why the latter solution must be used in the least possible excess; and also that the constant composition of the precipitate is doubtful (*Liebig* and *Kopp's* Annual Report II. 213, 1847-8; *Way* and *Ogston*, ibid. 1849, p. 397). The results of experiments made in my own laboratory by Mr. *D. Schirmer*, prove also that the composition of the precipitate varies with the greater or less excess used of the solution of acetate of sesquioxide of iron.

II. SEPARATION OF PHOSPHORIC ACID FROM THE BASES.

a. From the fixed alkalies.

α. The method I. *c*, in one of its modifications, is resorted to, or method I. *d*. The alkalies are found in the filtrate as nitrates or chlorides.

β. The method I. *b*. α, is applied, and the separation of the magnesia from the alkalies in the filtrate is effected in the manner described § 121.

γ. Salts composed after the formula 3 MO, PO_5, are dissolved in water and the solution is precipitated with neutral solution of silver; the yellow precipitate formed (3 AgO, PO_5,) is washed, dried, and ignited in the manner described § 36.

Phosphates, composed after the formula 2 MO, HO, PO_5, are ignited, the residue is dissolved in water, and precipitated with neutral solution of silver. The fluid is filtered off from the precipitate (which, in this case, consists of pyrophosphate of silver, 2 AgO, PO_5,) and the latter is washed dried, and ignited, (§ 36). For the properties of the precipitated phosphates of silver, see § 72, 4.

The bases in the filtrates are determined after the removal of the excess of silver used (see § 130).

The results are accurate; this method is particularly convenient, on account of the facility with which the alkalies in the filtrate may be estimated.

b. From the whole of the alkalies.

* A solution of iron alum (1:10), mixed with an equal quantity of solution of acetate of soda (1:10), and to which it is as well to add some free acetic acid, answer the same purpose.

α. The separation of the phosphoric acid is effected by the method I. *c.* *β.*, and the baryta and the alkalies in the filtrate are separated as directed § 121.

β. The aqueous solution is mixed with acetate of lead in slight excess, and the precipitate formed is allowed to subside; the fluid is then filtered off, and the alkalies in the filtrate are separated from the excess of the salt of lead used in the process, as directed in § 130. The quantity of the phosphoric acid originally present in the analysed compound may be inferred, in this case, from the loss, but it may also be determined directly by treating the washed precipitate of phosphate of lead according to § 106 II. *i.*

c. From baryta, strontia, lime, and oxide of lead.

The compound under examination is dissolved in hydrochloric or nitric acid, and the solution precipitated with sulphuric acid in slight excess. In the separation of phosphoric acid from strontia, lime, and oxide of lead, alcohol is added in conjunction with the sulphuric acid. The phosphoric acid in the filtrate is determined according to I. *b.* *α.* (in the case of strontia, lime, and oxide of lead after previous removal of the alcohol by evaporation.) The determination of the phosphoric acid is made the most accurate by saturating the fluid with carbonate of soda, evaporating to dryness, and fusing the residue with carbonate of soda and potassa. The fused mass is then dissolved in water, and the further process conducted as in I. *b.* *α.*

d. From magnesia.

The phosphoric acid is separated by *Berthier's* method, modified by *Kobell* (1. *c.* *β.*), and the magnesia and baryta in the filtrate are separated in the manner described § 122.

e. From the whole of the alkaline earths. (Comp. also § 106. II. *m* and *o.*)

α. The phosphoric acid is separated by the method I. *c.* *γ.* The alkaline earths remain in solution as chlorides with the alkaline acetate and alkaline chloride.

β. Dissolve in the least possible amount of nitric acid, add acetate of lead in slight excess, let the precipitate formed subside, wash the precipitate, which consists of phosphate and basic nitrate of lead, dry, ignite, (§ 36), and weigh. The residue is phosphate of lead + oxide of lead, or in other terms, phosphoric acid + oxide of lead. Put the crucible, with its contents, into a beaker glass, pour moderately dilute nitric acid over it, heat until it dissolves, decant the fluid into another glass, wash, add the rinsings to the solution, and determine the oxide of lead in it as sulphate (§ 92). Calculate from this the oxide of lead, and deduct the result from the weight of the first residue: the difference gives the quantity of the phosphoric acid. In the fluid filtered off from the first precipitate, the bases are separated from the excess of the salt of lead used,

in the manner described (§ 130). This method also gives satisfactory results.

f. From alumina (see also § 106 II. *m.* and *o.*).

α. (*Otto* and *Fresenius*). Dissolve in hydrochloric or nitric acid, dilute somewhat, add a tolerable quantity of tartaric acid, and then ammonia in excess. If you have added sufficient tartaric acid, the fluid must now appear clear. Add in slight excess a clear solution of sulphate of magnesia mixed with ammonia and chloride of ammonium, let the mixture stand at rest for several hours, after which filter, and wash the precipitate with dilute solution of ammonia; to free it completely from alumina, redissolve it in hydrochloric acid, add a little tartaric acid, and reprecipitate with ammonia. Treat the precipitate as directed in I. *b.* *α.* To obtain the alumina contained in the filtrate, add some nitrate of potassa, and a sufficient quantity of carbonate of soda to effect the decomposition of the chloride of ammonium present,* evaporate to dryness, and ignite the residue in a platinum vessel. Dissolve in hydrochloric acid by continued application of heat, and separate the alumina from the magnesia, as directed in § 124.

β. (*Berzelius.*) Pulverise the compound very finely, mix the powder with about one and a half parts of pure silicic acid† and six parts of carbonate of soda in a platinum crucible, and expose for half an hour to a strong heat. Digest the ignited mass with water, add bicarbonate of ammonia in excess, allow it to stand for some time, filter and wash. On the filter you have now silicate of alumina and soda, in the solution phosphate of soda, bicarbonate of soda, and carbonate of ammonia (were the solution filtered before the addition of the bicarbonate of ammonia, it would contain also some of the alumina compound). Determine the phosphoric acid in the solution by II. *a.*, and separate and determine the alumina in the insoluble residue in the manner described § 111.

γ. (*Fuchs.*) Dissolve in solution of potassa, and add solution of silicate of potassa. Dilute the mucilaginous mass which forms, with water, and boil. Filter off the precipitate of silicate of alumina and potassa. The filtrate contains the whole of the phosphoric acid. Acidulate it with hydrochloric acid, and separate the phosphoric acid and silicic acid in the manner described in § 135.

δ. (*Wackenroder* and *Fresenius.*) Precipitate the acid solution with ammonia, taking care not to use a great excess of that reagent, and add chloride of barium as long as a precipitate continues to form. Digest for some time, and filter. The precipitate contains the whole of the alumina and the whole of the phosphoric acid; the latter combined partly

* The ignition of alumina in presence of chloride of ammonium would entail loss by the formation and escape of chloride of aluminium.

† The safest way is to use artifically prepared silicic acid.

with alumina, partly with baryta. Wash it a little, and dissolve in the least possible quantity of hydrochloric acid. Saturate the solution at a high temperature with carbonate of baryta, add solution of soda in excess, apply heat, precipitate the baryta which the solution may contain, with carbonate of soda, and filter. You have now the whole of the alumina in the solution, the whole of the phosphoric acid in the precipitate. Acidulate the solution with hydrochloric acid, boil with some chlorate of potassa, and precipitate as directed § 83. Dissolve the precipitate in hydrochloric acid, precipitate the baryta with dilute sulphuric acid, filter, and determine the phosphoric acid in the filtrate by precipitation with solution of magnesia in the manner described in I. *b*. *a*. *Hermann* has applied a similar method in his analysis of Gibbsite.

g. *From sesquioxide of chromium.*

Fuse with carbonate and nitrate of soda, and separate the chromic acid and phosphoric acid in the manner described § 135.

h. *From the metallic oxides of the fourth group.*

a. Fuse with carbonate of soda and potassa. Keep in fusion for some time, and then boil the fused mass with water. Filter and wash the undissolved residue. The filtrate contains the phosphoric acid combined with soda; determine the acid as directed in II. *a*. Dissolve the residue, which generally retains an admixture of alkalies, in acid, and determine the respective metals in the solution by the appropriate methods (see §§ 85 to 90).

In the case of phosphate of manganese, carbonate of soda is used instead of carbonate of soda and potassa. Should a small portion of manganic acid have got into the solution, this is removed by a little sulphuretted hydrogen water.

β. Dissolve in hydrochloric acid, add tartaric acid, then ammonia, and finally, in a flask which is to be closed, sulphide of ammonium, put the flask in a moderately warm place, and allow it to deposit until the fluid appears of a pure yellow color, without the least tinge of green; filter, and determine the metals as directed in §§ 85 to 90. The phosphoric acid is calculated from the loss, or determined according to I. *b*. *a*. The solution of sulphate of magnesia may immediately be added to the filtrate, which contains sulphide of ammonium. This method is not well adapted for the analysis of phosphate of nickel. In the case of iron it is liable to give a little too much pyrophosphate of magnesia, and too little sesquioxide of iron (*Rose*.)

γ. (Special method to separate the phosphoric acid from the oxides of iron, *Fresenius*.) Reduce the peroxide of iron in the solution, if necessary, with sulphite of soda, add solution of soda or potassa in excess, boil until the precipitate has become black and granular, filter, and wash with boiling water. The precipitate on the filter is protosesquioxide of iron, free from

phosphoric acid. The phosphoric acid in the filtrate is determined as directed in I. *b.* *a.*

i. From the metals of the fifth and sixth groups.

Dissolve in hydrochloric or nitric acid, precipitate with sulphuretted hydrogen, filter, determine the bases by the methods given in §§ 91 to 102, and the phosphoric acid in the filtrate by I. *b.* *a.*, or, under circumstances, also by I. *a.* From oxide of silver the phosphoric acid is separated in a more simple way still, by adding hydrochloric acid to the nitric acid solution; from oxide of lead it is separated most readily by II. *c.*

k. From all the bases, except alumina and oxide of mercury (H. Rose).

The phosphoric acid is separated as phosphate of suboxide of mercury by *Rose's* method (§ 106, I. *b.* γ).

a. If the substance contained no iron, the fluid filtered off from the phosphate of suboxide of mercury, contains all the bases as nitrates, together with much nitrate of suboxide of mercury, and occasionally also some oxide. The former is removed by the addition of hydrochloric acid. The precipitated subchloride of mercury is free from other bases. If only a slight precipitate is produced by hydrochloric acid, the filtration is preceded by addition of ammonia. The bases in the filtrate are determined in the usual way. If the mercury has been separated by ammonia, the precipitate is dried and ignited (under a chimney with a good draught). If a residue remain, this must be more closely examined. If it consists of phosphates of the alkaline earths, the treatment with mercury and nitric acid must be repeated; if, on the contrary, it consists of pure magnesia or of carbonates of the alkaline earths, it is dissolved in hydrochloric acid, and the solution added to the fluid containing the chief portion of the bases. The following method is often advantageously resorted to instead of the one just described: the fluid filtered off from the phosphate of suboxide of mercury is evaporated to dryness in a platinum dish, and the residue ignited in a platinum crucible under a chimney with a good draught. If alkaline nitrates are present, some carbonate of ammonia must be added from time to time during the process of ignition, to guard against injury to the crucible from caustic alkali forming. The ignited residue is treated, according to circumstances, first with water and then with nitric acid, or at once with nitric acid.

β. If the substance contained iron, the greater part of that metal is left undissolved with the phosphate of suboxide of mercury. The dissolved part is separated from the other bases by the methods given below; the undissolved part is obtained, after ignition of the residue containing it, with carbonate of soda and potassa, and treating of the ignited mass with water, as sesquioxide of iron containing alkali. This is dissolved in hydrochloric acid, and the solution precipitated with ammonia; as alumina cannot be decomposed, like sesquioxide of iron, by fusion with carbonate of soda and potassa, whilst nitrate of alumina and nitrate of sesquioxide of

iron are both equally decomposed upon simple evaporation, the method just described is not applicable in presence of alumina.

l. From sesquioxide of iron, alumina, alkaline earths, and many other bases (*H. Rose*).

Mix the hydrochloric acid solution with carbonate of baryta in excess let the mixture digest some days in the cold, filter, and wash with cold water. The precipitate contains the whole of the phosphoric acid in combination with sesquioxide of iron, alumina, baryta, and besides also the excess of carbonate of baryta used. The other bases are in the filtrate. The precipitate is dissolved in the least possible quantity of dilute hydrochloric acid, the baryta cautiously precipitated with sulphuric acid, the fluid saturated with carbonate of soda, and, together with the precipitate, evaporated to dryness; the residue is mixed with an equal quantity of pure silicic acid, and six times as much carbonate of soda, and the mixture heated in a large platinum crucible, commencing with a gentle heat, which is then gradually increased to a very high degree. The remaining operations are conducted exactly as directed in II. *f.* β.

m. From many bases, especially from the alkaline earths and alumina (but not from sesquioxide of iron).

Precipitate the phosphoric acid as phosphate of binoxide of tin, in the manner directed in I. *d.* α. The filtrate contains the bases, free from admixture with any foreign body which it might be necessary to remove; this circumstance greatly facilitates the determination of the bases. It remains still to be ascertained which bases do not admit of the application of this otherwise very convenient method.

n. From sesquioxide of iron in large proportion and in presence of alkaline earths (as is often the case in the analysis of iron ores). (*Fresenius*, Journ. f. prakt. Chem. 45, 258).

The determination of the phosphoric acid in such compounds may indeed be accomplished by I. *c.* β. or γ., but the separation of a small quantity of phosphoric acid from a very large proportion of sesquioxide of iron is a most tedious task; it is therefore preferable in cases of the kind to proceed as follows: the hydrochloric acid solution is heated to boiling, then removed from the lamp, and solution of sulphite of soda added, until carbonate of soda produces a nearly white precipitate; the mixture is then boiled until the odor of sulphurous acid has gone off; the excess of free acid which might still be present is nearly neutralised with carbonate of soda, a few drops of chlorine water are added, and lastly, acetate of soda in excess. The minutest quantity of phosphoric acid shows itself at once by the formation of a white precipitate of phosphate of sesquioxide of iron.* More chlorine water is now added drop by drop, until the fluid

* Silicic acid and arsenic acid produce a similar precipitate, and must therefore, if they happen to be present, be previously removed.

appears reddish, it is then boiled, until the precipitate has well subsided; the latter is filtered off hot, and washed with hot water. The precipitate contains the whole of the phosphoric acid, together with a small portion of the iron; the filtrate contains the greater portion of the latter, together with alkaline earths. The precipitate is treated as directed § 106. II. *h*.

o. From all bases without exception.

Apply *Sonnenschein's* method (I. *b*. *β*.), and separate the bases from the molybdic acid in the fluid filtered off from the phospho-molybdate of ammonia. As molybdic acid comports itself with sulphuretted hydrogen and sulphide of ammonium like a metal of the sixth group, it is best to precipitate metals of the sixth and also of the fifth group from acid solutions with sulphuretted hydrogen before you proceed to precipitate the phosphoric acid with molybdic acid; you will thus have to separate the phosphoric acid only from the metals of the first four groups. The process is conducted as follows: mix the acid fluid in a flask that admits of being closed, with ammonia till it acquires an alkaline reaction, add sulphide of ammonium in sufficient excess, and digest the mixture. As soon as the solution appears of a pure yellow color, without the least tinge of green, filter off the fluid, which contains sulphide of molybdenum and ammonium, wash the residue with water, mixed with some sulphide of ammonium, and separate the remaining metallic sulphides and hydrated oxides of the fourth and third groups by the methods which will be found in Section V. Mix the filtrate cautiously with hydrochloric acid in moderate excess, and, if the fluid does not already smell strongly of sulphuretted hydrogen, add some of that agent; filter off the sulphide of molybdenum, and determine the alkaline earths and alkalies in the filtrate. This method of separating the phosphoric acid from the bases is highly recommended.

§ 107.

5. BORACIC ACID.

I. *Determination.*

The determination of boracic acid is always effected best in an indirect way, as there exists no compound of it sufficiently insoluble to admit of its being used to any advantage for the direct separation of the acid.

The determination of the boracic acid in an aqueous, or alcoholic solution cannot be effected by simply evaporating the solution and weighing the residue, as a notable portion of the acid volatilises and is carried off along with the aqueous or alcoholic vapor. This is the case also when the solution is evaporated with oxide of lead in excess.

The best way of determining the boracic acid is therefore the following:—mix the solution of the boracic acid with a weighed quantity of pure carbonate of soda,* about equal to the supposed amount of the

* Fused carbonate of soda answers the purpose best.

boracic acid, or exceeding it up to double the quantity. Evaporate the mixture to dryness, heat the residue to fusion, and weigh. The residue contains a known amount of soda, and unknown quantities of carbonic acid and boracic acid. Determine the carbonic acid by one of the methods given in § 110, and calculate the boracic from the difference (*H. Rose*).

II. *Separation of boracic acid from the bases.*

The boracic acid is generally calculated from the difference between the weight of the separated base and that of the analysed borate, as a direct determination of the acid, even though practicable, is yet always a task of very considerable difficulty.

a. From the whole of the fixed bases.

A portion of the very finely pulverised compound under examination is weighed, put into a platinum crucible, and digested with a sufficient quantity of hydrofluoric acid; pure concentrated sulphuric acid is then gradually added, drop by drop, and the mixture heated, gently at first, then more strongly, until the excess of the sulphuric acid is completely expelled. In this operation the boracic acid goes off in the form of fluoride of boron. ($BoO_3 + 3\ H\ Fl = B\ Fl_3 + 3\ HO$.) The residue contains the bases in the form of sulphates; the bases are determined by the appropriate methods, and the quantity of the boracic acid is inferred from the difference between the weight of the separated base and that of the analysed borate. The application of this method presupposes, of course, that the analysed compound is decomposable by sulphuric acid. Instead of the hydrofluoric acid, pure finely pulverised fluor-spar may be used in the proportion of four parts to one part of the borate; but in this case the determination of the base is somewhat more difficult, as the residuary sulphate contains a considerable admixture of sulphate of lime.

b. From the alkalies.

Dissolve a weighed quantity of the borate in water, add an excess of hydrochloric acid, and evaporate the solution on a water-bath. Towards the end of the operation add a few more drops of hydrochloric acid, and keep drying the residue on the water-bath, until no more hydrochloric acid vapors escape. Determine now the chlorine in the residue (§ 112), calculate from this the alkali, and the boracic acid from the difference.

E. Schweizer, with whom this method originated, states that it gave him very satisfactory results in his analysis of borax. It will, probably, answer also in the case of some other borates.

c. From baryta, strontia, lime, and oxide of lead.

The same method as in the case of phosphoric acid, § 106, II. *c*. The quantity of the boracic acid is inferred from the loss.

d. From magnesia.

Dissolve the compound in hydrochloric acid, supersaturate with ammonia, precipitate the magnesia by phosphate of soda (§ 82), and calculate

the boracic acid from the loss. The pyrophosphate of magnesia obtained by the process, contains a very minute admixture of boracic acid (*H. Rose*).

e. From the metallic oxides of the fourth, fifth, and sixth groups.

The metallic oxides are precipitated by sulphuretted hydrogen, or, as the case may be, sulphide of ammonium, and determined by the appropriate methods. The quantity of boracic acid is inferred from the loss. In cases where the metal has been precipitated with sulphuretted hydrogen from acid or neutral solutions, the boracic acid may also be determined in the filtrate by the methods given in I., after having been previously completely freed from sulphuretted hydrogen by the transmission of carbonic acid through the fluid.

§ 108.

6. OXALIC ACID.

I. *Determination.*

Oxalic acid is either precipitated as *oxalate of lime*, and the latter determined as *carbonate of lime*, or the proportion of it contained in a compound is inferred from the quantity of gold reduced by it, or from the amount of carbonic acid which it produces upon accession of one equivalent of oxygen.

a. Determination as carbonate of lime.

Precipitate with solution of acetate of lime added in moderate excess, and treat the precipitated oxalate of lime as directed in § 81. If this method is to yield accurate results, the solution must be neutral, or made slightly acid by *acetic acid*; it must not contain alumina, sesquioxide of chromium or oxides of the heavy metals, more especially sesquioxide of iron or oxide of copper; therefore where these conditions do not exist they must first be supplied.

b. Determination by inference from the amount of gold reduced by the acid.

α. In compounds which dissolve in water.

Add to the solution of the oxalic acid or the oxalate a solution of auro-perchloride of soda, or auro-perchloride of ammonium, and digest for some time at a temperature near ebullition, with exclusion of direct solar light. Collect the precipitated gold in a filter, wash, dry, ignite, and weigh it. One equivalent of gold (2458·33) corresponds to three equivalents of $C_2 O_3$ ($3 \times 450 = 1350$).

β. In compounds which do not dissolve in water.

Dissolve in the least possible amount of hydrochloric acid, dilute with a very large quantity of water, in a capacious flask, cleaned previously with solution of soda, add solution of gold in excess, boil the mixture some time, let the gold subside, taking care to exclude solar light, and then proceed as directed in *α*.

The method of determining oxalic acid by inference, from the amount of gold reduced by it, give very accurate results.

c. Determination as carbonic acid.

This may be effected either

a. By the method of organic elementary analysis (§ 142); or

β. By bringing oxalic acid into contact with finely pulverised binoxide of manganese in excess, and with sulphuric acid, in an apparatus so constructed that the disengaged carbonic acid is perfectly dried previously to escaping.

The theory of this method may be illustrated by the following equation:

$$C_2O_3 + MnO_2 + SO_3 = MnO, SO_3 + 2\ CO_2$$

For every one equivalent of oxalic acid we obtain accordingly two equivalents of carbonic acid. For the apparatus, and the process, refer to § 110. II. *b. β.*, and to the chapter on the examination of manganese ores. Here I may remark, that free oxalic acid must first be prepared for the process by slight supersaturation with ammonia, and also that nine parts of free oxalic acid require theoretically eleven parts of pure binoxide of manganese. Since an excess of the latter substance does not interfere with the accuracy of the results, it is easy to determine by simple estimation the amount to be added. The binoxide of manganese need not be pure, provided it contain no carbonate. This method is very expeditious, and gives highly accurate results, especially if the process is conducted in a light apparatus, so as to admit the use of a delicate balance.

Instead of binoxide of mangenese, chromate of potassa may be used; compare § 104. *c.*

II. *Separation of oxalic acid from the bases.*

a. The oxalic acid is determined by I. *b.*, and the gold separated from the bases in the filtrate by the methods given in Section V.

b. The methods I. *c. a.* and *β.* are applicable in all cases as far as the acid is concerned; but the determination of the bases in the same portion of the analysed substance is not very practicable in *a.*, and inconvenient in *β.*

c. In many neutral oxalates, the proportion of acid may be inferred from the loss of weight which the salt undergoes upon ignition in the air and consequent reduction to the metallic state (*e. g.* oxalate of silver), or to pure oxide (*e. g.* oxalate of lead), or to carbonate (the oxalates of the alkaline earths and of the alkalies). This method is particularly adapted to determine the bases in the oxalates.

d. In many soluble salts the oxalic acid may be determined by the method I. *a.;* separating the bases afterwards from the excess of the salt of lime, by the methods given in Section V.

e. All the oxalates whose bases are precipitated by carbonate of potassa or carbonate of soda, and are insoluble in an excess of the precipitant, may

be decomposed by boiling with solution of carbonate of potassa or carbonate of soda, into oxide or carbonate on the one, and alkaline oxalate on the other side.

f. All the salts of oxalic acid with the oxides of the fourth, fifth, and sixth groups, may be decomposed with sulphuretted hydrogen, or with sulphide of ammonium.

§ 109.

7. HYDROFLUORIC ACID.

I. *Determination.*

Free hydrofluoric acid in aqueous solution is determined best as *fluoride of calcium*. For this purpose, carbonate of soda is added in moderate excess, and then a solution of chloride of calcium as long as a precipitate continues to form; when the precipitate, which consists of fluoride of calcium and carbonate of lime, has subsided, it is washed, first by decantation, afterwards on the filter, and dried; when dry, it is ignited in a platinum crucible (§ 35); water is then poured over it in a platinum or porcelain dish, acetic acid added in slight excess, the mixture evaporated to dryness on the water-bath, and heated on the latter until all odor of acetic acid has gone off. The residue, which consists of fluoride of calcium and acetate of lime, is heated with water, the fluoride of calcium filtered off, washed, dried, ignited (§ 35), and weighed. If the precipitate of fluoride of calcium and carbonate of lime were treated with acetic acid, without previous ignition, the washing of the fluoride would prove a difficult task. Presence of nitric acid or of hydrochloric acid in the aqueous solution of the hydrofluoric acid does not interfere with the process (*H. Rose*).

II. *Separation of fluorine from the bases.*

a. Soluble fluorides.

In acid solutions the fluorine is determined by the method given in I., and the bases in the filtrate are separated from the excess of lime and from the soda, by the methods given in Section V. Neutral solutions are mixed with a sufficient quantity of chloride of calcium, and the mixture heated to boiling, in a platinum dish, or, but less appropriately, in a porcelain dish; the precipitate of fluoride of calcium is allowed to subside, thoroughly washed with hot water, by decantation, transferred to the filter, dried, ignited, and weighed. The bases in the filtrate are then separated from the excess of the salt of lime, by the appropriate methods. That the bases may be determined also in separate portions by the methods given in *b.*, need hardly be stated.

b. Insoluble fluorides.

a. Anhydrous insoluble fluorides.

The finely pulverised and accurately weighed substance under examination, is heated for some time with pure concentrated sulphuric acid, and

the residue finally ignited until the free sulphuric acid is completely expelled. The residuary sulphate is weighed, and the metal contained in it calculated. The difference between the calculated weight of the metal and that of the original fluoride shows the amount of fluorine originally present in the analysed compound. In cases where we have to deal with metals whose sulphate gives off part of the sulphuric acid upon ignition, or where the residue happens to contain several metals, it is necessary to subject the residue to a further analysis before this calculation can be made.

β. Hydrated insoluble fluorides.

A sample of the compound under examination is heated in a tube.

aa. The water expelled is perfectly neutral to litmus paper.

In this case the amount of water present is ascertained by igniting the hydrated compound, and the fluoride and metal are subsequently determined as directed in II. *b*. *a*.

bb. The water expelled manifests an acid reaction.

The hydrated fluoride under examination is, in the first place, treated with sulphuric acid as directed in II. *b*. *a*., to determine the metal on the one hand, and the water + fluorine on the other. Another weighed portion is then mixed in a small retort, with about six parts of recently ignited oxide of lead; the mixture is covered with a layer of oxide of lead, the retort weighed, and the water (which is now entirely free from admixture of hydrofluoric acid) expelled by the application of heat, increased gradually to redness. The weight of the expelled water is inferred from the loss. The first operation having given us the exact amount of the water + fluorine, the quantity of the latter substance may now be readily calculated by simply subtracting from the combined weight of the water + fluorine, the weight of the water expelled in the second operation.

In the fifth section we shall have occasion to speak of another method of determining fluorine (in the chapter on the separation of fluorine from silicic acid).

§ 110.

8. CARBONIC ACID.

I. *Determination.*

a. In a mixture of gases.

Measure the gases accurately in a graduated tube over mercury, insert into the tube a moistened ball of hydrate of potassa cast on a platinum wire in a pistol bullet-mould, and leave this in the tube for twenty-four hours, or until the volume of the gas ceases to show further diminution; withdraw the ball now, and measure the gas remaining; the amount of carbonic acid gas originally present is inferred from the difference, provided always, of course, that the gaseous mixture contained no other gas liable to absorption by potassa.

b. In aqueous solution.

Mix solution of chloride of barium with some solution of ammonia, let the mixture stand at rest, and should the fluid have become turbid, filter it into an appropriate glass vessel of sufficient capacity to hold ten times the quantity. Put in the stopper, determine the weight, and then carefully transfer to it the aqueous solution of the carbonic acid which you wish to examine, taking care not to fill the vessel to the brim ; insert the stopper, and weigh again. The difference between the first and second weighings shows the quantity of the water. If the water to be examined can be got into a syphon by slow immersion of that instrument, it will be found more convenient to determine the quantity in this way by measure.

Shake the vessel, let the turbid mixture stand four days, and then decant the fluid rapidly off on a filter secluded as much as possible from access of air ; fill the vessel with warm water, close, shake, allow it to deposit, decant again, and repeat this washing by decantation once more ; transfer the precipitate now to the filter, wash until the last rinsings remain clear upon addition of solution of silver, dry, ignite gently, and weigh (§ 36). The amount of the carbonic acid may now be calculated from the weight of the carbonate of baryta, provided always, of course, that the analysed solution contained, besides carbonic acid, no other substance liable to be precipitated by ammonia and chloride of barium. But should the latter be the case, and the precipitated carbonate of baryta accordingly contain an admixture of sulphate of baryta, phosphate of baryta, sesquioxide of iron, or other similar substances, the carbonic acid must be determined in the dried but not weighed precipitate, as directed in II. The filter, scraped as clean as possible had better be incinerated, and the ashes added to the precipitate. If the precipitate is very large it is best first to weigh the whole of it, and then to determine the carbonic acid in a weighed off portion of the uniformly mixed powder.

If the last particles of the precipitate cannot be removed from the glass by mechanical means, they are dissolved in a little dilute hydrochloric acid (the glass having previously been thoroughly washed), the solution is precipitated with carbonate of soda, and the trifling precipitate formed filtered off on a separate small filter, which latter is in that case incinerated with the larger one.

II. *Separation of carbonic acid from the bases.*

The following methods are all of them based upon the same principle, viz., the expulsion of the carbonic acid by a more powerful acid. The quantity of the carbonic acid is inferred either from the loss of weight suffered by the analysed compound, or from the increase of weight gained by the fluid which has been made to absorb the carbonic acid gas disengaged.

a. Separation of carbonic acid from bases which upon ignition readily and completely yield the carbonic acid with which they are combined.

Such are, for instance, the carbonates of the oxides of zinc, cadmium, lead, copper, magnesium, &c.

α. Anhydrous carbonates.

Heat the weighed substance in a platinum crucible (in the case of the oxides of cadmium and lead in a porcelain crucible) to ignition, and keep it in that state until the weight of the residue remains constant. The results are, of course, very accurate. Substances liable to absorb oxygen upon ignition in the air, are ignited in a bulb-tube, through which a stream of dry carbonic acid gas is conducted during the process. The carbonic acid is inferred from the loss.

β. Hydrated carbonates.

The carbonate is heated in a glass tube connected with a chloride of calcium tube and a potassa apparatus; the posterior part of the tube contains some fused chlorate of potassa. The process is the same as in organic elementary analysis (§ 143). The oxygen evolved from the chlorate of potassa serves to expel the last traces of carbonic acid from the tube. The chloride of calcium tube and the potassa apparatus are weighed about fifteen minutes after the termination of the process, to permit the atmospheric air to replace by simple diffusion the oxygen gas contained in them. In very accurate experiments the solution of potassa is saturated with oxygen gas before the process commences. (Compare § 143. *bb.*) That the carbonate intended to be analysed by this method must be entirely free from admixture of organic substances, is evident.

Or, the substance is ignited in a bulb-tube through which dried air, or, in presence of oxidisable substance, carbonic acid, is transmitted, and which is connected with a chloride of calcium tube by means of a dried close-fitting cork. During the ignition, the posterior end of the tube is, by means of a small lamp, kept sufficiently hot, to prevent the condensation of water in it, care being taken however to guard against burning the cork. The loss of weight of the tube gives the amount of the water + the carbonic acid; the increase of weight gained by the chloride of calcium tubes gives the amount of the water, and the difference accordingly that of the carbonic acid.

b. Separation of carbonic acid from all bases without exception.

α. Anhydrous carbonates.

The carbonate under examination is weighed in a platinum crucible, and about four times its weight of fused biborate of soda, § 44, 8, added, which has been heated once more just previously to weighing. The mixture is weighed, and heat is then applied to it, which is gradually increased to intense ignition, and maintained at this temperature until the contents of the crucible are in calm fusion. The crucible is now allowed

to cool, and, when cold, weighed. The loss of weight indicates the amount of carbonic acid originally present in the ignited compound. The results are accurate (*Schaffgottsch*).

β. Carbonates readily and completely decomposed by acids.

aa. Carbonates whose bases form soluble salts with sulphuric acid.

The process is conducted in the apparatus illustrated by Fig. 45.

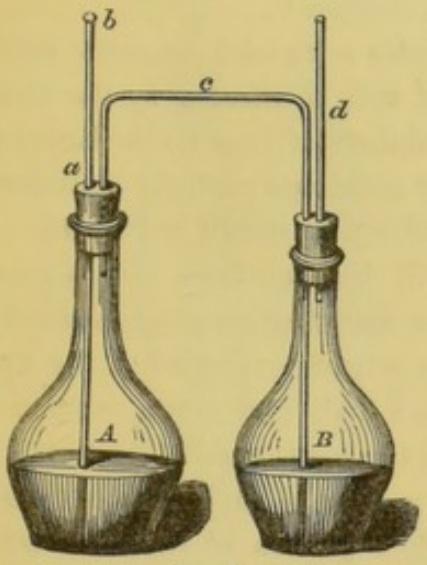


Fig. 45.

The size of the flasks depends upon the capacity of the balance which the operator may happen to possess. The tube *a* is closed at *b* by means of a small wax stopper; the other end of the tube *a* is open, and so are both ends of *c* and *d*. The flask B is nearly half filled with concentrated sulphuric acid; the tubes *a*, *c*, and *d* must fit air-tight in the perforations of the corks, and the latter equally so in the mouths of A and B. A weighed portion of the carbonate under examination is put into A; this flask is then filled to about one-third with water, the cork inserted, and the apparatus placed in equilibrium upon the balance.

A few bubbles of air are now sucked out of *d*, by means of a small suction tube, or of a perforated cork. This serves to rarify the air in A also, and causes the sulphuric acid in B to ascend in the tube *c*. The latter is watched for some time, to ascertain whether the column of sulphuric acid in it remains stationary, which is a proof that the apparatus is air-tight. Air is then again sucked out of *d*, which causes a portion of the sulphuric acid to flow over into A. The carbonate in the latter flask is decomposed by the sulphuric acid, and the liberated carbonic acid, completely dried in its passage through the concentrated sulphuric acid in B, escapes through *d*. When the evolution of the gas ceases, a fresh quantum of sulphuric acid is made to pass over into A by renewed suction through *d*, and the same operation is repeated until the whole of the carbonate is decomposed. A more vigorous suction is now applied, to make a larger amount of sulphuric acid pass over into A, whereby the contents of that flask are considerably heated; when the evolution of gas bubbles has completely ceased, the wax-stopper on *a* is slighty opened, and suction applied at *d* until the air sucked out tastes no longer of carbonic acid.

The apparatus is allowed to cool and then replaced upon the balance, and the equilibrium restored by additional weights. The sum of the weights so added indicates the amount of carbonic acid originally present in the analysed compound. The results are accurate.

If the flasks A and B are selected of a small size, the apparatus may be

so constructed that, together with the contents, it need not weigh above eighty grammes, admitting thus of being weighed on a very delicate balance. I have not as yet been able to convince myself that any one of the many proposed modifications of this apparatus affords essential advantages.

For the mode of proceeding in cases where the carbonate is mixed with a metallic sulphide or chloride, I refer to Section V.

bb. Carbonates whose bases form insoluble salts with sulphuric acid.

The analysis of such carbonates cannot well be effected by the method *aa*, as the insoluble sulphate formed (sulphate of lime for instance) protects the yet undecomposed portion of the carbonate partially from decomposition. The apparatus is therefore modified as shown in Fig. 46.

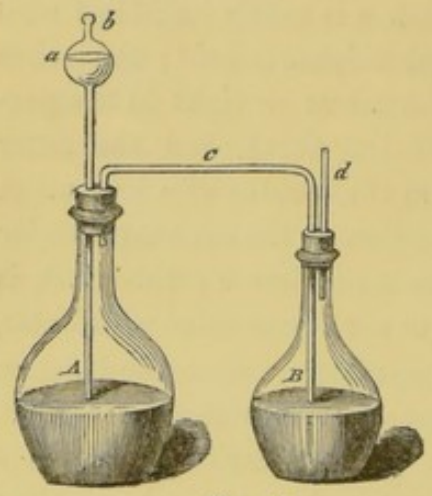


Fig. 46.

It will be seen from the engraving that the modification consists simply in the tube *a* being expanded at the upper end into a bulb, and drawn out to a fine point at the lower end.

The process is conducted as follows: A weighed portion of the carbonate is put into A, which flask is filled to about one-third with water. The bulb-tube *a* contains an amount of dilute nitric acid, more than sufficient for the decomposition of the carbonate, and which is prevented from flowing through the narrow aperture of this tube by the little wax stopper *b*. The point of this tube must not dip into the water in A, but simply reach to its surface. The apparatus, having been put in equilibrium on the balance, the tube *a* is carefully and cautiously moved down until its point nearly touches the bottom of A. The wax-stopper *b* is then slightly and momentarily raised, so as to permit a small quantity of nitric acid to flow out of tube *a*; and the same operation is repeated until the carbonate is completely decomposed. A is then placed in hot water, the wax-stopper is opened a little, and suction applied to the tube *d*, until the air tastes no longer of carbonic acid. The diminution of weight is ascertained when the apparatus is completely cooled.

It will be seen at a glance that a different construction may also be given to the apparatus; that, for instance, the tube *a* may be connected instead of with B, with a chloride of calcium tube, or with a tube fitted with pumice stone or asbestos moistened with sulphuric acid; also that the substance to be analysed may be put into a small tube, which is kept upright at first, but is subsequently, after weighing the apparatus, upset into the dilute acid in the flask. Such modifications, if they are judicious, do not alter the accuracy of the results.

Of the several modifications, the one proposed by *Geissler* (Journ. f. prakt. Chemie, 60, 35), and of which Fig. 47, gives a representation, is the most convenient.

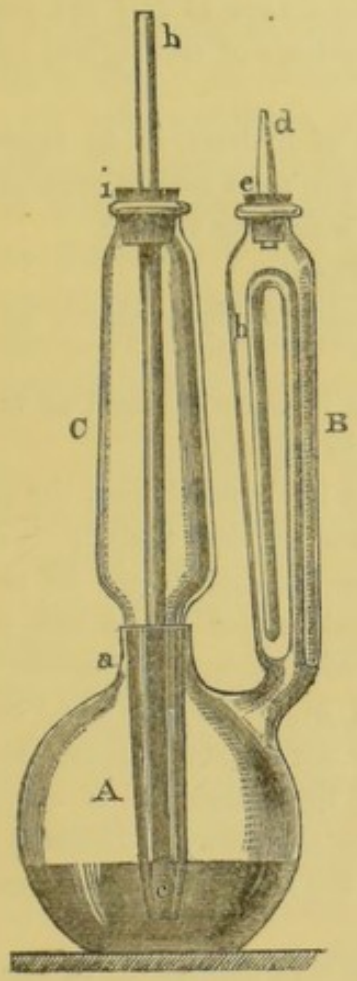


Fig. 47.

The apparatus consists of two parts, A B and C. C is ground into the neck of A (a), that it may close air-tight, and yet admit of its being readily removed, for the purpose of filling and emptying A. b c is a glass-tube, open at both ends, and ground water-tight into C, at the lower end (c); it is kept in the proper position by means of the moveable cork, i. The illustration shows the construction of the apparatus in other respects. The cork e must close air-tight, and so must the tube d in the cork. The weighed substance to be decomposed is put into A, water added to the extent indicated in the engraving, and the substance shaken towards the side of the flask. C is now filled nearly to the top with dilute nitric or hydrochloric acid, with the aid of a pipette, after having previously moved the cork i upwards, without raising b; the cork is then again turned down, C inserted into A; B filled somewhat more than half with concentrated sulphuric acid, and b closed at the top with a little wax stopper. After weighing the apparatus, the decomposition is effected by opening b a little, and thus causing acid to pass from C into A. The carbonic acid escapes through h into the sulphuric acid, where it is dried; it then leaves the apparatus through d. When the decomposition is effected, A is gently heated, the little wax-stopper on b opened, and the carbonic acid still remaining in the apparatus sucked out through by means of a perforated cork. The apparatus is then finally weighed when cold.

§ 111.

9. SILICIC ACID.

I. *Determination.*

The direct determination of silicic acid is invariably effected by converting the soluble modification of the acid into the insoluble modification,

which is effected by evaporating to dryness; the insoluble modification is then, after the removal of all foreign matter, ignited and weighed.

For the guidance of the student I have here to remark, that if he wishes to guard against mistakes he ought always to *test the purity of the weighed silicic acid.* The respective methods of testing will be found below.

If you have free silicic acid in the state of hydrate, in an aqueous or acid solution, free from other fixed bodies, you need simply evaporate the solution in a platinum dish, and ignite and weigh the residue.

II. *Separation of silicic acid from the bases.*

a. In all compounds which are decomposed by hydrochloric or nitric acid.

To this class belong the silicates soluble in water, as well as many of the insoluble silicates, as, for instance, all the zeolites.

The compound under examination is most finely pulverised, the powder dried at a temperature not exceeding 212°, and put into a platinum or porcelain dish, (in the cases of silicates whose solution might be attended with disengagment of chlorine, platinum must be avoided); a little water is then added, and the powder stirred up with it into a uniform paste. Moderately concentrated hydrochloric acid, or, if the substance contains lead or silver, nitric acid, is now added, and the mixture digested at a very gentle heat, with constant stirring, until the substance is completely decomposed, in other terms, until the glass rod, which is rounded at the end, encounters no more gritty powder, and the stirring proceeds smoothly and without the least grating noise.

The silicates of this class do not all comport themselves in the same manner in this process, but show some differences; thus most of them form a bulky gelatinous mass, whilst, in the case of others, the silicic acid separates as a light, pulverulent precipitate; thus again, many of them are decomposed readily and rapidly, whilst others require protracted digestion.

When the decomposition is effected, the mixture is evaporated to dryness on the water-bath, and the residue heated, with frequent stirring, until all the small lumps have crumbled to pieces, and the whole mass is thoroughly dry, and until no more acid vapors escape. It is always the *safest* way to conduct the operation of drying on the water-bath in cases where it may appear desirable to accelerate the desiccation by the application of a stronger heat, an air-bath may be had recourse to; which may be constructed in a simple way, by suspending the dish containing the substance by wire hooks in a somewhat larger dish of silver or iron, in a manner to leave everywhere between the two dishes a little free space of uniform width. Direct heating over the lamp is not advisable, as in the most strongly heated parts the silicic acid is liable to unite again with the sepa-

rated bases and to form compounds with them, which are not decomposed, or only imperfectly so, by hydrochloric acid.

When the mass is cold, it is thoroughly moistened with hydrochloric acid, after which it is allowed to stand for half an hour, without heating; it is then diluted with hot water, stirred, let deposit, and the fluid decanted through a filter; the sedimentary silicic acid is again treated with hot water, the mixture stirred, allowed to deposit, and the fluid once more decanted; the precipitate also is now transferred to the filter, thoroughly washed with hot water, well dried, and at last strongly ignited, in the manner directed in § 35. For the properties of the residue see § 72, 9. The results are accurate. The bases which are as chlorides in the filtrate, are determined respectively by the appropriate methods. Deviations from the instructions here given are likely to entail loss of substance; thus, for instance, if the mass is not *thoroughly* dried, a somewhat considerable portion of the silicic acid passes into the solution, whereas, in cases where the instructions are strictly complied with, only traces of the acid are dissolved; in accurate analyses, however, even such minute traces must not be neglected, but must be separated from the bases precipitated from the solution. This separation may be readily effected by dissolving the precipitated bases, after the processes of ignition and weighing, in hydrochloric or sulphuric acid, the operation being aided by the application of heat: the minute portion of silicic acid which has passed into the solution, and has been thrown down with the bases, is left behind. Again, if the silicic acid is not *thoroughly* dried previously to ignition, the aqueous vapour disengaged upon the rapid application of a strong heat, may carry along with it particles of the light and loose silica.

The *purity* of the silicic acid* is tested best in the following way:—heat a moderately concentrated solution of pure carbonate of soda to boiling, in a silver or platinum dish, or in a porcelain dish, and add a small quantity, of the silicic acid. If it dissolves completely, this is a proof of its purity; but if it leaves a residue, the remainder of the silicic acid must be weighed, and the substance which it contains in admixture must be determined as directed in *b*, and the result, of course, calculated upon the whole amount analysed. If you happen to have pure hydrofluoric acid at hand, you may also test the purity of the silicic acid in a very easy manner, by treating it with this acid in a platinum dish; upon the evaporation of the solution, the silicic acid, if *pure*, will volatilise completely (as fluoride of silicon). If there remains a residue, this is moistened once more with hydrofluoric acid, a few drops of sulphuric acid are added, the mixture is evaporated, and the residue ignited: the

* This testing is indispensable, more especiallyin cases where the silicic acid has separated, not in the gelatinous state, but in the pulverulent form.

residue consists of the sulphates of the bases which the silicic acid contains in admixture.—(*Berzelius.*)

b. Compounds which are not decomposed by hydrochloric acid or nitric acid.

α. The compound is fused with carbonate of soda, or carbonate of soda and potassa (see § 22, *a*). The red-hot crucible is put upon a cold iron plate, which will cause the solidified mass to come off readily. The mass is then dissolved in hydrochloric or nitric acid, and the solution treated as directed in II. *a*. This method is the one most commonly employed. That it cannot be used to determine alkalies in silicates is evident.

β. The finely-pulverised silicate is mixed in a platinum dish, with rather concentrated, slightly fuming hydrofluoric acid, the acid being added gradually, and the mixture stirred with a thick platinum wire. The mixture, which has the consistence of a thin paste, is digested some time on a water-bath, and pure hydrated sulphuric acid, diluted with an equal quantity of water, is then added drop by drop, in more than sufficient quantity to convert all the bases present into sulphates. The mixture is now evaporated on the water-bath to dryness, during which operation fluoride of silicon gas and hydrofluoric acid gas are continually volatilising; a strong heat is finally applied, with proper caution, until the excess of sulphuric acid added is completely expelled. The mass, when cold, is treated with concentrated hydrochloric acid, and allowed to stand at rest for one hour; water is then added, and a gentle heat applied. If the decomposition has fully succeeded, the whole must completely dissolve. If there remains a residue, the mixture is heated to gentle ebullition, and kept some time in that state; it is then allowed to deposit, the clear supernatant fluid is decanted off as far as practicable, and the residue dried, and then treated again with hydrofluoric acid and sulphuric acid, and, finally, with hydrochloric acid, which will effect complete solution, provided the analysed substance was very finely pulverised, and free from baryta, strontia, and lead. This solution is added to the first. The bases in the solution (which contains them as sulphates, and contains also some free hydrochloric acid), are determined by the methods which will be found in Section V.

This method, which is certainly one of the best to effect the decomposition of silicates, has *Berzelius* for its author. It has been but little used hitherto, because we did not know how to prepare hydrofluoric acid, except with the aid of a distilling apparatus of platinum, or, at least with platinum head; nor to keep it, except in platinum vessels. This difficulty, however, would appear to be overcome now, since *Städeler* (Annal. d. Chem. und Pharm. 87, 137) has made the discovery that gutta percha and vulcanised india-rubber resist the action of hydrofluoric acid. *Städeler* prepares the acid in a leaden retort having the shape of a

digesting glass, with the neck off. The retort has about five inches inner diameter; the width of the very short neck is one and three-quarter inches. A close fitting wide leaden tube of four inches length, is put into the mouth of the neck, which is made perfectly even, and smooth inside; the upper end of the tube is a little contracted, so that it may be closed with a common cork, which bears a double limbed thin leaden tube. The length of the longer limb of this tube is six inches; this limb is connected with a tube of stout vulcanised india-rubber, which opens into the gutta-percha flask intended to receive the hydrofluoric acid, but barely dips into the water in the receiver, by which precaution the receding of the acid is guarded against. Care must be taken to keep the receiver properly cooled. The gutta-percha flasks, in which the acid is kept, have the form of common bottles, and are closed with gutta-percha stoppers.* The execution of the method requires the greatest possible care both the fluid and the gaseous hydrofluoric acid being most dangerous substances. The treatment of the silicate with the acid and the evaporation must be conducted in the open air, otherwise the windows and all glass vessels and glass apparatus will be greatly injured. As the silicic acid is in this method simply inferred from the loss, a combination of the two methods, α and β, is often resorted to.

γ. Instead of the hydrofluoric acid dissolved in water, the gaseous acid also may be used to effect the decomposition of silicates. *Brunner* (*Pogg.* Annal. 44, 134) is the author of this method, which is very often employed. The process is as follows:—Put from one to two grammes of the silicate, very finely pulverised, in the thinnest possible layer, into a shallow platinum dish, and moisten the powder with water or with dilute sulphuric acid; put the dish on a leaden tripod, or some similar contrivance made of the same metal, into a leaden box, which may have a diameter of six inches, and a height of six inches, and in which you have just before stirred a layer of fluor-spar in powder, one half inch in depth, into paste, with concentrated sulphuric acid; in this latter operation, be cautious to avoid the escaping vapors; the mixing of the pulverised fluor-spar with the sulphuric acid is effected with a long glass rod, or better still with a long leaden rod. As soon as you have put the small dish, with the aid of a pair of pincers, into the box, cover the latter with the close-fitting leaden cover belonging to it, lute the joinings with gypsum paste, and put the box in a warm place for from six to eight days. If you wish to accelerate the process, you must not lute the joinings quite air-tight, and must heat the apparatus in the *open air* by means of a small spirit-lamp; in this manner you may succeed in a few hours to effect the decomposition of from one to two grammes of the pulverised silicate, provided the powder is spread in a very thin layer, or is stirred

* These flasks may be procured at the Gutta-percha Works, City Road.

from time to time, which latter operation requires caution. If the decomposition has succeeded well, the residue in the platinum dish consists of metallic silico-fluorides and (if you have used sulphuric acid to moisten the powder with) sulphates. Put the shallow dish now into a larger platinum dish, add, drop by drop pure sulphuric acid, in somewhat more than sufficient quantity to effect the conversion of the bases into sulphates; evaporate in the air-bath, expel finally the excess of hydrated sulphuric acid directly over the lamp, and treat the residue with hydrochloric acid and water in the manner directed in *β*. The decomposition can only be regarded complete if the residue is entirely dissolved.

δ. Fuse the most finely pulverised silicate with carbonate of baryta or hydrate of baryta—see § 22, *β*. Treat the hydrochloric acid solution obtained as directed in § 111. II. *a*. In the solution filtered off from the silicic acid, determine the bases by the methods which will be found in Section V. Test the purity of the silicic acid obtained as directed in *a*: if a residue remains, this is a proof that complete decomposition has not been effected. These methods, which were formerly often employed to determine the alkalies in silicates, have been in a measure supplanted by *γ*, since this latter method has been rendered more generally applicable.

Quite recently, *Deville** has called attention to the fact, that the proportion of carbonate of baryta usually employed to effect the decomposition of silicates (from four to six parts) is much larger than necessary. He states that one part of *orthoclase* fuses with as little as 0·8 parts of carbonate of baryta, at a moderate red heat, giving a vitreous transparent mass, decomposable by acids. He adds, that if carbonate of baryta is used in larger proportion, a notable amount of potassa volatilises, expelled by the agency of caustic baryta which forms in the process.

ε. *Deville** states also, that silicates undecomposable by acids, may be decomposed by fusing with small quantities of carbonate of lime (from 0·3 to 0·8 of carbonate of lime to one part of the silicate). The efficiency of this method has not yet been sufficiently proved by experiments in my own laboratory, to justify a detailed description of the process.

SECOND GROUP.

HYDROCHLORIC ACID—HYDROBROMIC ACID—HYDRIODIC ACID—HYDROCYANIC ACID—HYDROSULPHURIC ACID.

§ 112.

1. HYDROCHLORIC ACID.

I. *Determination.*

a. Hydrochloric acid is almost invariably determined as chloride of

* Ann. de Chim. et de Phys. 3. Ser. 38, 5. Or Journ. f. prakt. Chem. 60, 22.

silver. Solution of nitrate of silver, mixed with some nitric acid, is added in excess, to the solution under examination, the precipitated chloride is made to subside by the application of heat and shaking, washed by decantation, dried and ignited. The details of the process have been given in § 91, 1, *a*. *a*. Care must be taken not to heat the solution mixed with nitric acid before the solution of nitrate of silver has been added in excess. As soon as the latter is present in excess, the chloride of silver separates immediately and completely upon shaking the vessel, and the supernatant fluid becomes perfectly clear after standing a short time in a warm place. The determination of hydrochloric acid by means of silver is therefore more readily effected than that of silver by means of hydrochloric acid. In the case of smaller quantities of chloride of silver, the precipitate is often collected on a filter; see § 91, 1. *a*. *β*. Or the two methods may be combined in this way, that the chief portion of the precipitate is washed by decantation, dried in the porcelain crucible, and ignited, the decanted fluid being afterwards passed through a filter, to make quite sure that not a particle of chloride of silver has been lost. The filter is, after drying, incinerated on a platinum wire over the inverted cover of the porcelain crucible, the ashes are treated with a few drops of nitric acid, some hydrochloric acid is added, the mixture evaporated to dryness, the residue gently ignited, and the lid replaced in the proper position on the crucible in which the chloride has been heated to incipient fusion; a gentle heat is then once more applied, after which the crucible is allowed to cool under a bell-glass over sulphuric acid, and is then weighed.

b. If you have to determine hydrochloric acid in aqueous solution, no other substances being present, you may obtain satisfactory results also by evaporating a weighed portion of the solution with ammonia in excess, drying the residue on a water-bath, and weighing the chloride of ammonium obtained. Compare Experiment, No. 14.

c. Hydrochloric acid may also be accurately determined by analysis by measure.

a. A solution of silver of known strength is added as long as a precipitate continues to form. Compare § 91, 5.

Pelouze has used this method for the determination of several equivalent numbers. *Levol* has proposed a trifling modification, which, as he states, will serve to indicate more readily and accurately the exact point of complete precipitation. This modification consists in the addition of 0·1 volume of a saturated solution of phosphate of soda to the *neutral* fluid. When the whole of the chlorine has been precipitated by the silver, the addition of another drop of the solution of silver produces a yellow precipitate which does not disappear upon shaking the vessel. (Journ. f. prakt. Chem. 60, 384.)

β. *Liebig's* method (Annal. d. Chem. und Pharm. 85, 297). Recom-

mended more particularly for the determination of the chlorine in the chlorides contained in the urine, but applicable also in other cases.

aa. Principle of the method. Nitrate of oxide of mercury produces in a solution of urea immediately a thick, white precipitate; solution of chloride of mercury produces no such precipitate. When a solution of nitrate of oxide of mercury is mixed with the chloride of an alkali, there is formed chloride of mercury and nitrate of the alkali. If, therefore, a solution of urea is mixed with chloride of sodium, and a dilute solution of nitrate of oxide of mercury is dropped into it, a white turbidity will appear in the points of contact, which, however, will immediately disappear upon shaking, as long as the nitrate of oxide of mercury continues to decompose and transpose with the chloride of sodium in the manner just stated; but the moment this double decomposition is complete, an additional drop of the solution of the salt of mercury will produce a permanent white turbidity. Accordingly, if we know the measure and strength of the solution of the salt of mercury required to attain this point, we know also the amount of chlorine in the solution; since one equivalent of mercury in the mercurial solution used corresponds to one equivalent of chlorine.

bb. Preparation of the solution of nitrate of oxide of mercury. Take mercury of commerce and purify it as perfectly as possible (by *Ulex's** method, for instance), put ten grammes of the purified mercury into a beaker-glass, pour over it 50 grammes of nitric acid of 1·425 spec. gravity, and heat the mixture on a water-bath, with frequent addition of a few drops of nitric acid, until no more red fumes escape, and a drop of the fluid is no longer made turbid by solution of chloride of sodium; evaporate now to the consistence of syrup, and dilute with water to 550 cubic centimeters.

cc. Determination of the strength of the solution. This is effected with the aid of a solution of chloride of sodium of known strength, which *Liebig* prepares by mixing 20 cubic centimeters of a *saturated*† solution of pure rock salt, or chemically pure chloride of sodium, with 298·4 cubic centimeters of water. Every cubic centimeter of this solution contains 20 milligrammes of chloride of sodium.

* Triturate one pound of mercury with a quarter of an ounce of a solution of sesquichloride of iron of 1·48 spec. gravity and half an ounce of water, for ten minutes in a mortar, and digest the mixture several days, with occasional shaking; after which remove, by repeated washing with water, the solution of protochloride of iron formed, and which contains the foreign metals which the mercury held in admixture; boil the mercury now with hydrochloric acid, wash it once more and dry.

† Saturated at the common temperature.

Of this solution of chloride of sodium measure off 10 cubic centimeters into a small beaker-glass, and add 3 c. c. of a solution of urea containing in 100 c. c. four grammes of urea.

Let the solution of mercury, of which you wish to ascertain the strength, drop into this mixture, from a *burette* or from a *pipette*, provided with a compression stop-cock, until a perceptible precipitate forms, which agitation of the vessel fails to dissolve again.*

dd. When you have in this way ascertained how many c. c. of the mercurial solution correspond to the 10 c. c. of the solution of common salt = 0·2 grm. of chloride of sodium, you may use the mercurial solution in the analysis by measure, without further preparation, if you do not mind the trouble of a little calculation. But if you wish to avoid this, you must previously dilute the mercurial solution in a manner that every cubic centimeter corresponds to an integral number of milligrammes of chloride of sodium or chlorine. *Liebig* dilutes it to the extent that one cubic centimeter corresponds to 0·010 grm. of chloride of sodium.

ee. If the test fluid is intended to examine solutions containing a large amount of foreign salts, or an excess of urea, the 10 c. c. of the solution of the chloride of sodium must be mixed with 5 c. c. of a cold saturated solution of sulphate of soda† in addition to the 3 c. c. of the solution of urea, before the mercurial solution is added. The results are accurate.

II. *Separation of chlorine from the metals.*

a. In soluble chlorides.

The same method as in I. *a*. The metals in the filtrate are separated from the excess of the salt of silver added, by the methods which will be found in Section V.

Bichloride of tin, *chloride of mercury*, the *chlorides of antimony*, and the *green protochloride of chromium*, form exceptions from the rule, and are determined respectively by the following methods:—

a. From solution of *bichloride of tin* nitrate of silver would precipitate,

* The solution of chloride of sodium and urea is shaken occasionally during the addition of the mercurial solution: a mere opalescence of the fluid is disregarded, as this proceeds simply from a trace of foreign metals, which is readily seen from the circumstance that a further addition of the mercurial solution does not increase the turbidity.

† The reason of this addition is, that the nitrate of oxide of mercury and urea is more readily soluble in pure water than in saline water; to attain accurate results, therefore, it is necessary the solvent power of the fluids should be as nearly as possible the same in the preliminary determination of the strength of the mercurial solution as in the subsequent analytical process.

besides chloride of silver, a mixture of binoxide of tin and oxide of silver. To precipitate the tin, therefore, the solution is mixed with a concentrated solution of sulphate of soda or nitrate of ammonia, allowed to deposit, the fluid decanted, and filtered (compare § 101. *b.*, 1. *b.*), and the chlorine in the filtrate precipitated with solution of silver. *Löwenthal*, the inventor of this method, has proved its accuracy. (Journ. f. prakt. Chem. 56, 371.)

β. When a solution of *chloride of mercury* is precipitated with solution of nitrate of silver, the chloride of silver thrown down contains an admixture of mercury. The mercury is therefore thrown down from a solution of the chloride by sulphuretted hydrogen, which must be added in sufficient excess, and the chlorine in the filtrate is determined as directed in § 137, 5.

γ. *The chlorides of antimony* are also decomposed in the manner described in *β.* The separation of basic salt upon the addition of water may be avoided by addition of tartaric acid.

δ. Solution of silver fails to precipitate the whole of the chlorine from solution of the *green protochloride of chromium* (*Péligot*). The chromium is therefore first precipitated with ammonia, the fluid filtered, and the chlorine in the filtrate precipitated as directed in I. *a.*

b. *In insoluble chlorides.*

a. *Chlorides soluble in nitric acid.*

Dissolve the chloride in nitric acid, without applying heat, and proceed as directed in I. *a.*

β. *Chlorides insoluble in nitric acid* (chloride of lead, chloride of silver, subchloride of mercury).

aa. Chloride of lead and chloride of silver are analysed usually by reducing them to the metallic state, by means of hydrogen gas (see § 91, 4, and § 92), and estimating the chlorine from the loss. Chloride of silver may also be heated in conjunction with three parts of carbonate of soda and potassa, in a porcelain crucible, until the mass commences to agglutinate. Upon treating the mass with water, the metallic silver remains undissolved; the solution contains the alkaline chloride, which is then treated as directed in I. *a.*

bb. Subchloride of mercury is decomposed by digestion with solution of soda or potassa. The hydrochloric acid in the filtrate is determined as in II. *a.* The suboxide of mercury is dissolved in nitrohydrochloric acid, and the mercury determined as directed in § 94.

c. *The soluble chlorides of the metals of the fourth, fifth, and sixth groups* may all be decomposed also by sulphuretted hydrogen or, as the case may be, sulphide of ammonium. The hydrochloric acid in the filtrate is determined as directed in § 137, 5.

d. In many metallic chlorides, for instance, in those of the first and second groups, the chlorine may be determined also by evaporating the base with sulphuric acid, converting it thus into a sulphate, which is then ignited and weighed; the chlorine is calculated from the loss. This method is not applicable in the case of chloride of silver and chloride of lead, which are only imperfectly and with difficulty decomposed by sulphuric acid; nor in the case of chloride of mercury and bichloride of tin, which sulphuric acid fails altogether, or nearly so, to decompose.

Appendix:—*Determination of chlorine in the free state.*

The determination of chlorine in the free state, which was formerly a somewhat difficult task, is now comparatively easy.

The chlorine—either in the gaseous form or in aqueous solution—is mixed with an excess of solution of iodide of potassium in water. (Compare § 104, *d.* β.) Every equivalent of chlorine liberates one equivalent of iodine. By determining this iodine by *Bunsen's* method (see § 114), we also accurately learn the quantity of the chlorine.

In fluids containing with free chlorine also hydrochloric acid, or a metallic chloride, the chlorine existing in a state of combination may be determined in presence of the free chlorine, in the following way:—A weighed portion of the fluid is mixed with ammonia in excess; nitrogen escapes, and the solution contains the whole of the free chlorine as chloride of ammonium ($3Cl+4NH_3=N+3[NH_4Cl]$). By precipitating now with solution of silver, we learn the total amount of the chlorine. The quantity of the free chlorine is now determined in another weighed portion, by means of iodide of potassium; the difference gives the amount of chlorine which the analysed fluid contained in a state of combination.

Free chlorine may also be determined by the methods which will be found in the special part of this work, under the head of *Chlorimetry.*

Having thus seen in how simple a manner the quantity of free chlorine may be determined by *Bunsen's* method, it will be readily understood that all oxides and peroxides which evolve chlorine when heated with hydrochloric acid, may be analysed by heating them with concentrated hydrochloric acid, and determining the amount of chlorine evolved. The process is conducted the same way as with chromic acid. (§ 104, *d.* β.)

§ 113.

2. HYDROBROMIC ACID.

I. *Determination.*

a. Free hydrobromic acid is precipitated from its solution with nitrate of silver, and the further process conducted as in the case of chlorine (§ 112). For the properties of bromide of silver, see § 73, 2. The results are perfectly accurate.

*b. Heine's colorimetrical method.** The bromine is liberated by means of chlorine, and received in ether; the solution is compared in respect to color with an ethereal solution of bromine of known strength, and the quantity of bromine contained in it thus ascertained. *Fehling* obtained satisfactory results by this method. It will at once be seen that the amount of bromine contained in the fluid to be analyzed must be known in some measure, before this method can be resorted to. As the mother liquor examined by *Fehling* could contain at the most 0·02 grm. of bromine, he prepared ten different test fluids, by adding to ten several portions of 60 grammes each of a saturated solution of common salt, increasing quantities of bromide of potassium (containing respectively from 0·002 grm. to 0·020 grm. of bromine). He added an equal volume of ether to the test fluids, and then chlorine water, until there was no further change observed in the color of the ether. It being of the highest importance to hit this exact point, *Fehling* prepared three samples of each test fluid, and then chose the darkest of them for the comparison. Sixty grammes are now taken † of the mother liquor to be examined, the same volume of ether added as was added to the test fluids, and then chlorine water. Every experiment is repeated several times. Direct solar light must be avoided, and the operation conducted with despatch.

c. Figuier's colorimetrical method (Annal. de Chim. et de Phys. 33, 303, and Journ. f. prakt. Chem. 54, 293) also proposed as a useful method to effect the determination of bromine in mother liquors, &c.

This method is based upon the circumstance that one equivalent of chlorine (added in the form of chlorine water), liberates from a solution of a metallic bromide one equivalent of bromine, and that bromine imparts a yellow color to an aqueous solution, and escapes readily upon boiling, the yellow tint of the solution disappearing again with the escape of the bromine.

To carry this method into effect, the strength of the chlorine water is determined in the moment of its application, by making it act upon a solution of known strength of bromide of sodium, acidulated with a few drops of hydrochloric acid (or by *Bunsen's* method, § 112, Appendix), and then applied to the mother liquor. The latter is heated in a flask to near ebullition, chlorine water is then added from a *burette* covered with black paper, and the mixture heated for about three minutes, whereupon the yellow tint imparted to the fluid by the addition of the chlorine water, will disappear again; the mixture is now allowed to cool for two minutes, after which some more chlorine water is dropped into it, heat again applied, and the same process repeated until further addition of

* Journ. f. prakt. Chem. 36, 184, proposed as a useful method to effect the determination of bromine in mother liquors.

† The best way is to take them by measure.

chlorine water fails to impart a color to the fluid. Should the experiment last several hours, the strength of the chlorine water must be determined once more at the end of the process, and the calculation of the results based upon the mean of the two experiments. Alkaline fluids must be slightly acidulated with hydrochloric acid. Protoxide of iron, protoxide of manganese, iodine, and organic matter must not be present. Mother liquors colored yellow by the latter, are decolorised by acidulating them, adding a few drops of bromine, and heating. Larger quantities of organic matter must be destroyed by ignition. In the evaporation of the solutions to dryness, carbonate of soda must be added, since chloride and bromide of magnesium upon evaporation to dryness evolve hydrochloric and hydrobromic acids.

II. *Separation of bromine from the metals.*

The metallic bromides are analysed exactly like the corresponding chlorides (§ 112, II. *a.* to *d.*, the whole of these methods being applicable to bromides as well as chlorides. In the decomposition of bromides by sulphuric acid (§112, II. *d.*) porcelain crucibles must be used instead of platinum ones, as the liberated bromine would injuriously affect the latter.

Appendix: *Determination of free bromine.*

Free bromine in aqueous solution, or evolved in the gaseous form, is determined in the same way as free chlorine (see § 112, Appendix).

The determination of free bromine in the presence of hydrobromic acid, or a metallic bromide, is also effected in the manner described in that paragraph (Appendix). The addition of ammonia to the bromine requires caution. If bromine in solution is to be converted by ammonia into bromide of ammonium, the solution is poured into a capacious flask, a tolerably large quantity of water added, and then the ammonia through a funnel tube. The nitrogen gas escaping is transmitted by means of a bent tube, through dilute ammonia; the two fluids are then mixed together, and the remaining part of the process is conducted as directed in § 112, Appendix. By this means all loss is safely guarded against.

§ 114.

3. HYDRIODIC ACID.

I. *Determination.*

a. If you have hydriodic acid in solution, precipitate it with nitrate of silver, and proceed exactly as with hydrochloric acid (§ 112). For the properties of iodide of silver, see § 73, 3. The results are perfectly accurate.

b. The following method, recommended first by *Lassaigne*, is resorted to almost exclusively to effect the separation of hydriodic acid from hydro-

chloric and hydrobromic acids, for which purpose it is well adapted. Acidulate the solution slightly with hydrochloric acid, and add a solution of protochloride of palladium, as long as a precipitate continues to form; let the mixture stand from twenty-four to forty-eight hours in a warm place, filter the russet black precipitate off on a weighed filter, wash with warm water, and dry it at a temperature from about 158° to 176° until the weight of the precipitate remains constant. The drying may be greatly facilitated by replacing the water (after the operation of washing) by some alcohol, and the latter fluid again by a little ether. The best way, however, is to dry the precipitate *in vacuo* over a vessel containing sulphuric acid. For the properties of the precipitate, see § 73, 3. This method gives very accurate results, provided the drying be managed with proper care, but if the temperature is raised to near 212°, the precipitate will smell of iodine, and a trifling loss will be incurred.

Instead of simply drying the protiodide of palladium, and weighing it in that form, you may also ignite it in a crucible of porcelain or platinum,* and calculate the iodine from the residuary metallic palladium (*H. Rose*).

In addition to these, the following methods have been lately proposed:

Upon the circumstance that protochloride of palladium throws down the iodine from solutions of iodides,

c. Kersting† has founded a method of determining iodine by analysis by measure. This method requires,

α. A solution of pure iodide of potassium, containing exactly one part of iodine in 1000 parts of fluid. This is prepared by dissolving 1·308 grm. of ignited iodide of potassium in water, and diluting the solution to one litre of fluid.

β. An acid solution of protochloride of palladium, containing exactly one part of palladium in 2370 parts of fluid. This is prepared by dissolving one part of palladium in nitrohydrochloric acid, with application of heat, evaporating the solution to dryness at 212° adding 50 parts of concentrated hydrochloric acid and 2000 parts of water, and allowing to deposit. The exact strength of the clear solution is then ascertained by means of the solution of iodide of potassium, in the manner described in the *performance of the analytical process.*

γ. The solution of the iodide to be examined.—Dissolve the iodide, if possible, in water, and determine the amount of iodine in it approximately, in the manner described in the *performances of the analytical process;* dilute the rest of the solution now to a point that it may contain in about 1000 parts one part of iodine, and then determine the amount of iodine in it accurately by the same method.

Should the iodide be insoluble in water, or not well adapted for imme-

* This material is not injured by the operation.

† Annal. der Chem. und Pharm. 87, 25.

diate solution, on account of foreign admixtures, distil it with concentrated sulphuric acid, in a retort with neck directed upwards, and continue the application of heat until fumes of hydrate of sulphuric acid begin to be evolved. Take care to addat first from 20 to 100 c. c. of fluid, 20 c. c. of sulphuric acid (free from iodine). Should the distillate contain free iodine with hydriodic acid, add one or two drops of thin starch-paste,* and after this aqueous solution of sulphurous acid, until the blue coloraion is just disappearing. If the distillate contains sulphurous acid (as is the case, for instance, when urine containing iodine is distilled with sulphuric acid), add one or two drops of starch-paste, and then cautiously, solution of chloride of lime until the fluid just begins to show a blue tint, and dispel the blue coloration again by adding one or two drops of a weak aqueous solution of sulphurous acid. If the solution contains a very large amount of free acids, neutralise the latter partly with solution of soda.

Performance of the analytical process.

Pour 10 c. c. of the solution of protochloride of palladium into a white glass flask, of from 100 to 200 c. c. capacity, dilute slightly with water, put the cork in lightly, and place the flask in a water-bath of from 140° to 212. Add now some solution of iodide of potassium from the *burette*, shake, and heat a few seconds. When the fluid has cleared, which does not take long, pour some of it into two test tubes sufficient to fill them respectively to the height of two inches. By dropping some more solution of iodide of potassium into the one, and then comparing it with the other, you can readily see whether or not the iodide of potassium continues to produce a brown coloration in the fluid. Add now some more of the solution of iodide of potassium to the fluid in the flask, return to it also the sample from the test tubes, shake the flask, heat a few seconds, let the fluid clear, test it again in the way just now described, and repeat the same process until further addition of iodide of potassium ceases to produce a coloration in the fluid. Now filter off a sample of the fluid, and test it both with protochloride of palladium and iodide of potassium; if neither produce a perceptible brown coloration, the experiment is at an end. It will be readily understood that should too much iodide of potassium have been added, this error must be rectified by a further addition of 1 c. c. of solution of palladium.

The preliminary determination of the exact strength of the palladium solution is effected exactly in the same manner. Every 100 c. c. used of the solution of iodide of potassium (containing 0·100 of iodine) correspond to 0·042 grm. of palladium.

According to *Kersting's* experiments, the following bodies have no

* *Kersting* prepares this by boiling one part of starch and 0·1 part of sulphuric acid in twenty-four parts of waters.

adverse influence on the method; dilute hydrochloric acid, sulphuric acid, phosphoric acid, nitric acid, acetic acid, and the neutral salts of these acids, with potassa, soda, and ammonia; also chloride of calcium, and chloride of zinc; acetate of lead; sugar; uric acid, and the distillate of urine with sulphuric acid; alcohol, and ether; starch-paste; oil of lemon; also bromide of sodium, in presence of free acetic acid. The following bodies exercise an adverse influence on the process: bromide of sodium, in presence of free mineral acids, more especially upon heating; free alkalies; free chlorine, bromine, iodine, cyanogen; a large quantity of nitric acid, at a high temperature; sulphurous acid. These substances dissolve iodide of palladium, and prevent, consequently, the precipitation.

This method of *Kersting's* has been tested in my own laboratory, and found to give very accurate results.

d. Besides the method *c.*, *Kersting* has recommended also another and apparently still more convenient method of determining the iodine in iodides by analysis by measure (Annal. der Chem. und Pharm. 87, 29). This method, however, is less generally applicable than *c.*, the accuracy of its results being impaired by the presence of metallic chlorides and bromides, and free mineral acids; acetic acid, and the acetates also have an adverse influence. The method is founded upon the circumstance that, when chloride of mercury is added to the solution of a metallic iodide, tinged blue by addition of some starch-paste and bromine water, the decoloration of the iodide of starch ensues only upon the termination of the decomposition of the iodide. If the solution of the iodide is so highly dilute that it contains only one part of iodine in 10000 parts of fluid, the iodide of mercury formed remains in solution, and the decoloration of the iodide of starch may then be watched and ascertained with the greatest precision in the clear fluid. For the details of the process I refer to the original paper in the Annal. der Chem. und Pharm. 87, 29. Upon the same principle may also be founded a method of determining mercury by analysis by measure.

*e. Penny** has proposed to determine the iodine in iodides, by analysis by measure, by means of bichromate of potassa $3\,KI + KO,\,2CrO_3 + 7\,HCl = I_3 + 4\,KCl + Cr_2\,Cl_3 + 7\,HO$.

One equivalent of $KO, 2CrO_3$ corresponds accordingly to three equivalents of iodine, or in other terms, 0·3906 grm. of bichromate of potassa corresponds to 1·00 grm. of iodine. According to *Penny* no other decomposition takes place than the one given here, if application of heat is avoided. The process is conducted as follows: mix a solution of 0·3906 grm. of bichromate of potassa in 15 c. c. of water (or a measured off portion of solution of bichromate of potassa containing 0·3906 grm. of bichromate), with 6 c. c. of hydrochloric acid in the cold. On the other hand, dis-

* Chem. Gaz. 1852, 392, Journ. f. prakt. Chem. 58, 143.

solve a sufficient weighed quantity of the iodide in 50 c. c.=100° of water. Add this latter solution to the former until a sample of the mixture produces no longer a red coloration in a fresh prepared solution of protochloride of iron mixed with sulpho-cyanide of potassium. It need hardly be remarked here, that the method is inapplicable, or, at all events, not directly applicable, in cases where the solution of the iodide contains other bodies exercising a reducing action upon chromic acid.

Moride's methods of separating iodine, will be found in § 137, 2.

II. *Separation of iodine from the metals.*

The metallic iodides are analysed like the corresponding metallic chlorides. If you have to deal with iodides of the alkalies containing free alkali, and you wish to precipitate the iodine as iodide of silver, you must first saturate the free alkali almost completely with nitric acid, then add solution of nitrate of silver in excess, and finally nitric acid to strongly acid reaction. Were you to add the acid in excess at the beginning, free iodine might separate which is not converted completely into iodide of silver by the solution of nitrate of silver.

With respect to the salts insoluble in water, I have to observe that many of them are more advantageously decomposed by boiling with potassa, than by solution in dilute nitric acid, the latter process being apt to be attended with separation of iodine. This applies more particularly to protiodide of palladium, and to subiodide of copper, and subiodide of mercury. From iodides soluble in water the iodine may also be precipitated as protiodide of palladium.

Appendix :—*Determination of free iodine.*

Bunsen's method.

a. Principle of the method. The theory of this simple, beautiful, and accurate method, upon which a number of analytical processes are founded, is as follows :

α. Iodine and sulphurous acid, in presence of water, form hydriodic acid and sulphuric acid ($I+HO+SO_2=HI+SO_3$); but, on the other hand, sulphuric acid and hydriodic acid are decomposed again into iodine, sulphurous acid, and water ($HI+SO_3=I+HO+SO_2$). Which of these two reactions will ensue or predominate, depends upon the relative degrees of concentration of the solution. Now, *Bunsen* has ascertained, by accurate experiments that, when iodine is brought into contact with an aqueous solution of sulphurous acid containing no more than from 0·04 to 0·05 per cent by weight of anhydrous acid, the first reaction alone ensues ; under these circumstances, therefore, one equivalent of iodine converts one equivalent of sulphurous acid into sulphuric acid.

β. If therefore an unknown quantity of iodine, dissolved in iodide of potassium, is mixed with an excess of such highly dilute sulphurous acid of known strength, and the amount of the sulphurous acid remaining in

that form is then determined, the difference shows at once the amount converted into sulphuric acid, and hence also the amount of the iodine.

γ. The strength of the dilute solution of sulphurous acid is determined by ascertaining how much of a solution of iodine of known strength is required to convert the sulphurous acid in it into sulphuric acid.

b. Requisites for the process.—It results from *a* that the following fluids are required for the analytical process.

α. *A solution of iodine* of known strength.—This is prepared by dissolving 5 grammes of the purest possible iodine—dried for some time under a bell glass over sulphuric acid or chloride of calcium—with the aid of a concentrated solution of pure iodide of potassium,* in a measuring flask holding one litre, adding water up to the litre mark, and shaking the flask until perfect intermixture has taken place. As 1000 c. c. of this solution contains accordingly 5 grammes of iodine, every one c. c. contains 0·005 grm. and every one degree of the *burette* (=½ c. c.) 0·0025 grm. of iodine. But as iodine is mostly contaminated with traces of chlorine, which latter agent acts upon sulphurous acid the same way as iodine, but has another equivalent, the solution of iodine must be tested still to ascertain to how much absolutely pure iodine one degree of the *burette* corresponds in its action upon sulphurous acid.

This examination will be found in *c.* β.

β. *A solution of sulphurous acid.*—Saturate water completely with sulphurous acid at the common temperature, pour the solution into bottles, stop the latter tight, and place them inverted in water. Of this saturated solution add from 35 to 40 c. c. to 5000 c. c. of water.

γ. *A solution of iodide of potassium.*—Dissolve one part by weight of pure iodide of potassium (free from iodic acid) in about ten parts by weight of water. The solution must show no brown tint, neither upon standing in the air, nor immediately after addition of hydrochloric acid.

δ. *Starch-paste.*—This should be prepared fresh for every new experiment; it must be very thin, and almost perfectly clear.

c. Preliminary tests.

α. *Determination of the relative proportion between the solution of iodine and the solution of sulphurous acid.*

Measure off accurately, in a measuring flask or cylinder, or by means of a pipette, 100 c. c. of the dilute solution of sulphurous acid, and transfer from the measuring vessel to a flask, rinsing after or not, according to whether the measuring vessel used belongs to the system *e.* or to the system *a.* (see § 12, 4), *i.e.* whether it is regulated simply to *hold*, or actually to *give* the number of cubic centimeters marked on it. Add from three to four c. c. starch-paste, and then of the solution of iodine from a *burette*, until a per-

* This solution must be colorless, and must show no brown tinge, not even immediately after addition of acid.

sistent blue coloration appear; the flask must be shaken after every fresh addition of the solution of iodine.

Let us suppose we have found in this way, the proportion of our solution to be: 100 c. c.=200° of the dilute sulphurous acid to 54° of the solution of iodine; in other words, that 54° of the solution of iodine correspond to 200° of the dilute sulphurous acid.

As sulphurous acid suffers alteration from the oxidising action of the air, this preliminary determination must be repeated before every new series of experiments.

β. Testing the iodine solution, to ascertain to how much absolutely pure iodine one burette degree of it corresponds in its action upon sulphurous acid.

Weigh off about 0·35 grm. of the purest bichromate of potassa, thoroughly dried previously, and treat this with fuming hydrochloric acid, in the manner described in § 104, *d. β.* Conduct the chlorine evolved into an excess of solution of iodide of potassium, as directed in that paragraph. You will obtain accordingly for,

One equivalent of KO, 2 Cr O_3=1858, three equivalents of iodine=4758.

Supposing, therefore, you have weighed off 0·4 grm. of bichromate of potassa, the quantity of iodine liberated will amount to 1·024 grm. Add now to the solution of iodine in iodide of potassium so obtained, one measuring *pipette* (or cylinder or flask) full after another of the dilute sulphurous acid, until the brown coloration of the solution has completely disappeared. Suppose you have added in this way 800 c. c.

Add now to the fluid, which you have just mixed with 800 c. c. of dilute sulphurous acid, and which did contain 1·024 grm. of free iodine, a little starch-paste, and determine, by an experiment, how much of your iodine solution (*b. α.*) you have to add until blue coloration ensues. Suppose you have added 20° of your iodine solution.

The following simple calculation will now lead to the desired result: upon the supposition in *c. α.* you have required 54° of your iodine solution (*b. α.*) to convert 100 c. c. of your dilute sulphurous acid into sulphuric acid; the conversion of 800 c. c. of the dilute sulphurous acid into sulphuric acid would accordingly require $8 \times 54 = 432°$ of your iodine solution; but to convert the excess still remaining of sulphurous acid, you have required only 20°, accordingly $432° - 20° = 412°$, less than you would have required had the sulphurous acid not been acted upon already by free iodine. The quantity of this free iodine is, accordingly, exactly equal to that contained in 412° of your solution. Now, as the quantity of this free iodine amounts to 1·024 grm., you have in 412° of your iodine solution (*b. α.*) also 1·024 grm., or in 1° 0·00248 grm. of iodine, or, more correctly speaking, of a mixture of iodine with a trace of chlorine whose action is equal to that of the said quantity of pure iodine.

The number so found applies to the whole amount of the iodine solution prepared after b. α. As this solution keeps unaltered, and as it serves for the quantitative determination of a great variety of substances, it will be found advantageous to prepare a large quantity of it at once.

d. Performance of the analytical process.

Weigh off the iodine, best in a small flask, dissolve it in the iodide of potassium solution prepared after *b. γ.* (using about 5 c. c. of the solution of iodide of potassium to 0·1 grm. of iodine), add one measuring *pipette* (or cylinder or flask) full after another of the dilute sulphurous acid, until the fluid appear colorless; note the number of c. c., add 3 or 4 c. c. of starch-paste, and then solution of iodine (*b. α.*) until a blue coloration is just becoming perceptible, and note the quantity of solution of iodine added.

You have now simply to make the following calculation:

Deduct from the number of degrees of solution of iodine corresponding to the amount used of sulphurous acid, the number of degrees which you have been obliged to add to effect the conversion of the excess of the sulphurous acid into sulphuric acid. The result indicates the number of degrees of the solution of iodine which contain exactly the same amount of iodine as the examined sample.

The following example will serve to explain this more clearly:—

150 c. c. of dilute sulphurous acid, requiring 54° of solution of iodine to convert 100 c. c. of it into sulphuric acid, were added to 0·148 grm. of somewhat moist, but in other respects pure, iodine. The conversion of the excess remaining of the sulphurous acid took 23·6 of iodine solution.

To the 150 c. c. of sulphurous acid, correspond, of solution of iodine	81·0
The conversion of the excess remaining of sulphurous acid took .	23·6
Balance .	57·4

Now, as one degree of the iodine solution contains (upon the supposition in *c. β.*) 0·00248 grm. of iodine, 57·4° contain 0·1423 grm. The sample examined contained accordingly 0·1423 grm. of iodine.

If a fluid contains free iodine in presence of iodine in a state of combination, determine the former in one sample by *Bunsen's* method; add to another sample sulphurous acid until the fluid appears colorless, and then precipitate with solution of silver, as directed in § 114, I. *a.* Digest the precipitated fluid, previously to filtration, with nitric acid, in order to remove any sulphite of silver which might have been thrown down conjointly with the nitrate of the base originally combined with the iodine. The difference is equal to the amount of iodine originally present in a state of combination in the analysed fluid.

§ 115.

4. HYDROCYANIC ACID.

I. *Determination.*

a. If you have free hydrocyanic acid in solution, mix the solution, in a rather dilute state, with solution of nitrate of silver in excess, add a little nitric acid, and determine the precipitated cyanide of silver, as directed in § 91, 3.

If you wish to determine in this way, the hydrocyanic acid in bitter almond water or cherry laurel water, add ammonia after the addition of the solution of nitrate of silver, and then supersaturate slightly with nitric acid. This modification of the process is indispensable to precipitate from these fluids the whole of the hydrocyanic acid, as cyanide of silver.

b. Liebig's method of analysis by measure (Annal. der Chem. und Pharm. 77, 102). If hydrocyanic acid is mixed with potassa in excess, and a dilute solution of nitrate of silver is then added, a persistent turbidity—caused by the separation of cyanide of silver, or, if a few drops of solution of chloride of sodium have been added to the solution (which it is advisable to do) of chloride of silver—ensues only when the whole of the cyanogen is converted into double cyanide of silver and potassium. The first drop of solution of nitrate of silver added in excess produces the permanent precipitate. One equivalent of the silver used in the solution of the nitrate, corresponds therefore, exactly, to two equivalents of hydrocyanic acid ($2\,KCy + Ag\,O, NO_5 = Ag\,Cy, KCy + KO, NO_5$). For the examination of a dilute solution of hydrocyanic acid, a solution of nitrate of silver is used, containing in 500 c. c.=1000°, 2 grammes of metallic silver, and of which, accordingly, every one half c. c.=1° corresponds to 0·001 grm. of anhydrous hydrocyanic acid. *Liebig* has examined by this method hydrocyanic acid of various degrees of dilution, and has obtained results thereby corresponding exactly with those obtained by *a*. In this method it does not matter whether the hydrocyanic acid contains an admixture of hydrochloric acid or formic acid. Bitter almond water and medicinal hydrocyanic acid which it is intended to examine by this method, are diluted with from three to five volumes of water.

c. Fordos and *Gelis's method of analysis by measure** (Journ. de Chem. et de Pharm. 23, 48. Journ. f. prakt. Chem. 59, 255). This method is founded upon the reaction of free iodine upon cyanide of potassium; $KCy + 2\,I = KI + I\,Cy$. Two equivalents of iodine=3172, correspond accordingly to one equivalent of cyanogen=325, or to one equivalent of hydrocyanic acid=337·5, or to one equivalent of cyanide of potassium=814.

* Mentioned first by *Serullas* and *Wöhler*.

The process is conducted as follows: make a solution of iodine in alcohol, containing 40 grammes of iodine in the litre: ½ c. c. of this solution contains accordingly 0·020 grm. of iodine, corresponding to 0·0051 of cyanide of potassium. Mix the fluid containing the hydrocyanic acid, cautiously, with some solution of soda, and then add water containing carbonic acid, to convert a possible excess of alkali into bicarbonate; this addition of aërated water is necessary also in the examination of common cyanide of potassium by this method. Now drop your alcoholic solution of iodine into the mixture, until the fluid has acquired a persistent yellow color.

Fordos and *Gelis* recommend this method simply for the analysis of cyanide of potassium of commerce; it may, however, answer equally well also in scientific and pharmaceutical investigations. *Bunsen's* iodine solution (§ 114) might, in that case, be used instead of the alcoholic solution here recommended, 50 c. c.=100° of *Bunsen's* iodine solution (supposing them to contain exactly 0·25 grm. of iodine) correspond to 0·0256 of cyanogen.

II. *Separation of cyanogen from the metals.*

a. In soluble metallic cyanides (cyanide of mercury excepted).

Mix the solution of the cyanide with solution of nitrate of silver in excess, then add nitric acid to acid reaction, and proceed as in I. *a*. Determine the bases in the filtrate, after the removal of the excess of the salt of silver added; see Section V.

b. In insoluble metallic cyanides which dissolve readily in dilute nitric acid.

Dissolve the cyanide by shaking with extremely dilute nitric acid, in a flask closed with a glass-stopper, add nitrate of silver in excess, and proceed as in II. *a*.

c. In all insoluble metallic cyanides.

Ignite the cyanide, and determine the metal in the residue, either by at once weighing the residue, or by dissolving it, and precipitating it from the solution. The amount of cyanogen is either inferred from the loss, or determined by the method of organic elementary analysis. Many of the metallic cyanides may be decomposed also, by evaporation with hydrochloric acid, instead of by ignition, or by boiling with oxide of mercury. In the latter case, the oxides separate, mixed with the excess of the oxide of mercury, whilst basic cyanide of mercury dissolves.

d. In cyanide of mercury.

Precipitate the aqueous solution with sulphuretted hydrogen, and determine the mercury as directed in § 94, 3, and the hydrocyanic acid formed, in the manner described in § 137

The cyanogen may be advantageously determined also in another portion by the method of the quantitative determination of nitrogen (§ 152).

III. *Analysis of double protocyanides* (ferrocyanides, &c.)

*a. Bolley** has lately proposed the following simple method to effect the analysis of these compounds, which it is mostly found very difficult to decompose by acids, or by ignition, and which are also only imperfectly decomposed by boiling with oxide of mercury.

Weigh off a portion of the dried double cyanide, and mix this portion in a porcelain mortar with from three to four times the quantity of a mixture consisting of three parts of sulphate and one part of nitrate of ammonia; transfer the powder to a small tubulated retort, rinse the mortar with the mixture of the two ammonia salts, add the rinsings to the powder in the retort, join a receiver loose to the neck of the retort, and heat over a spirit-lamp, shaking the mixture in the retort occasionally. Complete decomposition ensues even at a moderate heat, attended with glimmering of the mass; the whole of the cyanogen volatilises in the form of cyanide of ammonium and of the products of the decomposition of the latter substance, whilst the metals remain behind as sulphates. As traces of these sulphates may have been carried over into the receiver, evaporate the fluid contained in the latter in a porcelain dish, volatilise the ammonia salts (if necessary), and dissolve what remains in the receiver in a little nitric acid. Dissolve the residue in the retort in water, adding, if necessary, some nitric acid, and then separate the metals in the clear solution by the appropriate methods which will be found in Section V. *Bolley* says he obtained very accurate results by this simple and easy method, in the decomposition of various ferro- and ferricyanides.

b. Mix a portion of the double cyanide with two parts of carbonate and two parts of nitrate of soda, and transfer the mixture in portions to a platinum† crucible, previously heated to gentle redness. Heat at last strongly, boil the residue with water, and determine the separated oxides by the proper methods which will be found in Section V. This method is not well adapted to compounds containing much alkali, on account of the more or less violent deflagration which ensues under these circumstances; nor is it adapted to compounds containing a volatile metal.

c. The estimation of the nitrogen and carbon (of the cyanogen) in such compounds is effected by the methods of organic elementary analysis (see Section VI.)

d. Liesching has proposed a method of analysis by measure, to determine ferricyanide of potassium when with ferrocyanide. This method is based upon the decomposition of the ferricyanide by the double compound of penta-sulphide of arsenic and sulphide of sodium. See Quart.

* Ann. der Chem. und Pharm. 87, 254.

† If there is reason to apprehend injury to this material, from the nature of the compound, you may substitute a crucible of porcelain; but the latter material is always strongly affected by the process.

Journal of the Chem. Society, vi. 31—36 ; Pharmaceut. Centralbl. 1853, page 388.

§ 116.

5. HYDROSULPHURIC ACID (Sulphuretted Hydrogen).

I. *Determination.*

Sulphuretted hydrogen in the free state is most readily and very accurately determined by means of iodine, by analysis by measure ; the sulphur in it may also be determined by converting it into sulphate of baryta and weighing.

a. The method of determining free sulphuretted hydrogen by analysis by measure, by means of a solution of iodine, was employed first by *Dupasquier*. That chemist used alcoholic solution of iodine for the purpose. But, as the action of the iodine upon the alcohol gradually alters the composition of this solution, it is better to use a solution of iodine in iodide of potassium. The decomposition ensues according to the formula :

$$HS + I = HI + S$$

One equivalent of I=1586 corresponds to one equivalent of HS=212·5. However, this exact decomposition can be relied upon with certainty only if the amount of sulphuretted hydrogen in the fluid to be analysed does not exceed 0·04 per cent of sulphuretted hydrogen (*Bunsen*). Fluids containing a larger proportion of sulphuretted hydrogen than this, must therefore first be diluted to the requisite degree, with water boiled and afterwards cooled again in a place from which the air is excluded.

If *Bunsen's* solution of iodine in iodide of potassium is used, 100°= 50 c. c. (containing exactly 0·2500 grm. of iodine), correspond to 0·0335 of HS or to 0·0315 of S. The calculation may be simplified also by preparing a solution of iodine containing in the litre 7·463 grammes of iodine ; every c. c. (= 2°) of this latter solution corresponds to 0·001 grm. of HS.

The analytical process is very simple : a weighed or measured off quantity of the sulphuretted hydrogen water* is poured into a capacious flask, diluted, if necessary, in the manner before directed, some thin starch-paste is added, and then solution of iodine, with constant shaking of the flask, until a persistent blue coloration ensues.

In exactly the same way free sulphurous acid may also be determined (Compare § 114, Appendix).

b. Measure or weigh off a certain quantity of the fluid containing the sulphuretted hydrogen, and mix it in a stoppered flask with solution of chloride of copper, or with a solution of arsenious acid in hydrochloric

* For the way of measuring off a certain quantity of sulphuretted hydrogen water from a larger amount of the same, see the Chapter on the Analysis of Mineral Waters.

acid in moderate excess; put in the stopper, shake the flask, allow it to deposit, filter, dry the precipitate, without previously washing it, or after slight washing only, and determine the sulphur in the dry precipitate as directed in II.

The method *a.* is always preferable in the case of mineral waters containing only a small proportion of sulphuretted hydrogen.

c. If the sulphuretted hydrogen is evolved in the gaseous state, conduct it into dilute solution of soda, and determine the sulphur in the sulphide of sodium formed, as directed in II. 2, *b.* *a.*

The last traces of the sulphuretted hydrogen gas are completely expelled, at the end of the evolution process, by pouring into the evolution flask, which still contains much free acid, some concentrated solution of bicarbonate of ammonia.

The absorption of the gas may be effected in the apparatus illustrated by Fig. 48.

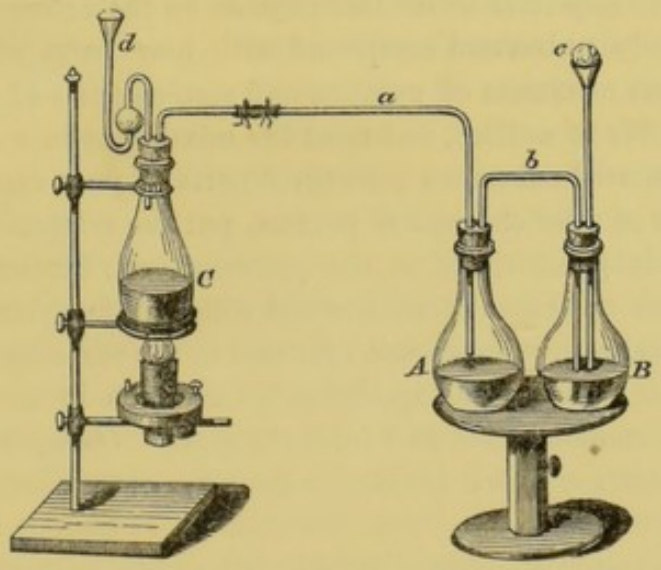


Fig. 48.

The construction and arrangement of the apparatus may be seen from the engraving. The tube *c* is cut off obliquely at the lower end, and hardly dips into the solution of soda. The funnel *c* contains asbestos moistened with the solution of soda. In cases where the sulphuretted hydrogen is evolved in conjunction with a larger proportion of another unabsorbed gas, *e. g.* hydrogen, the funnel on the tube *c* is replaced by a long and wide tube placed obliquely, and which contains broken pieces of glass or porcelain moistened with solution of soda. After the termination of the process, all the fluids are poured together, and the flasks and tube are rinsed with water boiled, and afterwards cooled again in a place from which the air is kept excluded.

II. *Separation and determination of sulphur in its combination with metals.*

1. *Methods in the dry way.*

a. In all sulphides which lose no sulphur by the action of heat.

Mix a weighed quantity of the pulverised substance with three parts of anhydrous carbonate of soda and four parts of nitrate of potassa, with the aid of a rounded glass rod, wipe the particles of the mixture which adhere to the rod, carefully off against some carbonate of soda, and add this to the mixture. Heat the latter in a platinum crucible—or also in one of porcelain, which, however, is somewhat affected by the process—at a gradually increased temperature to fusion, keep it in that state for some time, let it cool, heat the residue with water, filter, and determine in the filtrate, which contains the whole of the sulphur or alkaline sulphate, the sulphuric acid as directed in § 105. The metal, metallic oxide, or carbonate, which remains undissolved, is determined, according to circumstances, either by direct weighing, or in some other appropriate way.

b. In metallic sulphides which lose sulphur by the action of heat.

Mix the finely pulverised compound with four parts of carbonate of soda, eight parts of nitrate of potassa, and sixteen parts of pure and perfectly dry chloride of sodium, and treat the mixture as in *a*. Or, mix the very finely triturated substance with three parts of pure carbonate of soda and three parts of pure chlorate of potassa, put the mixture into a tube of difficultly fusible glass, closed at the posterior end, fill the anterior part of this tube with carbonate of soda mixed with a little chlorate of potassa, and heat the tube in a combustion furnace in the same way as in an elementary analysis. Treat the ignited saline mass as in *a*. The solution will, of course, contain silicic acid from the glass. (*Kemp.*)

c. In sulphosalts of more complex composition (after *Berzelius* and *H. Rose*).

Use the apparatus illustrated by Fig. 49, or an apparatus of similar construction.

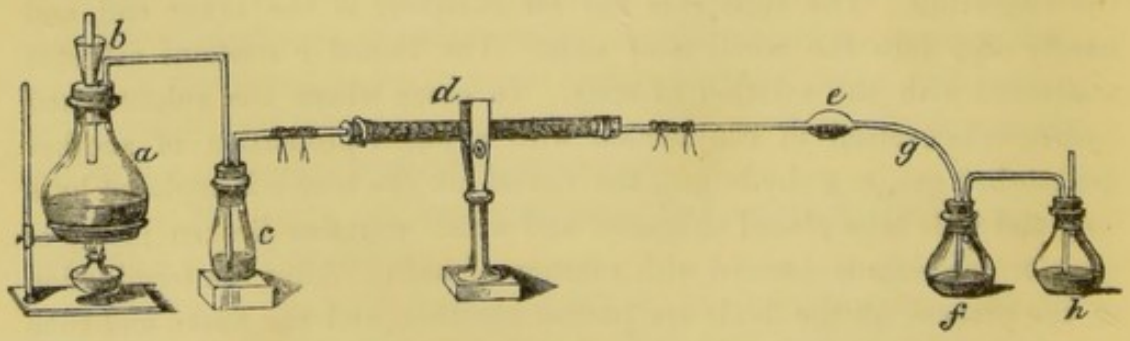


Fig. 49.

a is a flask from which chlorine is evolved in a slow stream; *b* serves to convey into *a* additional portions of hydrochloric acid; *c* contains con-

centrated sulphuric acid; *d* chloride of calcium—both intended for the drying of the chlorine evolved; *e* is a bulb-tube intended to receive the substance to be analysed; this tube dips to near the surface of the water in *f* (in presence of antimony, a solution of tartaric acid in dilute hydrochloric acid is substituted for the water in *f*); the flask *f* is connected with *h*, the connecting tube reaching down to the bottom of the fluid in the latter; the chlorine issuing from *h* is conducted into milk of lime, or into alcohol, or out of the window.

When the apparatus is arranged, the sulphide to be examined is weighed in a narrow glass tube, closed at one end, and subsequently cautiously transferred from this tube to the bulb *e*, in the manner illustrated by Fig. 50, to prevent any portion of the substance getting into the ends of the bulb-tube.

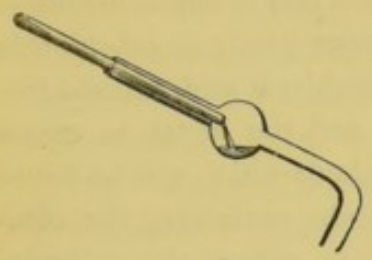


Fig. 50.

When the apparatus is filled with chlorine, *e* is connected with *d* by means of a vulcanized india-rubber tube, and the chlorine is allowed to act on the sulphide, at first without the aid of heat. When no further alteration is observed, a very gentle heat is applied to the bulb, care being taken also to keep the tube *g* warm, securing that tube thus from being stopped up by the sublimed volatile metallic chloride. The sulphide is completely decomposed by the chlorine, the metals being converted into chlorides, which partly remain in the bulb, partly—(viz. the volatile ones, as chloride of antimony, chloride of arsenic, chloride of mercury)—pass over into the receiver; the sulphur combines with the chlorine to form chloride of sulphur, which passes over into the flask *f*, where, coming into contact with water, it decomposes with the latter, forming hydrochloric acid, and hyposulphurous acid, with separation of sulphur. The hyposulphurous acid decomposes again into sulphur and sulphurous acid, which latter is finally, by the action of the chlorine water in *f*, converted into sulphuric acid. The final result of the decomposition is consequently sulphuric acid, and a greater or less amount of sulphur. The operation is concluded when no more products of distillation—with the exception perhaps of sesquichloride of iron the complete expulsion of which need not be awaited—pass over from the bulb. Heat is then applied to *e*, proceeding from the bulb towards the bend, so as to force all the chloride of sulphur which may remain in this part to pass over into *f*.

The apparatus is still left together a short time, after which the tube *e* is cut off under the bend at *g*, and the separated end, which contains a portion of the volatile chlorides, is closed by inverting over it a glass-tube closed at one end, and moistened inside. The whole is now allowed to stand twenty-four hours, to let the volatile chlorides absorb moisture, and

dissolve in water without heat; the metallic chlorides in the tube are then dissolved in dilute hydrochloric acid, the tube is rinsed, and the solution added to the contents of the flasks *f* and *h*; a very gentle heat is now applied until the free chlorine is expelled, and the fluid in them allowed to stand until the sulphur has solidified. The sulphur is filtered off on a weighed filter, washed, dried, and weighed. The filtrate is precipitated with chloride of barium (§ 105), by which operation the amount of that portion of the sulphur is determined which had been converted into sulphuric acid. The fluid filtered off from the sulphate of baryta contains, besides the excess of chloride of barium added, also the volatile metallic chlorides; which latter are finally determined in it by the proper methods which will be found in Section V.

The chloride remaining in the bulb-tube is either at once weighed as such (chloride of silver, chloride of lead), or when this is impracticable—as in the case of copper, for instance, which remains partly as subchloride partly as chloride—it is dissolved in water, hydrochloric acid, nitrohydrochloric acid, or some other appropriate solvent, and the metal or metals in the solution are determined by the proper methods which will be found in Section V. To be enabled to weigh the bulb-tube containing the chloride of silver or chloride of lead, it is advisable to reduce the chlorides by hydrogen gas, and to dissolve the metals then in nitric acid.

2. *Methods in the humid way.*

*a. In all solid metallic sulphides, with the exception of the sulphides of lead, barium, strontium, and calcium.**

a. Weigh the finely pulverised sulphide in a small glass tube closed at one end, and place the tube into a tolerably capacious flask with a glass stopper, and which contains red fuming nitric acid (perfectly free from sulphuric acid) in more than sufficient quantity to effect the decomposition of the sulphide. Immediately after having placed in the tube, close the flask firmly. When the action, which is very impetuous at first, has somewhat relaxed, shake the flask a little; when the shaking of the flask ceases to cause renewed reaction, and the fumes in the flask have condensed, take off the stopper, rinse this with a little nitric acid, letting the rinsings run into the flask, and then heat the latter gently.

aa. The whole of the sulphur has been oxidised, the fluid is perfectly clear.

Dilute with much water, and determine the sulphuric acid formed, as directed in § 105. (Do not neglect to wash the precipitate thoroughly with hot water, and to ascertain, after weighing, whether the precipitate is absolutely insoluble in dilute hydrochloric acid.) Separate the bases in

* The analysis of sulphide of lead has been given already in § 92, 6; the other three may be analysed in a similar manner; it is preferable, however, to decompose them in the dry way.

the filtrate from the salt of baryta added in excess, by the proper methods which will be found in Section V.

bb. Undissolved sulphur floats in the fluid.

Add chlorate of potassa in small portions, or strong hydrochloric acid, and digest some time in a water-bath. This process will often succeed in dissolving the whole of the sulphur. Should this not be the case, and should the separated sulphur appear of a pure yellow color, dilute with water, collect the sulphur on a weighed filter, wash carefully, dry, and weigh. After weighing, ignite the whole, or a portion of it, to ascertain whether it is perfectly pure. If a fixed residue remains (consisting commonly of quartz, &c.) deduct its weight from that of the impure sulphur. In the filtered fluid determine the sulphuric acid as in *aa.*, calculate the sulphur in it, and add the amount to that of the separated sulphur.

In the presence of bismuth, the addition of chlorate of potassa or of hydrochloric acid is not advisable, as the presence of chlorine interferes with the determination of bismuth.

β. Mix the finely pulverised metallic sulphide by shaking in a dry flask with chlorate of potassa (free from sulphuric acid), and add concentrated hydrochloric acid in small portions. Cover the vessel with a watch-glass, or with an inverted small flask. When the whole of the chlorate of potassa is decomposed, heat gently on the water-bath, until the fluid smells no longer of chlorine. Proceed now as directed in *a. aa.* or *bb*, according to whether the sulphur is completely dissolved or not. In the latter case you must immediately dilute and filter. The oxidation of the sulphur may be effected also by heating with nitric acid and chlorate of potassa.

γ. Strong nitrohydrochloric acid is also often used instead of the oxidising agents named in *α.* and *β.*; however, with this the complete conversion of the sulphur into sulphuric acid succeeds more rarely.

b. In dissolved sulphides of the alkalies and alkaline earths.

(Sulphides containing an admixture of hyposulphites or sulphates, are analysed as directed in § 136.)

a. The sulphides contain no excess of sulphur.

aa. Dilute the solution so much that the fluid contains only about 0·04 per cent of sulphur, and proceed exactly as directed in § 116, I. *a.* (KS+I=KI+S.)

Should the solution contain, besides the sulphide, a caustic alkali, the dilute fluid must be slightly acidified, before proceeding with the operation; if it contains an alkaline carbonate, chloride of barium may be added, instead of a free acid (*Filhol*).

bb. Mix the solution with an excess of a solution of arsenious acid in

hydrochloric acid, supersaturated with ammonia, or of a solution of chloride of copper, superatured with ammonia, add hydrochloric acid, and then proceed as directed in I. *b*.

β. The sulphides contain an excess of sulphur.

Decompose the sulphide with hydrochloric acid in the apparatus described in I. *c*, and proceed as there directed. When the whole of the sulphuretted hydrogen gas has been expelled, and the separated sulphur has subsided, filter through a tared filter, dry and weigh. The chlorides of the metals are found in the filtrate.

THIRD GROUP.

NITRIC ACID.—CHLORIC ACID.

§ 117.

1. NITRIC ACID.

I. *Determination.*

Free nitric acid in a solution containing no other acid is determined most simply by analysis by measure, neutralising it with a dilute solution of soda of known strength (compare the special part, Section Acidimetry). The following method also effects the same purpose: mix the solution with baryta-water, until the reaction is just alkaline, evaporate the solution in the air slowly, nearly to dryness, dilute the residue with water, filter, wash the carbonate of baryta formed by the action of the carbonic acid of the atmosphere upon the excess of the baryta-water, add the washings to the filtrate, and determine in the latter the baryta as directed in § 79. Calculate for every equivalent of baryta found, an equivalent of nitric acid. The correctness of the results depends entirely upon the accuracy of the execution of the analytical process. Avoid the use of a large excess of baryta-water, and take care not to filter the evaporated fluid before its alkaline reaction has completely disappeared.

II. *Separation of nitric acid from the bases, and its determination in a state of combination.*

a. In all nitrates, according to *Pelouze.*

Add a weighed quantity of the nitrate to an excess of a solution of protochloride of iron in hydrochloric acid. A portion of the protochloride corresponding to the amount of the nitric acid present, is hereby converted into sesquichloride. By determining now the quantity of protochloride remaining (as directed in § 89, 2), you learn from this the quantity which has been oxidised, and thus also the amount of the nitric acid. $6\,FeCl + KO, NO_5 + 4\,HCl = 4\,HO + KCl + NO_2 + 3\,Fe_2Cl_3$. 168 of iron, con-

verted thus from the state of protochloride to that of sesquichloride, correspond accordingly to 54 of nitric acid.*

The process is best conducted as follows: Dissolve 2 grammes of pianoforte wire in from 80 to 100 grammes of pure hydrochloric acid, in a flask holding about 150 c. c., and closed with a cork into which a glass tube is fitted; promote the solution by the application of heat. When the wire is dissolved, add 1·2 grm. of the nitrate of potassa or an equivalent quantity of another nitrate, to be analysed, replace the cork, and heat to boiling. After from five to six minutes, pour the fluid, which has again become clear, into a capacious flask, dilute largely with water, and proceed as directed in § 89,2. Assuming you find 0·2 iron remaining in the state of protoxide, you make your calcuation as follows: (2·0−0·2=1·8). 168 : 54 :: 1·8 : x.−x=0·578, *i. e.* in the 1·2 grm. of nitrate of potassa are contained 0·578 of nitric acid; or 2 : 1·2 :: 1·8 : x. −x=1·08, *i. e.* in the 1·2 grm. of impure nitre are contained 1·08 grm. of pure nitrate of potassa.

Determine the base in another weighed portion by the proper method. If the analysed salt was pure and anhydrous, the quantity of the acid calculated from the loss must be equal to that found by the direct analysis.

b. In salts with alkaline base, according to *J. Stein.*

Mix the compound with three times its weight of arsenious acid, dissolve the mixture in concentrated hydrochloric acid, evaporate to dryness, dissolve the residue in water, supersaturate the solution with ammonia, precipitate with a mixture of chloride of ammonium and sulphate of magnesia, and determine the precipitated arseniate of ammonia and magnesia as directed in § 102, 2. One equivalent of arsenic acid obtained corresponds, according to *Stein*, exactly to one equivalent of nitric acid.

c. In all anhydrous nitrates with fixed base.

Mix the triturated compound with from two to three parts of perfectly anhydrous biborate of soda, put the mixture into a platinum crucible, weigh this with its contents, heat very gradually, until the mass is in a state of calm fusion, cool, and weigh again. The diminution of weight gives the quantity of the nitric acid originally present. The results are accurate. (*Schaffgottsch, Poggend.* Annal. 57, 260.)

d. In hydrated salts.

Determine in one portion the bases, in another the water and the acid (the latter from the volume of the nitrogen gas), by the method of organic elementary analysis (§ 153). If you have not the requisite quantity of

* *Pelouze* found that it required on an average 1·216 grm. of nitrate of potassa, to oxidise 2 grms. of pianoforte wire, dissolved in from 80 to 100 grms. of hydrochloric acid. According to the above formula, it would have required 1·200 grm., assuming the pianoforte wire to contain 99·7 per cent of iron.

mercury, determine simply the water and the base, and calculate the nitric acid from the loss. If you propose to determine the water, and the nitrogen, you must expel the air from the combustion tube with carbonate of lead heated to incipient decomposition, instead of with bicarbonate of soda, as directed in § 153.

e. In soluble salts whose bases are completely precipitated by baryta, sulphide of barium, or carbonate of baryta.

Mix the solution with baryta water, or, as the case may be, sulphide of barium, until the fluid is alkaline; determine the base in the precipitate by the proper method, evaporate the filtrate to dryness, treat the residue with water, and proceed with the solution of nitrate of baryta obtained (which must no longer show alkaline reaction), as directed in I. *a*. If you have used sulphide of barium as precipitant, treat the evaporated mass as directed in II. *f*. as the excess of that agent changes, upon evaporation in the air, into insoluble sulphate and hyposulphite of baryta. If the bases are such as are precipitated completely by carbonate of baryta, the analysis is still more simple, since you need in that case only filter, and determine in the filtrate the dissolved nitrate of baryta.

f. In the salts of baryta, strontia, and lime.

Mix the solution with sulphuric acid in the least possible excess, and in the case of the strontia and lime salts, add alcohol, to make the separation of the sulphates more complete. Drop baryta-water into the filtrate, until the reaction is feebly alkaline; evaporate the mixture without filtering it previously, on the water-bath to dryness, heat the residue with water (which must not thereby acquire an alkaline reaction), filter, wash the residue with boiling water, until the filtrate is no longer rendered turbid by sulphuric acid, and treat the solution of nitrate of baryta obtained, as in I.

g. In soluble salts of the fifth and sixth groups.

Mix the highly dilute solution in a stoppered flask with strong sulphuretted hydrogen water in the least possible excess,* allow it to deposit, filter, and treat the filtrate as in II. *f*. (The sulphide of barium formed upon the saturation of the filtrate with baryta-water absorbs oxygen upon the evaporation of the mixture in the air, and is thereby converted into insoluble sulphate and hyposulphite of baryta.)

§ 118.

2. CHLORIC ACID.

I. *Determination.*

Free chloric acid in aqueous solution may be determined by converting

* The best way to hit the exact point, is to add the sulphuretted hydrogen water in small portions, and to shake the flask after every fresh addition.

it into hydrochloric acid by the agency of sulphuretted hydrogen, and determining the amount of the acid formed, as directed in § 137, or by saturating it with solution of soda, evaporating the fluid, and treating residue as directed in II. *a*.

II. *Separation of chloric acid from the bases, and its determination in a state of combination.*

a. *Bunsen's* method (Ann. der Chem. und. Pharm. 86, 282).

When hot hydrochloric acid is made to act upon chlorates, the latter are reduced; as this reduction is not attended with separation of oxygen the following decompositions may take place :—

$$\begin{array}{llllllllll} ClO_5 & \left\{\begin{array}{l}ClO\\ ClO_3\\ HO\end{array}\right. & ClO_5 & \left\{\begin{array}{l}3\ ClO\\ 2\ HO\end{array}\right. & ClO_5 & \left\{\begin{array}{l}2\ ClO\\ 2\ Cl\\ 3\ HO\end{array}\right. & ClO_5 & \left\{\begin{array}{l}ClO\\ 4\ Cl\\ 4\ HO\end{array}\right. & ClO_5 & \left\{\begin{array}{l}6\ Cl\\ 5\ HO\end{array}\right. \\ HCl & & 2\ HCl & & 3\ HCl & & 4\ HCl & & 5\ HCl & \end{array}$$

Which of these products of decomposition may actually be formed, whether all, or only certain of them, cannot be foreseen. But no matter which of them may be formed, they all of them agree in this, that when in contact with solution of iodide of potassium, they liberate for every equivalent of chloric acid in the chlorate, six equivalents of iodine. 9516 of iodine liberated correspond accordingly to 943·28 of chloric acid. The analytical process is conducted exactly as described in the determination of chromic acid (compare § 104, *d*. *β*.).

b. The bases are appropriately determined in a separate portion by converting the chlorate into chloride, either by very cautious ignition, or by heating with hydrochloric acid.

Appendix: *Determination of chlorous and hypochlorous acids in their salts* (according to *Bunsen*).

Mix the solution of the salt with solution of iodide of potassium, add hydrochloric acid to slightly acid reaction, and determine the quantity of iodine separated, as directed in § 114, Appendix.

The decompositions which ensue in the process, and whereon the calculations are to be based, are as follow:

$$ClO + HCl + 2\ KI = 2\ KCl + HO + 2\ I$$

and

$$ClO_3 + 3\ HCl + 4\ KI = 4\ KCl + 3\ HO + 4\ I.$$

Accordingly two equivalents of iodine=3172 correspond to one equivalent of hypochlorous acid=543·28; and four equivalents of iodine=6344 to one equivalent of chlorous acid=743·28.

SECTION V.

SEPARATION OF BODIES.

§ 119.

HAVING thus disposed of the methods which serve to determine the bases and acids in *simple* compounds, we will now proceed to discuss the various processes which are applied to effect the analysis of *complex* compounds or mixtures, and the determination of their several constituents,—in other words, to effect the separation of bodies from one another.

This end may be attained by two different ways, namely, *a.* by the way of *direct* analysis; and *b.* by that of *indirect* analysis.

By *direct* analysis, we understand the *actual* separation of the several individual acids, or bases present in a compound, or mixture. Thus we separate potassa from soda by means of bichloride of platinum; copper from bismuth by means of cyanide of potassium; arsenic from iron by means of sulphuretted hydrogen; iodine from chlorine by means of nitrate of protoxide of palladium; phosphoric acid from sulphuric acid by means of baryta; carbon from nitrate of potassa by means of water, &c., &c. The principle of the methods of direct analysis is accordingly to convert one of the two substances which it is intended to separate, into an insoluble form, under circumstances which cause the solution of the other, or *vice versâ*. This mode of analysis is preferable to the *indirect* way, and therefore is had recourse to wherever the circumstances of the case will permit.

We term an analysis *indirect*, when it does not effect the *actual* separation of the substances which we wish to determine, but causes certain changes enabling us to infer, or calculate the respective quantities of the individual bases, or acids present in the analysed compound or mixture. Thus, for instance, the respective quantities of potassa and soda jointly present in a compound, or mixture, may be estimated by converting these two bases into sulphates, weighing the latter, and determining the proportion of sulphuric acid contained in them (§ 120, 3); thus, sesquioxide of iron may be estimated in presence of alumina, by weighing the mixed body, then determining the iron by analysis by measure, and calculating the alumina from the difference, &c.

Indirect analysis, though applicable in an exceedingly great number of cases, is generally had recourse to only to supply the deficiency of good methods of *actual* separation. It is impossible to point out every *special* case in which indirect analysis may be preferable to direct analysis; I have, therefore, confined myself to the indication of the more frequently occurring instances. For the calculations of indirect analyses, I generally

refer to Subdivision B. (CALCULATION OF THE RESULTS). In certain instances, however, I have appended the mode of calculation to the description of the process.

For the sake of greater perspicuity and simplicity, I have retained our former subdivision into groups, and, as far as practicable, systematically arranged, first, the *general* separation of all the substances belonging to one group from those of the preceding group, or groups; secondly, the separation of *individual* substances of one group from *all* or from *individual* substances of the preceding group, or groups; and thirdly and finally, the separation of substances of one and the same group from one another. I think I need scarcely observe that the general methods which serve to separate the whole of the substances of one group from those of another group, are equally applicable to the separation of every individual substance of this group from one or several substances of the other group. I beg, moreover, to remark that I do not intend to assert that the *special* methods given subsequently are preferable to the *general* methods, or that no other methods besides those which I have selected for description in this work, might not be applied with equal, or even better success in special cases. A wide field is left open here to individual sagacity.

In my selection of general and special methods from the great number that have been proposed, I have been guided entirely by experience, and I have given the preference invariably to those which yield the most accurate results. In cases where two equally accurate methods presented themselves, I have either given both, or selected the more simple of the two. I have, moreover, endeavored to point out, as far as possible, the particular circumstances under which either the one or the other of several methods deserve the preference. Methods which experience has shown to be defective, or fallacious have been altogether omitted.

The methods given in this work are based in general upon the supposition that the base, or acid to be separated exists in the free state, or in the form of a salt soluble in water. Wherever this is not the case, special mention is made of the circumstance.

Where the precision of an analytical method has been established already, in Section IV., no further allusion is made to the subject here. Paragraphs of former Sections deserving particular attention are referred to in parentheses.

The extension of chemical science introduces almost every day new analytical methods of every kind, which are, right or wrong, preferred to the older methods; the present time may therefore be looked upon in this, as in many other respects, as a period of transition, in which the new strives with more than usual efforts to overcome and to supplant the old. I make this remark here, to show the impossibility of adding always to the description of a method an opinion of its usefulness and

accuracy, and also to point out how important a proper generalisation is in such periods. To assist the student I have in this Section arranged the various analytical methods upon the basis of their scientific principles, firmly persuaded that this will greatly tend to facilitate the study of the methods, and will lead to essays to apply known and approved analytical methods to other bodies besides those to which they are already applied, or to discover new principles where experience has proved the old ones fallacious, and the methods based on them defective. To enable the student, on the other hand, to find readily the methods adapted to effect the separation of bodies, I have, wherever I deemed it necessary, placed at the head of the several paragraphs an index, which I think will answer the purpose of a guide in this respect.

I conclude this introduction to Section V. with the important caution to the student, never to look upon a separation as successfully effected, if he has not convinced himself, by the proper tests, that the separated substances are actually and truly free from the least traces of the body or bodies from which they have been separated.

I. SEPARATION OF THE BASES FROM ONE ANOTHER.

FIRST GROUP.

POTASSA—SODA—AMMONIA.

§ 120.

Index: Potassa from soda: 1, *a.*; 3;—from ammonia: 2.
Soda from potassa: 1, *a.*; 3;—from ammonia: 1, *b.*; 2.
Ammonia from potassa: 2;—from soda: 1, *b.*; 2.

1. *Methods based upon the different degrees of solubility in alcohol, of the double chlorides of the alkali metals with bichloride of platinum.*

a. POTASSA FROM SODA.

It is an indispensable condition in this method that the two alkalies should exist in the form of chlorides. If, therefore, they are present in any other form, they must be first converted into chlorides, which, in most cases, may be done by evaporation with hydrochloric acid in excess; but in presence of sulphuric acid, phosphoric acid, and boracic acid, this simple way will not suffice. For the methods of separating the alkali from the two latter acids, and converting them into chlorides, see §§ 106 and 107. The presence of sulphuric acid being a circumstance of rather frequent occurrence, the way of meeting this contingency is given below.

Determine the total quantity of the chloride of sodium and chloride of

potassium,* dissolve them in a small portion of water, add an aqueous solution of bichloride of platinum in excess, evaporate on the water-bath nearly to dryness, treat the residue with alcohol of from 76—80 per cent., cover the beaker-glass or the dish with a glass plate, and let the contents stand a few hours, with occasional stirring. If the fluid above the precipitate appears of a deep yellow color, this is a proof that a sufficient quantity of bichloride of platinum has been used; if not, another portion of it must be added. When the sodio-bichloride of platinum has completely dissolved, and the potassio-bichloride of platinum at the bottom of the glass or dish appears as a heavy yellow powder, with no crystalline scales of larger size discernible in it, filter the fluid from the precipitate, and treat the latter as directed in § 76. The quantity of the soda is usually estimated by subtracting from the united weight of the chloride of sodium and chloride of potassium the weight of the latter, deduced from that of the potassio-bichloride of platinum.

To make quite sure that the potassa has completely separated, it is advisable to add to the filtrate some more bichloride of platinum, to evaporate in the water-bath to dryness, and treat the residue in the manner just described. Should this operation again leave an undissolved sediment of potassio-bichloride of platinum, let the separated particles quietly subside, decant the yellow fluid off from the trifling precipitate, wash the latter repeatedly with small quantities of spirits of wine by decantation, then transfer it to the filter which contains the principal precipitate, and wash the latter, if necessary, again once or twice with small quantities of spirits of wine.

I prefer this way to ensure the complete separation of the potassa, to the usual process of evaporating the filtrate to dryness, igniting the residue with addition of some oxalic acid, treating with water, and determining the chloride of sodium in the solution obtained; since, after all, the estimation of the soda here is only *apparently* direct: if the chloride of potassium has not completely separated, the portion still remaining in the filtrate will, of course, be obtained now with the chloride of sodium. The latter method can therefore only afford a control, whether or not the operation has been attended with loss of substance.

Should the solution contain sulphuric acid, it may be in presence of chlorine, or of some volatile acid, convert the alkalies first into neutral sulphates (§§ 76 and 77), and weigh them in that form. Dissolve them in a little water, and add an alcoholic solution of chloride of stron-

* Never weigh the chlorides of the alkali metals before you have convinced yourself of their purity by dissolving them in water, which should give a clear solution, and testing this solution with ammonia and carbonate of ammonia, which must throw down no precipitate. It may be thought, perhaps, that a matter so simple need not be mentioned here; still I have found that neglect in this respect is by no means uncommon.

tium, taking care to let the latter but little predominate.—The quantity of spirits of wine in the fluid must be kept within limits which will not permit the separation of chloride of sodium, or chloride of potassium.—Allow it to deposit, filter, and wash the sulphate of strontia (which may be weighed, as a control of the analysis—compare § 120, 3) with weak spirits of wine as long as the washing leaves a residue upon evaporation on a watch-glass; evaporate the filtrate nearly to dryness, adding in the last stage bichloride of platinum in excess, and proceed as directed in the preceding part. The minute portion of chloride of strontium added in excess, dissolves, either in that form, or as strontio-bichloride of platinum, together with the sodio-bichloride of platinum, in spirits of wine.

Instead of this, the following method may also be employed. Dissolve the weighed sulphates of the alkalies in water, add solution of acetate of baryta (free from chloride of barium), in the least possible excess, allow it to deposit, filter, evaporate the filtrate to dryness, ignite the residue, treat it with water, saturate cautiously with hydrochloric acid, and treat the solution of the chlorides of the alkali metals, as directed above. Instead of acetate of baryta, you may also use acetate of lead, removing the excess of lead by sulphuretted hydrogen and evaporating the filtrate with hydrochloric acid to dryness (*L. Smith*). Or you may mix the sulphates with chloride of ammonium in powder, in a crucible, ignite, add a few drops of water and again some chloride of ammonium, ignite once more, and repeat this until the weight remains constant (*H. Rose*).

Repeated experiments have shown that the process of separating potassa and soda, as described above, gives always a little less potassa than is really present. If the process is properly conducted, the loss of potassa amounts to about one per cent. I have found that the loss is usually greater where the concentrated solution of the metallic chlorides is mixed with bichloride of platinum, and then with a rather large quantity of alcohol.

b. AMMONIA FROM SODA.

The process is conducted exactly as in *a*. See also § 78, 2.

2. *Methods based upon the volatility of ammonia and its salts.*

AMMONIA FROM SODA AND POTASSA.

a. The salts of the alkalies to be separated contain the same volatile acid, and admit of the total expulsion of their water by drying at 212°, *without losing ammonia* (*e. g.* the metallic chlorides).

Weigh the total mass of the salts in a platinum crucible, and heat with the lid on, gently at first, but ultimately for some time to faint redness; let the mass cool, and weigh. The decrease of weight gives the quantity of the ammonia salt. If the acid present is sulphuric acid, you must, in the first place, take care to heat very gradually, as otherwise you will suffer loss from the decrepitation of the sulphate of ammonia; and in the

second place, bear in mind that part of the sulphuric acid of the sulphate of ammonia remains with the sulphates of the fixed alkalies, and that you must accordingly convert them into neutral salts, by ignition in an atmosphere of carbonate of ammonia, before proceeding to determine their weight (compare §§ 76 and 77). Chloride of ammonium cannot be separated in this manner from sulphates of the fixed alkalies, as it converts them, upon ignition, partly or totally into chlorides.

b. Some one or other of the conditions given in a. is not fulfilled.

If it is impracticable to alter the circumstances by simple means so as to make the method *a.* applicable, the fixed alkalies and the ammonia must be estimated separately in different portions of the compound under examination. The portion in which it is intended to determine the soda and potassa, is ignited, until the ammonia is completely expelled. The fixed alkalies are converted, according to circumstances, into chlorides or sulphates, and treated as directed § 120, 1. The ammonia is estimated in another portion, in the manner directed § 78, 3.

3. *Indirect methods.*

Of course, of these a great many may be devised ; but the following is generally employed.

Potassa from soda.

Both alkalies are converted into neutral sulphates (§§ 76 and 77), and weighed in that form ; the amount of sulphuric acid in them is estimated (§ 105) ; and the respective quantities of the soda and potassa are calculated from these data (see below "Calculation of the Analyses," § 168).

SECOND GROUP.

BARYTA—STRONTIA—LIME—MAGNESIA.

I. Separation of the oxides of the second group from those of the first.

§ 121.

Index : Baryta from potassa and soda: A. 1, B. 1 ;—from ammonia: A. 2.
Strontia from potassa and soda : A. 1, B. 2 ;—from ammonia : A. 2.
Lime from potassa and soda : A. 1, B. 3 ;—from ammonia : A. 2.
Magnesia from potassa and soda : A. 1, B. 4 ;—from ammonia : A. 2.

A. *General method.*

1. The whole of the alkaline earths from potassa and soda.

Principle on which the method is based : Carbonate of ammonia precipitates from a solution containing chloride of ammonium, only baryta, strontia, and lime ; and chloride of magnesium is decomposed by oxide of mercury.

Mix the solution, in which the bases are assumed to be contained in the form of chlorides, with a sufficient quantity of chloride of ammonium to prevent the precipitation of the magnesia by ammonia; add some ammonia, then carbonate of ammonia in slight excess, let the mixture stand covered for twelve hours in a moderately warm place, filter, and wash the precipitate with water to which a few drops of ammonia have been added.

The precipitate, which contains the *baryta, strontia,* and *lime,* is treated as directed in § 122; the filtrate contains the *magnesia* and the *alkalies,* and, besides these, exceedingly minute traces of lime, and somewhat more considerable traces of baryta, as the carbonates of these two earths are not absolutely insoluble in a fluid containing chloride of ammonium. In ordinary analyses these minute admixtures may be disregarded; but in cases where a higher degree of accuracy is required, they must be removed. To accomplish this, add to the filtrate three or four drops (but not much more) of dilute sulphuric acid, then a few drops of oxalate of ammonia, and let the fluid stand again for twelve hours at a gentle heat. If a precipitate forms, collect this on a small filter, wash it, and treat it on the filter with some dilute hydrochloric acid, which dissolves the oxalate of lime, and leaves the sulphate of baryta undissolved.

Evaporate the filtrate containing the *magnesia* and the alkalies according to circumstances, either at once or after previous removal of the traces of lime and baryta, to dryness, and remove the ammonia salts by gentle ignition in a covered crucible, or in a covered small dish of platinum or porcelain.* Heat the residue with some water (in which it dissolves with the exception of a little magnesia, which separates), add some most minutely divided oxide of mercury, diffused in water, and proceed exactly as directed § 82, 3, *b*.

In the fluid filtered from the magnesia, determine the alkalies as directed § 120. This method of *Berzelius,* to separate magnesia and the alkalies, gives good results. Do not make the labor of the process more difficult than need be, by adding more oxide of mercury than is necessary; but for precaution's sake, always test the solution of the chlorides of the alkali metals for magnesia.

2. THE WHOLE OF THE ALKALINE EARTH FROM AMMONIA.—The same principle and the same process, as in the separation of potassa and soda from ammonia (see § 120).

B. *Special methods.*

SINGLE ALKALINE EARTHS FROM POTASSA AND SODA.

1. BARYTA FROM POTASSA AND SODA.

* This operation effects also the removal of the small quantity of sulphuric acid added to precipitate the traces of baryta, as sulphates of the alkalies are converted into chlorides of the alkali metals upon ignition in presence of a large proportion of chloride of ammonium.

Precipitate the baryta with dilute sulphuric acid (§ 79, 1, *a*), evaporate the filtrate to dryness, and ignite the residue, with addition of carbonate of ammonia (§ 76, 1—77, 4). Take care to add a sufficient quantity of sulphuric acid to convert the alkalies also completely into sulphates.

This method is, on account of its greater accuracy, preferable to the one in A., in cases where the baryta has to be separated only from one of the two fixed alkalies; but if both alkalies are present, the other method is more convenient, since the alkalies are obtained in it as chlorides.

2. Strontia from potassa and soda.

Strontia may be separated from the alkalies, like baryta, by means of sulphuric acid; but this method (precipitation of the strontia as sulphate) is not preferable to the one in A., is cases where the choice is permitted (compare § 80).

3. Lime from potassa and soda.

Precipitate the lime with oxalate of ammonia (§ 81, 2, *b*. *a*.), filter, evaporate the filtrate to dryness, and determine the alkalies in the ignited residue. In determining the alkalies, dissolve the residue freed by ignition from the ammonia salts, in water, and filter the solution from the undissolved sediment; acidulate the filtrate with hydrochloric acid or sulphuric acid, as the case may be, and then evaporate to dryness: since oxalate of ammonia partially decomposes chlorides of the alkali metals, upon ignition, and converts the bases into carbonates, except in presence of a large proportion of chloride of ammonium. The results are still more accurate than in A., except where oxalate of ammonia has been used, after the precipitation by carbonate of ammonia, to remove the minute traces of lime from the filtrate.

4. Magnesia from potassa and soda.

a. Methods based upon the sparing solubility of magnesia in water.

α. Make a solution of the bases, as neutral as possible, and free from ammonia salts (whether the acid is sulphuric acid, hydrochloric acid, or nitric acid, is indifferent), add baryta-water as long as a precipitate continues to form, heat to boiling, filter the fluid off from the precipitate, and wash the latter with boiling water. The precipitate contains the magnesia as hydrated oxide; the magnesia is determined either as directed in § 82, 1, *b*., or the precipitate is dissolved in hydrochloric acid, the baryta thrown down with sulphuric acid, and the magnesia as phosphate of magnesia and ammonia (82, 2). The alkalies which, according to circumstances, are in the solution as chlorides, nitrates, or caustic alkalies, are separated from the baryta as directed in A. or B. 1. *Liebig*, who was the first to employ this method, proposes crystallised sulphide of barium as precipitant. The method gives good results, but is a little tedious.

β. Precipitate the solution with a little pure milk of lime, boil, filter, and wash. Separate the lime and the magnesia in the precipitate, as directed

§ 122; the lime and the alkalies in the filtrate, as directed in A. or B. 3. This method is advantageously employed in cases where it is desirable to remove the magnesia from a fluid containing lime, and alkalies, which latter alone it is intended to determine.

b. Methods based upon the sparing solubility of carbonate of magnesia.

a. Convert into chlorides, ignite gently, dissolve in water, and boil with carbonate of silver diffused in water (prepared by precipitating nitrate of silver with carbonate of ammonia, and washing the precipitate), until the supernatant fluid shows strongly alkaline reaction. Filter off the fluid hot, remove the trace of the salt of silver which may have dissolved, with hydrochloric acid, filter, and determine the alkalies, as directed § 120. Treat the precipitate with warm hydrochloric acid, and throw down the magnesia as directed in § 82, 2 (*Sonnenschein*).*

β. Convert into nitrates, heat them gently in a platinum dish, add some water, then pure crystallised oxalic acid in excess, and evaporate. During the evaporation, nitric acid is evolved, and ultimately hydrate of oxalic acid sublimes on the sides of the dish. Decompose the oxalates by ignition, and separate the pure magnesia and the carbonate of magnesia from the carbonates of the alkalies, by boiling water (*Deville.*).†

c. Method based upon the precipitation of magnesia by phosphate of ammonia, or arseniate of ammonia.

Add to the solution containing magnesia, potassa, and soda, ammonia in excess, and some chloride of ammonium, should this not be present already; precipitate the magnesia with phosphate of ammonia (free from soda), added in slight excess. Filter, remove the free ammonia from the filtrate by evaporation, and then precipitate the phosphoric acid with acetate of lead as a combination of phosphate of lead and chloride of lead. Remove the excess of oxide of lead from the still hot fluid, with ammonia and carbonate of ammonia, filter, and determine the potassa and soda in the filtrate as directed §§ 76 and 77 (*O. L. Erdmann*,‡ *Heintz*‖). I cannot concede the preference to this method over the one of *Berzelius*, given in A. The following process is much more simple: precipitate the magnesia, instead of with phosphate of ammonia, with arseniate of ammonia, and estimate it as arseniate of magnesia and ammonia, as directed § 102. 2. Evaporate the filtrate to dryness, and heat the residue in a porcelain crucible. Should the mass not have contained sufficient chloride of ammonium, add some of the latter substance to the residue, and then ignite once more. As this operation effects the ready

* *Pogg.* Annal. 74, 313. *Liebig* and *Kopp's* Annual Report 1847 and 1848, 227.

† Journ. f. prakt. Chem. 1853. 60, 17.

‡ Journal f. prakt. Chem. 41, 89.

‖ *Pogg* 73, 119. *Liebig* and *Kopp's* Annual Report. 1847 and 1848, 226.

and complete volatilisation of the arsenic acid, the alkalies are left behind as pure chlorides. I need hardly mention that proper arrangements to secure the safe removal of the arsenical fumes are indispensable.

II. Separation of the oxides of the second group from each other.

§ 122.

Index: Baryta from strontia: B. 1;—from lime: B. 1 and 2;—from magnesia: A. B. 2.
Strontia from baryta: B. 1;—from lime: B. 4 and 5;—from magnesia: A.
Lime from baryta: B. 1 and 2;—from strontia: B. 4 and 5;—from magnesia: A. B. 3.
Magnesia from baryta: A. B. 2;—from strontia: A.;—from lime: A. B. 3.

A. *General Method.*

THE WHOLE OF THE ALKALINE EARTHS FROM EACH OTHER.

Proceed as in § 121, A. 1. The magnesia is precipitated from the filtrate with phosphate of soda. The precipitated carbonates of the baryta, strontia, and lime, are dissolved in hydrochloric acid, and the bases separated as directed in B. 1.

B. *Special Methods.*

1. *Methods based upon the insolubility of the silicofluoride of barium.*

BARYTA FROM STRONTIA AND FROM LIME.

Mix the neutral or slightly acid solution with hydrofluosilicic acid in excess, add a volume of spirits of wine, equal or somewhat inferior to that of the fluid (*H. Rose*), let the mixture stand twelve hours, filter the precipitate of *silicofluoride of barium* on a weighed filter, wash it with a mixture of equal parts of water and spirits of wine, until the washings cease to show even the least trace of acid reaction (but no longer), and dry it at 212°. Precipitate the strontia, or lime from the filtrate by dilute sulphuric acid (§ 80, 1, *a*, and § 81, 1). The results are satisfactory. For the properties of the silicofluoride of barium, see § 50. If both strontia and lime are present, the sulphates are weighed, converted into carbonates (§ 105, II. *b.*), and the two bases are then separated as directed in 4 or 5.

2. *Methods based upon the insolubility of sulphate of baryta.*

a. BARYTA FROM MAGNESIA.

Precipitate the baryta with sulphuric acid (§ 79, 1, *a.*), and the magnesia from the filtrate with phosphate of soda and ammonia (§ 82, 2).

b. Baryta from lime.

Mix the solution with hydrochloric acid, then with highly dilute sulphuric acid (1 part acid to 300 water), as long as a precipitate continues to form; allow it to deposit, and determine the sulphate of baryta as directed in § 79, 1, *a.* Add to the filtrate the washings concentrated previously by evaporation, neutralise the acid with ammonia, and precipitate the lime as oxalate (§ 81, 2, *b.* *a.*). The results are accurate.

3. *Methods based upon the insolubility of oxalate of lime in chloride of ammonium and in acetic acid.*

Lime from magnesia.

a. Mix the properly diluted solution with sufficient chloride of ammonium to prevent the formation of a precipitate by ammonia, which latter reagent is added in very slight excess; then add oxalate of ammonia as long as a precipitate continues to form, let the mixture stand twelve hours at a gentle heat, and then filter off the fluid from the oxalate of lime, which latter treat as directed § 81, 2, *b.* *a.* When you begin washing the precipitated oxalate of lime on the filter, remove the vessel with the filtrate, and replace it by an empty vessel to receive the washings; concentrate the latter subsequently by evaporation, adding, in the last stage of this process, some hydrochloric acid in excess; and then add the concentrated fluid to the filtrate, and precipitate the magnesia as directed § 82, 2.

b. In the case of lime and magnesia combined with phosphoric acid, dissolve in the least possible quantity of hydrochloric acid, add ammonia, until a permanent precipitate forms; redissolve this by addition of acetic acid, and precipitate from the solution the lime with oxalate of ammonia (§ 81, 2, *b.* *β.*); precipitate the magnesia from the filtrate as directed § 82, 2.

4. *Methods based upon the insolubility of nitrate of strontia in alcohol.*

Strontia from lime.

Treat the nitrates with absolute alcohol. Filter the fluid from the undissolved nitrate of strontia, wash the latter with alcohol, dissolve it in water, and determine it as sulphate of strontia (§ 80, 1). Precipitate the lime from the filtrate by sulphuric acid. The results are approximate. This method is applicable only where the proportion of lime is large, that of strontia small.

5. *Indirect method.*

Strontia and lime.

Determine both bases first as carbonates, then as sulphates (§§ 80, 81), and calculate the amount of both from the data found.

THIRD GROUP.

ALUMINA—SESQUIOXIDE OF CHROMIUM.

I. Separation of the oxides of the third group from the alkalies.

§ 123.

1. From ammonia.

a. Salts of alumina and of sesquioxide of chromium may be separated from salts of ammonia by ignition. However, in the case of alumina, this method is applicable only in the absence of chlorine (volatilisation of chloride of aluminium). The safest way, therefore, is to mix the compound, with carbonate of soda, previously to ignition.

b. Determine the ammonia by *Schlösing's* method (§ 78, 3). If the ammonia is expelled, instead of with milk of lime, with hydrate of potassa—of which a lump is laid on a tripod, close over the fluid, so that, in proportion as it absorbs moisture, it drips into the latter—alumina and sesquioxide of chromium may be determined without difficulty in presence of each other (as directed 2).

2. From potassa and soda.

a. Mix the solution with some chloride of ammonium; add ammonia to alkaline reaction, heat some time, and filter. Alumina and sesquioxide of chromium are precipitated as hydrates (§ 83, *a.*, and § 84, 1, *a.*); the filtrate contains the alkalies, which are then freed from the salt of ammonia formed, by evaporation to dryness, and ignition.

b. Alumina may be separated also from potassa and soda, by heating the nitrates of the three bases (see § 124, 1, A. 2).

II. Separation of the oxides of the third group from the alkaline earths.

§ 124.

Index: 1. *Alumina* from baryta: A. 1 and 2; B. 1 and 3;—from strontia: A. 1 and 2; B. 1 and 3;—from lime: A. 1 and 2; B. 1, 2, 3;—from magnesia: A. 1 and 2; B. 1 and 2.

2. *Sesquioxide of chromium* from the alkaline earths.

1. Separation of alumina from the alkaline earths.

A. *General methods.*

The whole of the alkaline earths from alumina.

1. *Method based upon the precipitation of alumina by ammonia, and upon its solubility in solution of soda.*

Mix the solution with chloride of ammonium, and add pure ammonia, (free from carbonic acid) to feeble predominance ; heat the fluid in a well-covered beaker for some time gently, filter from the precipitate (taking care to prevent the access of the carbonic acid of the atmosphere by keeping the funnel covered with a glass-plate), and wash rapidly with hot water. The solution contains the baryta, strontia, and lime, with the greater part of the magnesia, a small portion of the maguesia being with the hydrate of alumina, in combination. The precipitate often contains, notwithstanding every precaution used to avoid it, minute quantities of carbonates of baryta, strontia, and lime. Dissolve the hydrate of alumina in hydrochloric acid, by transferring the hydrate with a spatula as far as practicable into a platinum or porcelain dish, treating the filter with warm hydrochloric acid, to extract the last adhering particles of the hydrate, and employing the hydrochloric acid running off, to effect the solution of the precipitate in the dish ; add to the fluid pure solution of soda or potassa (compare § 128, B. 1, *a*, note), until the precipitate of hydrate of alumina which first forms, is redissolved, heat, filter off hot from the hydrate of magnesia which separates, wash the latter carefully with hot water, dissolve it in some hydrochloric acid, and add the solution to the filtrate of the first operation, which contains the larger portion of the magnesia. It will be seen that in this way the minute quantities of carbonates of bartya, strontia, and lime, which have precipitated with the hydrate of alumina, are restored to the bulk of these substances in that filtrate. The further separation of the alkaline earths is effected as directed § 122. The alumina is precipitated from the alkaline solution by strongly acidulating with hydrochloric acid, boiling with some chlorate of potassa (to destroy the traces of organic matters which the solution of soda or potassa has dissolved from the filter, and which interfere with the precipitation of the alumina) and then adding ammonia (§ 83, *a*).

2. *Method based upon the unequal decomposability of the nitrates at a moderate heat* (*Deville*).*

To make this method applicable, the bases must be present as pure nitrates. Evaporate to dryness in a covered platinum dish, and heat gradually, in the sand, or air-bath, to about from 390° to 480°, until a glass rod, moistened with ammonia, ceases to indicate further evolution of nitric acid fumes. You may also, without risk, continue to heat until nitrous acid vapors form. The residue consists of alumina, nitrates of baryta, strontia, and lime, nitrate and basic nitrate of magnesia.

Moisten the mass with a concentrated solution of nitrate of ammonia, and heat. Repeat this operation until no further evolution of ammonia is perceptible. (The basic nitrate of magnesia, insoluble in water, dissolves

* Journal f. prakt. Chem. 1853, 60, 9.

in nitrate of ammonia, with evolution of ammonia, as neutral nitrate of magnesia.) Add water, and let the mixture digest at a gentle heat.

If the nitrate of ammonia has liberated only imperceptible traces of ammonia, pour hot water into the dish, stir, and add a drop of dilute ammonia; this must cause no turbidity in the fluid; should the fluid become turbid, this proves that the heating of the nitrates has not been continued long enough; in which case you must again evaporate the contents of the dish, and heat once more.

The alumina remains undissolved in the form of a dense granular substance. Decant after digestion, and wash with boiling water; ignite strongly in the same vessel in which the separation has been effected, and weigh. Separate the alkaline earths as directed § 122. In the same way alumina may be separated also from potassa and soda.

B. *Special methods.*

SOME OF THE ALKALINE EARTHS FROM ALUMINA.

1. *Methods based upon the precipitation of alumina by ammonia.*

ALUMINA FROM LIME, BARYTA, STRONTIA.

The method A. 1, is modified as follows: mix the warm fluid with chloride of ammonium and ammonia (free from carbonic acid), place the vessel on a dish containing some solution of soda, milk of lime, or solution of ammonia, and invert a bell-glass over it; wait until the alumina has subsided. Decant the clear fluid now rapidly into another beaker-glass, treat the alumina with boiling water, stir, and replace the beaker under the bell-glass. Filter the decanted fluid. Repeat this operation three times. Now change the vessel under the funnel, pour some warm hydrochloric acid over the filter, wash it, heat the solution so obtained of the trifling contents of the filter to boiling, and precipitate the trace of alumina, which may chance to be present, with ammonia; filter the fluid, transfer also to the filter the main bulk of the hydrate of alumina, and wash with hot water. In this manner the adverse influence of the carbonic acid of the atmosphere may be entirely avoided. Or, precipitate as in A. 1, filter, wash the precipitate twice, or three times with hot water, then dissolve it in hydrochloric acid, heat the solution to boiling, reprecipitate with ammonia, allow it to deposit, filter, and add the filtrate, which now contains the trace of lime thrown down with alumina in the first precipitation, to the filtrate of the first operation, which contains the principal bulk of the lime. This latter modification, A. 1, is advantageously resorted to in cases where the quantity of alumina is small, that of lime large.

2. *Methods based upon the precipitation of alumina by bicarbonate of soda or carbonate of baryta.*

a. ALUMINA FROM MAGNESIA (and from small portions of LIME).

Add to the somewhat dilute, moderately acid solution, in a flask or beaker with a cover, a cold prepared solution of bicarbonate of potassa or

soda, as long as effervescence ensues and a precipitate continues to form; allow the fluid to stand twelve hours, then decant, filter (§ 31), and wash with water containing carbonic acid.* The precipitate is hydrate of alumina containing an admixture of alkali; the whole of the magnesia is in the solution. Dissolve in hydrochloric acid, and throw down the alumina with ammonia, after addition of chloride of ammonium, in the manner directed § 83, *a*. Precipitate the magnesia from the solution as basic phosphate of magnesia and ammonia (§ 82, 2). The results are accurate.

This method may be employed also to effect the joint separation of both lime and magnesia from alumina; but satisfactory results can only be expected if the quantity of lime is small. In cases of this kind the fluid must be largely diluted before the bicarbonate of soda is added, and the precipitation must be effected in a stoppered flask.

b. ALUMINA FROM MAGNESIA AND LIME.

Mix the slightly acid dilute fluid with well washed carbonate of baryta diffused in water in moderate excess, let the mixture stand in the cold twelve hours, then decant and filter (§ 31), and determine the alumina in the precipitate as directed § 124, *b*. 3; the magnesia and lime in the filtrate as directed in § 122.

3. *Methods based upon the insolubility of some salts of the alkaline earths.*

a. BARYTA AND STRONTIA FROM ALUMINA.

Precipitate the baryta and strontia with *sulphuric acid* (§§ 79 and 80); and throw down the alumina from the filtrate as directed § 83, *a*. To effect the separation of baryta from alumina, this method is preferable to any other.

b. LIME FROM ALUMINA.

Add ammonia to the solution, until a persistent precipitate forms, then acetic acid until this precipitate is redissolved; then some acetate of ammonia, and after this, *oxalate of ammonia* in slight excess (§ 81, 2, *b*. *β*.); allow the oxalate of lime to deposit in the cold, filter, and precipitate the alumina from the filtrate as directed § 83, *a*.

2. SEPARATION OF SESQUIOXIDE OF CHROMIUM FROM THE ALKALINE EARTHS.

The best way to effect the separation of sesquioxide of chromium from all the alkaline earths at the same time, is to convert the sesquioxide into chromic acid. For this purpose, the pulverised substance is mixed with two parts of pure *carbonate of soda* and two and half parts of *nitrate of potassa*, and the mixture heated in a porcelain crucible to fusion. On treating the fused mass with hot water, the chromium dissolves as alka-

* This may be readily prepared by adding to a highly dilute solution of bicarbonate of potassa or soda, a small quantity of hydrochloric acid, insufficient to saturate the base.

line chromate; the residue contains the alkaline earths as carbonates, or also (magnesia) in the caustic state. The chromium in the solution is determined as directed § 104.

I need hardly observe that sesquioxide of chromium may also be separated from *baryta* and, though less perfectly, from *strontia*, by means of *sulphuric acid* added to the acid solution of the substance.

Sesquioxide of chromium cannot be separated by ammonia from the alkaline earths, since, even though carbonic acid be completely excluded, particles of the alkaline earths are thrown down in conjunction with the sesquioxide of chromium. From solution containing salt of sesquioxide of chromium, lime cannot be precipitated completely by oxalate of ammonia; but it may be by sulphuric acid and alcohol (§ 81. 1).

III. Separation of sesquioxide of chromium from alumina.

§ 125.

Fuse the oxides with two parts by weight of nitrate of potassa and four parts of carbonate of soda, in a platinum crucible, treat the fused mass with boiling water, rinse the contents of the crucible into a porcelain dish or beaker, add a somewhat large quantity of chlorate of potassa, supersaturate slightly with hydrochloric acid, evaporate to the consistence of a syrup, and add, during the latter process, some more chlorate of potassa in portions, to remove the free hydrochloric acid. Dilute now with water, and precipitate the alumina by ammonia or carbonate of ammonia, as directed in § 83, *a*. The alumina falls down free from sesquioxide of chromium. The chromium in the filtrate is determined as directed § 104. If you omit the evaporation with hydrochloric acid and chlorate of potassa, part of the chromic acid will be reduced by the nitrous acid in the fluid, and sesquioxide of chromium will accordingly, upon addition of ammonia, precipitate with the alumina (*Dexter*).*

FOURTH GROUP.

OXIDE OF ZINC—PROTOXIDE OF MANGANESE—PROTOXIDE OF NICKEL—PROTOXIDE OF COBALT—PROTOXIDE OF IRON—SESQUIOXIDE OF IRON.

I. Separation of the oxides of the fourth group from the alkalies.

§ 126.

A. *General Methods.*

1. All the oxides of the fourth group from ammonia.

Proceed as for the separation of sesquioxide of chromium and alumina

* *Pogg.* Ann. 89, 142.

from ammonia (§ 123). It must be borne in mind here that the oxides of the fourth group comport themselves, upon ignition with chloride of ammonium, as follows: sesquioxide of iron is partly volatilised as sesquichloride; the oxides of manganese are converted into protochloride of manganese containing protosesquioxide of that metal; the oxides of nickel and cobalt are reduced to the metallic state; oxide of zinc volatilises, with access of air, as chloride of zinc (*H. Rose*).

2. ALL OXIDES OF THE FOURTH GROUP FROM POTASSA AND SODA.

Mix with ammonia until the fluid is neutral, add *sulphide of ammonium*, and filter off the sulphides of the metals from the fluid containing the alkalies. The precautionary measures recommended in the case of sulphide of nickel (§ 87, *b*.) must be carefully attended to, otherwise part of that sulphide will remain in solution. Acidulate the filtrate with hydrochloric acid, concentrate by evaporation, filter from the sulphur, evaporate to dryness, ignite the residue, to effect the removal of the ammonia salts, and determine the alkalies by the methods given in § 120.

B. *Special methods.*

1. OXIDE OF ZINC FROM POTASSA AND SODA, by precipitating the zinc from the solution of the acetates, with sulphuretted hydrogen (see § 128, B. 2, *a*).
2. PROTOXIDE OF NICKEL AND PROTOXIDE OF COBALT FROM THE ALKALIES, by igniting the chlorides of the metals in a stream of hydrogen gas (see § 128, B. 4).
3. SESQUIOXIDE OF IRON FROM POTASSA AND SODA, by precipitating the sesquioxide of iron with ammonia (see § 124, 1, A. 1), or by heating the nitrates (see § 124, 1, A. 2).
4. PROTOXIDE OF MANGANESE FROM THE ALKALIES.
   a. Saturate the solution with chlorine, and precipitate the manganese with *ammonia* (as hydrated sesquioxide). See § 127, 4, *a*. *δ*.
   b. Precipitate the manganese with peroxide of lead (*Gibbs*); see § 127, 4, *a*. *α*. The acid with which the bases are combined may be hydrochloric acid, nitric acid, or sulphuric acid. If the choice is allowed, select the first.
   c. Heat the nitrates (*Deville*). See § 127, 4, *a*. *γ*.

II. SEPARATION OF THE OXIDES OF THE FOURTH GROUP FROM THE ALKALINE EARTHS.

§ 127.

Index: Oxide of zinc from baryta: A.; B. 1, 2, 5;—from strontia: A.; B. 1, 2, 5;—from lime: A.; B. 2, 5;—from magnesia: A.; B. 2.

Protoxide of manganese from baryta: A.; B. 1, 4;—from strontia: A.; B. 1, 4;—from lime: A.; B. 4;—from magnesia: A.; B. 4.

The *Protoxide of nickel and cobalt* from baryta and strontia: A.; B. 1, 5, 7;—from lime: A.; B. 5, 7;—from magnesia: A.; B. 6.

Sesquioxide of iron from baryta and strontia: A.; B. 1, 3;—from lime: A.; B. 3;—from magnesia: A.; B. 3.

A. *General method.*

ALL OXIDES OF THE FOURTH GROUP FROM THE ALKALINE EARTHS.

Add chloride of ammonium (and, if the solution is acid, also ammonia), and precipitate with sulphide of ammonium, as in § 126, A. 2. Take care to use sulphide of ammonium perfectly saturated with sulphuretted hydrogen, and free from carbonate of ammonia, and to employ it in sufficient excess. Wash the precipitate quickly and, as far as practicable, excluded from the access of air, with water to which some sulphide of ammonium has been added. Acidulate the filtrate with hydrochloric acid, heat, filter from the sulphur, and separate the alkaline earths, as directed in § 122.

B. *Special methods.*

1. BARYTA AND STRONTIA FROM THE WHOLE OF THE OXIDES OF THE FOURTH GROUP.

Precipitate the baryta and strontia from the acid solution with sulphuric acid (§§ 79 and 80). This method is preferable to any other to effect the separation of baryta from the oxides of the fourth group.

2. OXIDE OF ZINC FROM THE ALKALINE EARTHS.

Convert the bases into acetates, and precipitate the zinc from the solution as directed in § 85, *b*.

3. SESQUIOXIDE OF IRON FROM THE ALKALINE EARTHS.

a. Precipitate the dilute solution with bicarbonate of soda, or with carbonate of baryta (see § 124, B. 2).

b. Precipitate the sesquioxide of iron with succinate of ammonia (§ 90, 1, *c*).

c. Decompose the nitrates by heat (§ 124, A. 2).

d. Add carbonate of soda to the moderately diluted solution, until the fluid is nearly neutral and has acquired a deep brownish-red tint; add acetate of soda, boil, and filter the fluid from the brownish-red precipitate, which contains all the sesquioxide of iron in form of a basic salt; keep the fluid boiling during filtration, and wash the precipitate with boiling water.

e. (Not applicable in the case of magnesia). Precipitate with *ammonia*, conducting the operation exactly as directed in § 124, B. 1. If you wish to use this method in presence of magnesia,

you must re-dissolve in hydrochloric acid the hydrated sesquioxide of iron containing magnesia, and precipitate with bicarbonate of soda.

4. PROTOXIDE OF MANGANESE FROM THE ALKALINE EARTHS.

a. Methods based upon the separation of manganese as sesquioxide or binoxide.

α. Gibbs's method.* Add to the *perfectly* neutral solution of the bases, which may be combined with hydrochloric acid or nitric acid,† or, in the case of magnesia, with sulphuric acid, pure binoxide of lead,‡ in the proportion of 5 grammes of the binoxide to 1 gramme of substance; digest for an hour at about 185°, with repeated stirring, filter the fluid from the precipitate, which contains the whole of the manganese, probably as sesquioxide, and wash with boiling water. If magnesia is present, a few drops of nitric acid are added, previously to filtration, to the cooled solution. Determine the alkaline earths (and alkalies) in the filtrate, as directed in §§ 121 and 122. Ignite the precipitate, dissolve in strong nitric acid, and separate the manganese and lead as directed in § 130. This method is a little complicated. Presence of free hydrochloric acid does not interfere with the process, but presence of free nitric acid and sulphuric acid does; compare *Will*, Annal. der Chem. und Pharm. 86, 62.

β. Schiel's method.§ Add to the hydrochloric acid solution carbonate of soda, until the fluid is nearly neutralised, mix with acetate of soda, and then conduct *chlorine gas* into the mixture. The acetate of protoxide of manganese is hereby decomposed, and the whole of the manganese separates as binoxide. The alkaline earths remain in solution.

γ. Deville's method.‖ The bases must be present as nitrates. Heat in a covered platinum dish to from 392° to 482°, until the formation of fumes has completely ceased, and the mass has become black; and proceed in all other respects as directed in § 124, 1, A. 2. The presence of a small quantity of organic matter, or the action of a too intense heat, may cause the reduction of traces of binoxide of manganese, and their solution in nitrate of ammonia; these traces of manganese are in that case found with the magnesia.

δ. Saturate the solution with chlorine gas, or, if the quantity of manga-

* Annal. der Chem. und Pharm. 86, 54.

† Hydrochloric acid deserves the preference if, besides the alkaline earths, alkalies are present; if not, nitric acid is preferable.

‡ The binoxide of lead prepared from minium is not adapted for use in this process, on account of the impurities which it contains. Pure binoxide may be obtained by treating the hydrated oxide diffused in water, with chlorine, washing the product with boiling water, digesting with nitric acid, and washing.

§ *Sillim.* Journal 15, 275.

‖ Journ. f. prakt. Chem. 60, 11.

nese is very minute, with chlorine water, and precipitate the manganese as hydrated oxide, with bicarbonate of soda or carbonate of baryta (*H. Rose*). If a considerable quantity of lime, baryta, or strontia, is present, precipitate first with ammonia, filter, wash, redissolve the precipitate in hydrochloric acid, and then precipitate with bicarbonate of soda. Care must be taken not to form chloride of nitrogen by continuing too long to conduct chlorine into a solution containing much chloride of ammonium.

b. Methods based upon the volumetrical determination of manganese, according to *Bunsen* and *Krieger*.*

α. MANGANESE FROM MAGNESIA.

Precipitate with solution of soda (§ 86, 1, *b*). Wash the precipitate thoroughly, ignite and weigh. If the quantity of magnesia present is sufficient, the residue has the formula.

$$Mn_2O_3, MgO + x\ MgO.$$

Treat a weighed sample of it as directed in § 112, appendix; this will give the quantity of the manganese (one equivalent of chlorine, or, as the case may be, one equivalent of liberated iodine, corresponds to one equivalent of Mn_2O_3); from the difference you may calculate the quantity of the magnesia.

β. FROM BARYTA.

Precipitate with carbonate of soda (§ 86, 1, *a*.), and wash the precipitate thoroughly. It has the formula

$$Mn_2O_3, BaO + x\ BaO, CO_2.$$

Treat a sample of it as in *a*.; this will give the quantity of the manganese. To find that of the carbonate of baryta deduct the weight of the sesquioxide of manganese from that of the weighed precipitate, and add to the difference so much carbonic acid as has been expelled by the sesquioxide of manganese, that is, for every equivalent of Mn_2O_3, an equivalent of CO_2.

The separation of MANGANESE from STRONTIA is effected in the same way.

γ. FROM LIME.

Proceed as in β.; but after ignition moisten repeatedly with carbonate of ammonia, evaporate again, and ignite gently, until the weight remains constant.

N.B. This method of volumetrical determination of manganese presupposes the presence of more than one equivalent of Mg O, CO_2, &c., to one equivalent of Mn_2O_3; for if the case is different, the residue contains, besides Mn_2O_3, also Mn_2O_3, MnO. To adapt the method also to cases of the latter description, *Krieger* recommends the following process: dissolve a sample of the weighed precipitate, add half its weight of oxide of zinc, precipitate with carbonate of soda, ignite the precipitate some

* Annal der Chemie und Pharm. 87, 268.

time in the air, determine the quantity of the residue, and use the latter, or a weighed portion of it, for the volumetrical determination. This residue contains the whole of the manganese as Mn_2O_3.

5. PROTOXIDE OF COBALT, PROTOXIDE OF NICKEL, AND OXIDE OF ZINC, FROM BARYTA, STRONTIA, AND LIME.

Mix with carbonate of soda in excess, add cyanide of potassium, heat very gently, until the whole of the precipitated carbonates of protoxide of cobalt, protoxide of nickel, and oxide of zinc, are redissolved, and filter the solution of the cyanides of the metals in cyanide of potassium, from the carbonate of the alkaline earths. Dissolve the latter in dilute hydrochloric acid, and separate them as directed in § 122. Separate the metals as directed § 128.

6. PROTOXIDE OF COBALT AND PROTOXIDE OF NICKEL FROM MAGNESIA.

Precipitate with a mixture of solution of hypochlorite of potassa and solution of caustic potassa. The precipitate consists of peroxide of nickel, sesquioxide of cobalt, and hydrate of magnesia; wash it thoroughly, and digest it still moist, at a temperature of from 86° to 104°, with an excess of solution of chloride of mercury. In this process a double salt is formed of MgCl+3 HgCl, and the magnesia is dissolved, whilst a corresponding quantity of basic chloride of mercury precipitates (*Ullgren, Berzel.* Jahresber. 21, 146). Evaporate the solution and washings with addition of pure oxide of mercury, and determine the magnesia as directed § 82, 3. *b*. Remove the mercury from the oxides of nickel and cobalt by ignition, and separate the two metals as directed below.

7. THE PROTOXIDES OF COBALT AND OF NICKEL FROM BARYTA, STRONTIA, AND LIME.

Ignite the chlorides of the metals in hydrogen gas (§ 128, B. 4).

III. SEPARATION OF THE OXIDES OF THE FOURTH GROUP FROM THOSE OF THE THIRD, AND FROM EACH OTHER.

§ 128.

Index: Alumina from sesquioxide of chromium: B. 1, *a.*;—from oxide of zinc: A. 1 and 2; B. 2, *a.*; 8, *a.*;—from protoxide of manganese: A. 1 and 2; B. 1, *a.*; 5, *b.* and *c.*; 10, *c.*;—from protoxide of nickel: A. 1 and 2; B. 1, *b.*; 8, *a.*;—from protoxide of cobalt: A. 1 and 2; B. 1, *b.*; 8, *a.*;—from protoxide of iron: A. 1 and 2; B. 1, *a.* and *b.*;—from sesquioxide of iron: A. 2; B. 1, *a.* and *b.*; 3, *a.*; 10, *a.*

Sesquioxide of chromium from alumina: B. 1, *a.*;—from oxide of zinc, protoxide of manganese, protoxide of nickel, protoxide of cobalt, and protoxide of iron: A. 1 and 2; B. 5, *a.*;—from sesquioxide of iron: A. 2; B. 3, *a.*; 5, *a.*

Oxide of zinc from alumina: A. 1 and 2; B. 2, *a.*; 8, *a.*;—from sesquioxide of chromium: A. 1 and 2; B. 5, *a.*;—from protoxide of manganese: B. 2, *a.*; 5, *b.* and *c.*; 10, *d.*;—from protoxide of nickel: B. 2, *a.* and *c.*; 3, *c.*; 9;—from protoxide of cobalt: B. 2, *a.* and *c.*; 3, *c.*; 8, *c.*; 9—from sesquioxide of iron: A. 1; B. 2, *a.*; 6, 9, *b.*

Protoxide of manganese from alumina: A. 1 and 2; B. 1, *a.*; 5, *b.* and *c.*; 10, *c.*;—from sesquioxide of chromium: A. 1 and 2; B. 5, *a.*;—from oxide of zinc: B. 2, *a.*; 5, *b.* and *c.*; 10, *d.*;—from protoxide of nickel: B. 2, *b.* and *c.*; 4, 5, *b.* c. and *d.*;—from protoxide of cobalt: B. 2, *b.* and *c.*; 4, 8, *d.*;—from sesquioxide of iron: A. 1; B. 5, *c.*; 6, 10, c.

Protoxide of nickel from alumina: A. 1 and 2; B. 1, *b.*; 8, *a.*;—from sesquioxide of chromium: A. 1 and 2; B. 5, *a.*;—from oxide of zinc: B. 2, *a.* and *c.*; 3, *c.*; 9;—from protoxide of manganese: B. 2, *b.* and *c.*; 4, 5, *b.* *c.* and *d.*;—from protoxide of cobalt: B. 5, *d.*; 8, *b.*;—from sesquioxide of iron: A. 1; B. 2, *b.*; 6.

Protoxide of cobalt from alumina: A. 1 and 2; B. 1, *b.*; 8, *a.*;—from sesquioxide of chromium: A. 1 and 2; B. 5, *a.*;—from oxide of zinc: B. 2, *a.* and *c.*; 3, *c.*; 8, *c.*; 9;—from protoxide of manganese: B. 2, *b.* and *c.*; 4, 8, *d.*;—from protoxide of nickel: B. 5, *d.*; 8, *b.*;—from sesquioxide of iron: A. 1; B. 2, *b.*; 6, 7.

Protoxide of iron from alumina: A. 1 and 2; B. 1, *a.* and *b.*;—from sesquioxide of chromium: A. 1 and 2;—from sesquioxide of iron: A. 1; B. 3, *b.*; 10, *b.*; 11.

Sesquioxide of iron from alumina: A. 2; B. 1, *a.* and *b.*; 3, *a.*; 10, *a.*;—from sesquioxide of chromium: A. 2; B. 3, *a.*; 5, *a.*;—from oxide of zinc: A. 1; B. 2, *a.*; 6, 9, *b.*;—from protoxide of manganese: A. 1; B. 5, *c.*; 6, 10, *c.*;—from protoxide of nickel: A. 1; B. 2, *b.*; 6;—from protoxide of cobalt: A. 1; B. 2, *b.*; 6, 7;—from protoxide of iron: A. 1; B. 3, *b.*; 10, *b.*; 11.

A. *General methods.*

1. *Method based upon the precipitation of some oxides by carbonate of baryta.*

SESQUIOXIDE OF IRON, ALUMINA, AND SESQUIOXIDE OF CHROMIUM, FROM ALL OTHER OXIDES OF THE FOURTH GROUP.

Mix the properly diluted solution, which must contain a little free acid,* in a flask, with carbonate of baryta diffused in water in moderate excess; insert the stopper, and let the mixture stand some time in the cold, with occasional shaking. The sesquioxide of iron, alumina, and sesquioxide of chromium, are completely separated hereby,† whilst the other

* If there is much free acid, the greater part of it must be previously saturated with carbonate of soda.

† The separation of the sesquioxide of chromium requires the most time.

bases remain in solution, with the exception perhaps of traces of protoxide of cobalt, which will mostly fall down with the precipitated oxides. Decant, stir the sediment up with cold water, allow it to deposit, decant once more, filter, and wash with cold water. The precipitate contains, besides the precipitated oxides, carbonate of baryta; and the filtrate, besides the non-precipitated oxides, a salt of baryta.

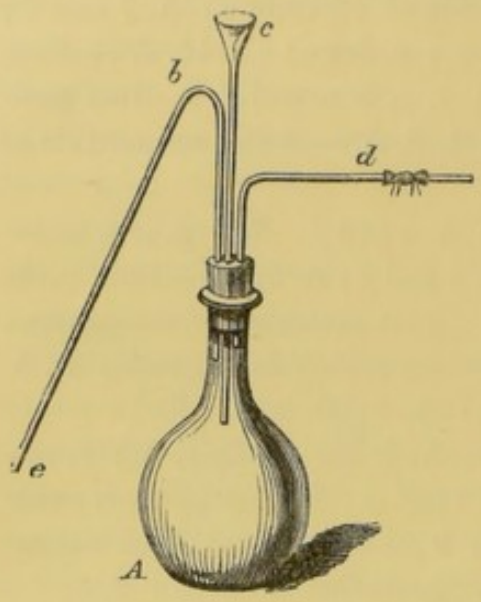


Fig. 51.

If protoxide of iron is present, and it is wished to separate it by this method from sesquioxide of iron, &c., the air must be excluded during the whole of the operation. In that case the solution of the substance, the precipitation, and the washing by decantation, are effected in a flask (see Fig. 51, A), through which carbonic acid is transmitted (*d*). The washing water is poured in through a funnel tube (*c*), and the fluid drawn off by means of a moveable syphon (*b*); both *b* and *c* are fitted air-tight into the cork.

To effect the separation of the sesquioxide from the protoxide of iron, *Scheerer* uses the solution prepared, in an atmosphere of carbonic acid, by heating with concentrated sulphuric acid; he allows the solution to cool, adds ice to the proper degree of dilution, nearly saturates with carbonate of ammonia, and boils the fluid some time with very finely pulverised magnesite (carbonate of magnesia), conducting all the while carbonic acid into it. By this process complete precipitation of the sesquioxide of iron is effected.

2. *Methods based upon the precipitation of the oxides of the fourth group, by sulphide of sodium, from alkaline solution effected with the aid of tartaric acid.*

ALUMINA AND SESQUIOXIDE OF CHROMIUM FROM THE OXIDES OF THE FOURTH GROUP.

Mix the solution with tartaric acid, then with solution of soda or potassa, until the fluid has cleared again; add sulphide of sodium as long as a precipitate continues to form; allow to deposit until the supernatant fluid no longer exhibits a greenish, or brownish tint; decant, stir the precipitate up with water containing sulphide of sodium, decant again, transfer the precipitate, which contains all the metals of the fourth group, to a filter, wash with water containing sulphide of sodium, and separate the metals as directed in B. Add to the filtrate nitrate of potassa, and evaporate to dryness; fuse the residue, and separate the alumina from the chromic acid formed, as directed § 125.

B. *Special methods.*

1. *Methods based upon the solubility of alumina in caustic alkalies.*

a. ALUMINA FROM PROTOXIDE AND SESQUIOXIDE OF IRON, SESQUIOXIDE OF CHROMIUM, AND SMALL QUANTITIES OF PROTOXIDE OF MANGANESE (but not from protoxide of nickel and protoxide of cobalt).

Heat the rather concentrated acid solution in a flask to boiling, remove from the gas or sand-bath, and reduce the sesquioxide of iron present by sulphide of soda. Replace the fluid on the sand-bath, keep boiling some time, and then neutralise with carbonate of soda, add pure solution of soda or potassa* in excess, and boil for some time.

If the analysed substance contains much iron, the precipitate will be black and granular, which is a proof that the iron has been converted into protosesquioxide. The tendency to bumping preceding the actual ebullition of the fluid, may be guarded against by means of a spiral coil of platinum wire placed in the liquid, or by constant agitation of the latter; when ebullition has once set in, there is no further need of these precautions. Remove the fluid now from the sand-bath, allow it to deposit, pass the clear fluid through a filter, which must not be over-porous, boil the precipitate, for security, once more with a fresh quantity of solution of soda, then wash it, first by decantation, and afterwards on the filter, with hot water. Acidulate the alkaline filtrate with hydrochloric acid, boil with some chlorate of potassa (§ 124, 1, A. 1), concentrate by evaporation, and precipitate the alumina as directed § 83, *a.* (Journal f. prakt. Chem. 45, 261.) The boiling of the precipitated oxides with the solution of soda is effected best in a somewhat capacious silver or platinum dish. The use of solution of soda containing alumina and silica, must be particularly avoided.

If sesquioxide of chromium was present in the analysed substance, you will find the principal portion of this with the sesquioxide of iron; but a small quantity has been oxidised in the process and converted into chromic acid, and is accordingly found in the fluid filtered from the alumina.

b. ALUMINA FROM SESQUI AND PROTOXIDE OF IRON, PROTOXIDE OF COBALT, AND PROTOXIDE OF NICKEL.

Fuse the oxides with hydrate of potassa in a silver crucible, boil the mass with water, and filter the alkaline fluid, which contains the alu-

* *Wöhler* has recently recommended the following method for the preparation of pure solution of soda or potassa: Put 1 part of nitrate of potassa and 2 or 3 parts of sheet copper cuttings, in alternate layers, in an iron or copper crucible, cover the latter, and expose it for half an hour to a moderate red heat. (If you have a copper crucible so much the better; if not, you must use an iron one.) Allow the mass to cool, treat it with water, let the solution—which is perfectly free from copper—deposit in a tall cylinder, and then take it up by means of a syphon. The best way of keeping it is that recommended by *Mohr*, namely, in a bottle, closed with a cork, into which a tube is fitted air-tight, open at both ends and filled with a coarse mixture of sulphate of soda and caustic lime (Annal. d. Chem. und Pharm. 87, 373).

mina, from the oxides, which are free from alumina, but contain potassa (*H. Rose*).

2. *Methods based upon the different deportment of the several sulphides with acids, or of the acetic acid solutions with sulphuretted hydrogen.*

a. OXIDE OF ZINC FROM ALUMINA AND THE OXIDES OF THE FOURTH GROUP.

The solution of the acetates, which must be free from inorganic acids, and must contain a sufficient excess of acetic acid, is precipitated with sulphuretted hydrogen, which throws down the zinc only (§ 85, *b*). The oxides are usually most readily obtained, in acetic acid solution, by converting them into sulphates, and adding a sufficient quantity of acetate of baryta. Sulphuretted hydrogen is then conducted, without application of heat, into the unfiltered fluid, to which, if necessary, some more acetic acid has been added. Should the precipitate, as will sometimes happen, look gray, this may be remedied if the coloration proceeds from admixture of sulphide of iron in the precipitate, by applying a gentle heat, and once more conducting sulphuretted hydrogen into the fluid. The precipitate, which consists of a mixture of sulphide of zinc and sulphate of baryta, is washed with water containing sulphuretted hydrogen. It is then heated with hydrochloric acid, the solution filtered, and the zinc in the filtrate determined as directed § 85, *a*. The other oxides in the fluid filtered off from the sulphide of zinc are, after previous removal of the baryta by precipitation, determined by the proper methods.

b. PROTOXIDE OF COBALT AND PROTOXIDE OF NICKEL FROM PROTOXIDE OF MANGANESE AND THE OXIDES OF IRON.

The solution of the oxides, which must be free from nitric acid, is, after previous neutralisation of the free acid which may be present, by ammonia, precipitated with sulphide of ammonium, and highly dilute hydrochloric acid (*H. Rose*), or acetic acid (*Wackenroder*) is then added. This serves to dissolve the sulphide of manganese and the sulphide of iron, whilst the sulphide of cobalt and the sulphide of nickel, though the latter less completely, remain undissolved. The sulphides of the metals are reprecipitated from the filtrate by addition of ammonia and sulphide of ammonium, and the precipitate is treated once more with dilute hydrochloric acid. The results are nearly accurate.

c. PROTOXIDE OF COBALT AND PROTOXIDE OF NICKEL FROM PROTOXIDE OF MANGANESE AND OXIDE OF ZINC.

a. Put the weighed mixture of the oxides in a small boat-shaped porcelain, or platinum vessel, insert the latter into a tube, heat the mixture to dull redness, conducting all the while sulphuretted hydrogen gas over it. Let the sulphides of the metals formed cool in the gaseous stream, and then digest them for several hours with cold dilute hydrochloric acid, which dissolves only the sulphide of manganese, and the sulphide of zinc.

The sulphides of nickel and cobalt are left behind free from admixture of the other sulphides (*Ebelmen*).*

β. Precipitate with carbonate of soda, filter, wash, and ignite; mix one part of the residue with 1·5 parts of sulphur and 0·75 of carbonate of soda, and heat the mixture in a small retort as strongly as possible for half an hour. Allow the mixture to cool, and treat the sulphide of zinc (and sulphide of manganese) formed, with dilute hydrochloric acid (one part of acid to ten of water), *Brunner*.†

3. *Methods based upon the different deportment of the several oxides with hydrogen gas at a red heat.*

α. SESQUIOXIDE OF IRON FROM ALUMINA AND SESQUIOXIDE OF CHROMIUM.

α. *Rivot's* method.‡ Precipitate with ammonia, heat, filter, ignite, weigh, triturate, and weigh off a portion of the powder in a small porcelain boat. Insert this latter now into a porcelain tube, lying in an horizontal position and having one end closed with a cork into which a narrower open glass tube is fitted. Conduct into the other end hydrogen gas, dried by transmission through sulphuric acid and chloride of calcium. When the air has been expelled from the apparatus, heat the porcelain tube gradually to redness, and maintain it at that temperature as long as water continues to form (about one hour). Allow the tube now to cool, continuing all the while the transmission of the hydrogen gas, then remove the little boat, and weigh it. The loss of weight indicates the quantity of oxygen which was combined with the iron in the sesquioxide of that metal.

If you wish to determine the oxides separately, which may be deemed more particularly necessary, if the analysed substance contains much alumina and little sesquioxide of iron, treat the mixture of alumina, sesquioxide of chromium, and metallic iron, with highly dilute nitric acid (1 part of acid to 30 or 40 parts of water), or with water to which very little nitric acid is gradually added. The iron is dissolved, the alumina and sesquioxide of chromium remain undissolved. The latter are weighed directly; the iron is precipitated from the filtrate by ammonia, after ebullition of the fluid. The results of *Rivot's* experimental analyses were highly satisfactory.

β. *Deville* transmits through the tube, when the reduction by hydrogen is effected as in *α*, first hydrochloric acid gas, and then again hydrogen. This leaves the alumina behind in a state of purity, the iron volatilises as

* Annal. der Chem. und Pharm. 72, 329. *Ebelmen* has given his method simply for the separation of CoO and NiO from MnO.

† Annal. der Chem. und Pharm. 80, 364. *Brunner* has given his method simply for nickel and zinc.

‡ Ann. de Chim. et de Phys. xxx. 188. Journ. f. prakt. Chem. 51, 338.

protochloride, and is either determined directly, or calculated from the loss. If it is intended to do the former, the protochloride in the tubes and in the tubulated receiver is dissolved by heating dilute hydrochloric acid to boiling, and conducting the fumes into the porcelain tube; the tube of the receiver is directed downwards in this operation. *Deville* has employed his method simply to effect the separation of sesquioxide of iron from alumina; but it is obvious that it is equally adapted for the separation of sesquioxide of iron from sesquioxide of chromium.

APPENDIX: *Decomposition of chrome-iron (Rivot).**

Treat the finely pulverised and elutriated mineral as directed in *a*. An hour's application of a bright red heat suffices to effect the complete reduction of the protoxide of iron. The mass is allowed to cool in the stream of hydrogen gas, and then digested twenty-four hours with dilute nitric acid, which dissolves the iron, lime, and magnesia, leaving behind the sesquioxide of chromium, alumina, and silicic acid.

b. SESQUIOXIDE OF IRON FROM PROTOXIDE OF IRON.

Compounds containing only sesquioxide and protoxide of iron, or, at all events, besides these two, no other substances liable to undergo alteration by ignition in a stream of hydrogen gas, are accurately weighed, intensely ignited in hydrogen gas, allowed to cool in the gaseous stream, and then again weighed: the loss of weight indicates the quantity of oxygen originally combined with the iron. The quantity of the iron may be determined, according to circumstances, either by simply weighing the residue, or by an ulterior analysis of the latter. The operation may be conducted either as in *a*., or in the manner described in § 88, and illustrated by Fig. 40. If, by way of controlling the analysis, you wish to weigh the water generated in the process of reduction, you may use the apparatus described in § 19, and illustrated by Fig. 18. The gasometer is, in that case, to be filled with hydrogen gas instead of atmospheric air.

c. PROTOXIDE OF COBALT AND PROTOXIDE OF NICKEL FROM OXIDE OF ZINC.

Ullgren's method. (*Berzelius's* Jahresbericht, 21, 145.)

Precipitate the solution with carbonate of soda, in the manner and with the precautions directed in § 85, *a*. Wash the precipitates carefully with boiling water, dry, ignite, and weigh. Triturate finely, introduce a weighed portion of the powder into the bulb of a bulb-tube, and heat the latter to incipient redness, transmitting a slow stream of hydrogen gas through it during the operation. As soon as the formation of water ceases, stop the application of heat, and allow the mass to cool in the hydrogen stream. The mass contains the whole of the cobalt and nickel in the metallic state, the whole of the zinc as oxide. Close one end of the tube by fusion, fill with a concentrated solution of carbonate of ammonia,

* Journal f. prakt. Chem. 51, 347.

insert a cork into the other end, and keep exposed for twenty-four hours to a gentle heat (about 105°). The oxide of zinc dissolves completely in this process; the undissolved portion, which consists of the cobalt and nickel, is washed repeatedly with solution of carbonate of ammonia, then dried and weighed. The quantity of the oxide of zinc is found by cautiously evaporating the ammoniacal solution, and igniting the residue.

4. *Methods based upon the different deportment of the chlorides of the metals with hydrogen at a red heat.*

PROTOXIDE OF COBALT AND PROTOXIDE OF NICKEL FROM PROTOXIDE OF MANGANESE.

The oxides are thrown down from the solution; if the latter is free from salts of ammonia, this is effected by precipitating with solution of soda; but in presence of a considerable proportion of salts of ammonia, the best way is to precipitate with sulphide of ammonium, wash the sulphides of the metals thrown down, dissolve them in nitrohydrochloric acid, and precipitate with solution of soda.

The oxides, or a weighed portion of them, are introduced into a bulb-tube, and exposed, in a current of dry hydrochloric acid gas, to a moderate red heat, until they are completely converted into chlorides, and consequently, until the formation of water has entirely ceased, which takes a long time to accomplish. A strong heat is now applied to the bulb, and dry hydrogen gas transmitted over the chlorides until a light vapor only is perceptible upon approaching a glass rod moistened with ammonia to the mouth of the tube. The protochlorides of nickel and cobalt are reduced to the metallic state in this process, whilst the protochloride of manganese remains unaltered. The mass is allowed to cool in the current of hydrogen gas, and the bulb-tube is then placed in a cylinder with water. The greater part of the protochloride of manganese dissolves, a small portion floating about in the fluid, in the shape of brown flakes; the cobalt and nickel speedily subside. The fluid, with the suspended light flakes in it, is decanted from the reduced metals, and the latter washed on a weighed filter—first with a little highly dilute hydrochloric acid, then with water—dried, and weighed (compare also § 88, *b.*). The decanted fluid, with the washings and some hydrochloric acid added to it, is concentrated by evaporation, and the manganese precipitated with carbonate of soda (§ 86). The results are accurate (*H. Rose*).

5. *Methods based upon the different capacity of the several oxides to be converted by oxidising agents into higher oxides, or by chlorine into higher chlorides.*

a. SESQUIOXIDE OF CHROMIUM FROM ALL THE OXIDES OF THE FOURTH GROUP.

Fuse the oxides with nitrate of potassa and carbonate of soda (compare § 125), boil the mass with water, add a sufficient quantity of spirits of

wine, and heat for several hours. Filter, and determine in the filtrate the chromium as directed § 104, and in the residue the bases of the fourth group. The following is the theory of this process: the oxides of zinc, cobalt, nickel, iron, and partly that of manganese, separate upon fusion with nitrate of potassa and carbonate of soda, whilst, on the other hand, manganate (perhaps also some ferrate) and chromate of potassa are formed. Upon boiling with water, part of the manganic acid of the manganate of potassa is converted into permanganic acid at the expense of the oxygen of the other part, which is reduced to the state of binoxide; the latter separates, whilst the permanganate of potassa and the chromate of potassa are dissolved. The addition of alcohol, with the application of a gentle heat, effects the decomposition of the permanganate of potassa, and the reduction of the permanganic acid to the state of binoxide of manganese, which separates. Upon filtering the mixture, we have now the whole of the chromium in the filtrate as alkaline chromate, and all the oxides of the fourth group on the filter.

The analysis of the native compound of sesquioxide of chromium with protoxide of iron (chrome-iron), requires the most careful levigation and elutriation of the mineral, and long protracted fusion with the proper flux. However, in most cases, even the strictest attention to these points will not prevent part of the mineral remaining undecomposed; in which case the residue left undissolved by water will not completely dissolve in hydrochloric acid. In cases of this kind, the weight of the undecomposed portion of the mineral is determined, and subtracted from the total amount analysed.

Calvert recommends to effect the decomposition of the chrome-ores, by mixing the finely pulverised minerals with from three to four parts of soda-lime, and one part of nitrate of soda, and fusing the mixture for two hours.

b. PROTOXIDE OF MANGANESE FROM ALUMINA, PROTOXIDE OF NICKEL, AND OXIDE OF ZINC (but not from protoxide of cobalt and the oxides of iron).

Gibbs's method.* Precipitate the manganese with binoxide of lead, and conduct the process exactly as in the separation of manganese from magnesia (§ 127, B. 4, *a.* *a.*)

c. PROTOXIDE OF MANGANESE FROM ALUMINA, SESQUIOXIDE OF IRON, PROTOXIDE OF NICKEL, AND OXIDE OF ZINC (but not from protoxide of cobalt).

Schiel's method.† Conduct chlorine gas into the solution mixed with acetate of soda (see § 127, B. 4, *a.* *β.*).

* Annal. d. Chem. u. Pharm. 66, 56.

† *Sillim.* Journ. 15, 275. *Schiel* speaks only of the separation of the manganese from

d. PROTOXIDE OF COBALT AND PROTOXIDE OF MANGANESE FROM PROTOXIDE OF NICKEL (according to *H. Rose—Pogg.* Annal. 71, 545).

Dilute the hydrochloric acid solution in a capacious flask, with one litre of water to two grms. of metallic oxides in the solution, conduct chlorine gas into the flask, until the fluid is saturated, and the flask is completely filled with the gas; add, well washed, freshly precipitated carbonate of baryta in excess, let the mixture stand in the cold from twelve to eighteen hours, taking care to shake it repeatedly; and then filter the fluid, which contains the whole of the nickel, from the precipitated sesquioxide of cobalt and manganese.

Henry used bromine instead of chlorine as the oxidising agent; he obtained satisfactory results. *Denham Smith* recommends addition of a dilute solution of chloride of lime which has been completely decomposed by addition of sulphuric acid, so as to leave no particle of undecomposed hypochlorite (otherwise nickel would be thrown down with the other oxides).

6. *Method based upon the different deportment of the succinates of the several oxides.*

SESQUIOXIDE OF IRON FROM OXIDE OF ZINC, PROTOXIDE OF MANGANESE, PROTOXIDE OF NICKEL, AND PROTOXIDE OF COBALT.

Add to the solution, if not strongly acid, chloride of ammonium and then neutralise it with ammonia in a manner to precipitate a very small portion of the sesquioxide of iron, leaving the greater part in solution; add now a solution of neutral succinate (or benzoate) of ammonia, and filter the fluid from the succinate of sesquioxide of iron; the filtrate contains the other metallic oxides. For the details of the process see § 90, 1, *c.* With proper care, the separation is complete; the process is more particularly adapted in cases where the relative proportion of the sesquioxide of iron is rather large.

7. *Method based upon the different deportment of the oxalates of the several oxides.*

PROTOXIDE OF COBALT FROM SESQUIOXIDE OF IRON.

Mix the solution, which must be as neutral as possible, with binoxalate of potassa (or with oxalic acid and a sufficient quantity of carbonate of potassa to leave the reaction only moderately acid), and allow the mixture to stand at rest for three or four days, shaded from sunlight. The oxalate of protoxide of cobalt separates completely, and free from iron. Wash it with cold water, ignite it in a stream of hydrogen gas, and weigh the metallic cobalt. The results are satisfactory (*H. Rose*).

8. *Methods based upon the different deportment of the several oxides with cyanide of potassium.*

iron and nickel; but it is obvious that the method will equally answer to effect its separation from alumina and zinc.

a. ALUMINA FROM OXIDE OF ZINC, PROTOXIDE OF COBALT, AND PROTOXIDE OF NICKEL.

Mix the solution with carbonate of soda, add cyanide of potassium in sufficient quantity, and digest in the cold, until the precipitated carbonates of the oxide of zinc and the protoxides of cobalt and manganese are dissolved. Filter the fluid from the undissolved alumina, wash the latter, and remove the alkali which it contains by solution in hydrochloric acid, and reprecipitating by ammonia.

b. PROTOXIDE OF COBALT FROM PROTOXIDE OF NICKEL.

Liebig's method.* Mix the solution of the two oxides, which must be free from other oxides, with hydrocyanic acid, then with solution of potassa, until the precipitate which first formed is completely redissolved. (Cyanide of potassium, free from cyanate, may be used instead of hydrocyanic acid and potassa.) The solution looks reddish-yellow; heat it to boiling, to remove the free hydrocyanic acid. By this process the double cyanide of cobalt and potassium (KCy,CoCy) in the solution, is converted, with evolution of hydrogen, into cobalticyanide of potassium (a compound of one equivalent of sesquicyanide of cobalt with three equivalents of cyanide of potassium Co_2Cy_6 3 K),† whilst the double cyanide of nickel and potassium in the solution remains unaltered. Add to the hot solution very finely divided elutriated oxide of mercury and boil. By this operation the whole of the nickel is precipitated partly as sesquioxide partly as protocyanide, the mercury combining with the liberated cyanogen. If the fluid was neutral before the addition of the oxide of mercury, it shows alkaline reaction after boiling with the latter. The precipitate looks greenish at first, or, if the oxide of mercury has been added in excess, yellowish-gray. Wash and ignite. The residue is pure sesquioxide of nickel.

To determine the cobalt in the filtrate, supersaturate with acetic acid, boil, precipitate boiling with sulphate of copper, keep in ebullition for some time longer, then filter the fluid from the precipitated cobalticyanide of copper (Co_2Cy_6, 3 Cu+7 HO), decompose the latter by boiling with solution of potassa, and calculate the quantity of the cobalt from that of the oxide of copper obtained. The following method, recommended by *Wöhler*) ‡ is more simple and convenient. The filtrate is nearly neutralised with nitric acid (a slightly alkaline reaction is of no consequence), and a solution, as neutral as possible, of nitrate of suboxide of mercury added; the white precipitate of cobalticyanide of mercury, which contains the whole of the cobalt, may be readily washed, and gives,

* Annal. d. Chem. und Pharm. 65, 244.

† 2 (Co Cy, K Cy)+K Cy+Cy H=(Co_2Cy_6 3 K)+H.

‡ Annal. d. Chem. und Pharm. 70, 256.

upon ignition with free access of air, pure sesquioxide of cobalt; the reduction of the latter is effected best with hydrogen. See § 88.

Instead of precipitating the nickel with oxide of mercury, you may proceed as follows: when you have expelled the free hydrocyanic acid by boiling, let the solution cool, supersaturate it with chlorine, and redissolve the precipitate of cyanide of nickel which forms, by addition of solution of soda or potassa. The chlorine does not act upon the cobalticyanide of potassium, but it decomposes the double cyanide of nickel and potassium, and throws down the whole of the nickel as black peroxide (*Liebig*).*

c. PROTOXIDE OF COBALT FROM OXIDE OF ZINC.

Add to the solution of the two oxides, which must contain some free hydrochloric acid, common cyanide of potassium (prepared after *Liebig's* method), in sufficient quantity to redissolve the precipitate of protocyanide of cobalt and cyanide of zinc which forms at first; then add a little more cyanide of potassium, and boil some time, adding occasionally one or two drops of hydrochloric acid, but not in sufficient quantity to make the solution acid. Mix the solution with hydrochloric acid in an obliquely placed flask, and boil, until the cobalticyanide of zinc which precipitates at first, is redissolved, and the hydrocyanic acid completely expelled. Add solution of soda or potassa in excess, and boil until the fluid is clear; the solution may now be assumed to contain all the cobalt as cobalticyanide of potassium, and all the zinc as a mixture or compound of oxide of zinc and alkali. Precipitate the zinc by sulphuretted hydrogen (§ 85). Filter, and determine the cobalt in the filtrate, as directed § 128, 8, *b*. The process is simple and the separation complete.

d. PROTOXIDE OF COBALT FROM PROTOXIDE OF MANGANESE.

Mix the solution of the two oxides with hydrocyanic acid, then with solution of potassa and soda, and heat the mixture. If the quantity of hydrocyanic acid added was sufficient, the protocyanide of cobalt which precipitated at first, redissolves completely, whilst the greater portion of the precipitated protocyanide of manganese remains undissolved. Filter, and treat the filtrate exactly as directed § 128, 8, *b*. (separation of cobalt from nickel). Ignite the two manganese precipitates together. When the oxide of mercury which the second manganese precipitate contains in admixture, has been expelled, there remains protosesquioxide of manganese. This shows that cobalt may be separated also both from nickel and manganese at the same time; in which case the dissolved portion of the manganese is obtained with the protoxide of nickel.

9. *Methods based upon the volatility of zinc.*

a. PROTOXIDE OF COBALT AND PROTOXIDE OF NICKEL FROM OXIDE OF ZINC.

Berzelius (Jahresbericht, 21, 144,) recommends the following methods

* Annal. d. Chem. und Pharm. 87, 128.

for the absolute separation of cobalt and nickel from zinc. Precipitate with solution of potassa in excess, boil, and filter the fluid, which contains the greater portion of the zinc dissolved in the caustic potassa, from the precipitated hydrate of protoxide of nickel and cobalt, which also contains some of the zinc; wash the precipitate *thoroughly* with boiling water, and determine the zinc in the filtrate as directed § 85. Dry the precipitate, ignite, and weigh; then mix it in a porcelain crucible with pure sugar (recrystallized from solution in alcohol), and heat slowly until the sugar is completely carbonised. Place the crucible, with the lid on, into a bath of magnesia in a larger-sized covered clay crucible, and expose, for the space of one hour, to the very highest degree of heat attainable by a wind furnace. This process causes the reduction of the metals: the whole of the zinc present rises in vapor, the nickel and cobalt, mixed with charcoal, remain. Treat the residue with nitric acid, and determine the oxides by precipitating with solution of potassa, and weighing the precipitate. The difference between this weight and that obtained before shows the quantity of the oxide of zinc which has been thrown down with the other oxides. This method gives very accurate results only in the separation of nickel from zinc. (Compare § 88, *b*.)

b. Zinc from iron, in alloys.

Bobierre states that these alloys may be readily and accurately analysed by igniting them in a stream of hydrogen gas (see § 130, B. 4, *b*.).

10. *Methods based upon the volumetrical determination of one of the components, and the calculation of the other from the difference.*

a. Sesquioxide of iron fron alumina.

Precipitate both substances with ammonia (§ 83, *a*., and § 90, 1). Dissolve the weighed residue, entirely or in part, by digestion with concentrated hydrochloric acid, or by fusion with bisulphate of potassa and treating with water containing hydrochloric acid; and determine the iron by analysis by measure, as directed § 90, 3. Calculate the alumina from the difference. This method is to be recommended more particularly in cases where the relative proportion of the sesquioxide of iron present is small. Instead of estimating the iron by analysis by measure, you may also precipitate it, after addition of tartaric acid and ammonia, with sulphide of ammonium.

b. Sesquioxide of iron from protoxide of iron.

a. Determine in a portion of the substance the total amount of the iron as sesquioxide, or by analysis by measure. Dissolve another portion by heating with hydrochloric acid in a flask through which carbonic acid is conducted, to exclude the air; dilute the solution, and determine the protoxide of iron volumetrically (§ 89, 2). The difference gives the quantity of the sesquioxide. This convenient and accurate method will probably replace the more complicated methods hitherto employed, to determine

protoxide of iron in presence of sesquioxide. Iron may also be determined by analysis by measure in presence of oxide of zinc, protoxide of nickel, &c.

β. Bunsen's method. Fill the little flask, *a*. (Fig. 44, § 104) two-thirds with fuming hydrochloric acid, and expel the air by carbonic acid, by throwing some fragments of carbonate of soda into it. Weigh a portion of the substance to be analysed in an open short tube; weigh in a similar tube a quantity of bichromate of potassa slightly in excess; drop the two tubes into the flask, put on the evolution tube, and proceed for the rest as directed § 104, *d. β.* Of course you will obtain less free iodine than you would if no protoxide of iron had been dissolved with the chromate of potassa, as a portion of the liberated chlorine is used to convert the protochloride of iron into sesquichloride; every one equivalent of iodine obtained less than corresponds to the chromate of potassa used, is calculated as two equivalents of protoxide of iron.

If you wish to ascertain the total quantity of iron contained in the substances, dissolve another portion of it in hydrochloric acid in the flask *a*, and effect the reduction of the sesquioxide of iron to protoxide, by means of a ball of chemically pure zinc, cast on a fine platinum wire. To exclude all access of air, close the flask *a*, during the ebullition, with the apparatus *b b* (Fig. 52).

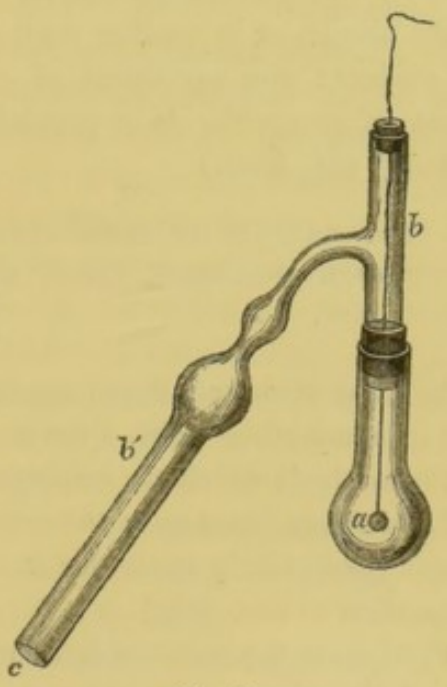


Fig. 52.

As soon as the colorless condition of the fluid shows that the reduction is completed, cool the flask in cold water, lift the upper cork, throw a few grains of carbonate of soda into the acid, draw the zinc ball up the tube *b*, wash the fluid adhering to the ball off into the flask, and remove *b b*. Add quickly a weighed portion of bichromate of potassa in excess, put on the evolution tube, and proceed for the rest as just directed.

c. PROTOXIDE OF MANGANESE FROM ALUMINA AND SESQUIOXIDE OF IRON (according to *Krieger*—Annal. d. Chem. u. Pharm., 87, 261).

Precipitate with carbonate of soda, digest the precipitate some time with the fluid, wash properly, first, by decantation, then on the filter, dry, ignite, and determine in a sample the manganese as directed § 112, ap-

pendix. Bear in mind that the precipitate contains the manganese as Mn_3O_4.

d. PROTOXIDE OF MANGANESE FROM OXIDE OF ZINC (according to *Krieger*).

Precipitate boiling with carbonate of soda, wash the precipitate with boiling water, dry, and ignite. If the analysed substance contained a sufficient quantity of zinc, the precipitate consists of $Zn\,O + x\,Mn_2O_3$. Weigh a portion, and determine in this the manganese, as directed § 112, appendix. If the quantity of zinc present is insufficient, proceed as directed § 127, B. 4, *b*. N.B.

11. *Indirect method.*

SESQUIOXIDE OF IRON FROM PROTOXIDE.

Of the many indirect methods proposed I will only give the following: Dissolve as in 10, *b.*, add a solution of sodio-chloride of gold (auro-perchloride of sodium) in excess, close the flask, and allow the reduced gold, which separates, to deposit; filter the fluid from the gold, and determine the latter as directed § 98. Determine the total quantity of the iron in the filtrate, or in another portion of the substance. The calculation is self-evident: one equivalent of gold separated corresponds to six equivalents of protochloride or protoxide of iron ($6\,FeCl + AuCl_3 = 3\,Fe_2\,Cl_3 + Au$). (*H. Rose.*)

IV. SEPARATION OF SESQUIOXIDE OF IRON, ALUMINA, PROTOXIDE OF MANGANESE, LIME, MAGNESIA, POTASSA, AND SODA.

§ 129.

As these oxides are found together in the analysis of most silicates, and also in many other cases, I devote a distinct paragraph to the description of the methods which are employed to effect their separation.

1. *Methods based upon the employment of carbonate of baryta as precipitant* (particularly applicable in cases where the mixture contains a small proportion of lime only).

Precipitate the iron—which must be present in the form of sesquioxide—and the alumina by carbonate of baryta (§ 128, A. 1),* and separate the two metals by one of the methods given in § 128. Precipitate the manganese from the filtrate, either by sulphide of ammonium, or, after addition of a little hydrochloric acid and saturation with chlorine, by carbonate of baryta, or, as *Gibbs* recommends, by binoxide of lead. If you have used sulphide of ammonium, dissolve the precipitated sulphide of manganese in hydrochloric acid, mix the solution with some sulphuric acid, filter off, and determine the manganese as directed § 86,

* Before adding the carbonate of baryta it is *absolutely indispensable* to try whether a solution of it in hydrochloric acid is completely precipitated by sulphuric acid, so that the filtrate leaves no residue upon evaporation on platinum.

1, *a*. If you have used carbonate of baryta as precipitant, separate the manganese as directed § 127 ; if binoxide of lead, proceed as directed § 130. Precipitate the dilute solution now with dilute sulphuric acid, wash the precipitate, until the water running off is no longer rendered turbid by chloride of barium ; if you have used binoxide of lead, throw down the last traces of lead with sulphuretted hydrogen, and then the lime with oxalate of ammonia. Evaporate the filtrate to dryness, ignite the residue, and separate the magnesia from the alkalies by one of the methods given in § 121.

In cases where the proportion of the alumina is large, that of the iron and manganese small, the solution may be saturated first with chlorine, and the sesquioxide of iron, alumina, and sesquioxide of manganese may then be jointly precipitated with carbonate of baryta, the precipitate dissolved in hydrochloric acid, the baryta thrown down from the solution by sulphuric acid in the least excess, then the three bases by carbonate of soda, and the precipitate thoroughly washed, dried, ignited, and weighed ; it contains the manganese as Mn_3O_4. If this and the sesquioxide of iron are now determined by the volumetrical method, the difference will give the quantity of the alumina. It will be readily seen that one and the same sample may be used, first, for the determination of the manganese, and then for that of the iron ; compare § 112, appendix, and § 128, B. 10, *b*. *β*. There is only one objection to this method, viz., that it is apt to give a trifling excess of alumina, as that substance, when precipitated with a fixed alkali, can hardly ever be altogether freed from the latter by washing. The joint precipitation of the alumina, iron, and manganese, may also be effected with ammonia, after previous saturation of the fluid with chlorine, or addition of hypochlorous acid. But in that case it is advisable to let the precipitated fluid stand some time before proceeding to filtration. Care must also be taken to ascertain that the filtrate contains no manganese, which may be done by adding sulphide of ammonium, and allowing it to stand some time.

2. *Method based upon the application of ammonia as precipitant.*

Precipitate the hydrochloric acid solution, to which, if necessary, some chloride of ammonium has been added, with ammonia, and filter the fluid from the precipitate, which consists principally of alumina and sesquioxide of iron, but contains also small quantities of protoxide of manganese, lime, and magnesia. Wash it thoroughly, dry, ignite, and weigh. Dissolve it by digestion with concentrated hydrochloric acid, or by fusion with bisulphate of potassa. Boil the solution, first with some sulphite of soda, then with solution of soda, by which means the alumina will be completely dissolved (§ 128, B. 1, *a*.). Wash the residue thoroughly, dissolve it in hydrochloric acid, precipitate the sesquioxide of iron with succinate of ammonia, and determine either in the filtrate separately the

small quantities of manganese, lime, and magnesia—which is the safer way on account of the possible presence of an alkali—or unite the filtrate with the fluid filtered from the precipitate produced by ammonia, and treat the mixture as directed in 1.

If the fluid is saturated with chlorine previously to the addition of the ammonia, the whole of the manganese is obtained in the first precipitate; if the quantity of manganese is small, addition of chlorine water suffices; indeed, as a rule, this may be said to be the best way.

3. *Method based upon the application of sulphide of ammonium as precipitant.*

Mix with ammonia until a precipitate just begins to form, then with sulphide of ammonium, allow the precipitate, which contains iron, manganese, and alumina, to subside, and then filter the fluid from it. Separate the lime, magnesia, and alkalies, in the filtrate, as directed § 121. Dissolve the precipitate in hydrochloric acid, and separate the alumina from the iron and manganese by solution of soda, and then finally the iron from the manganese by succinate of ammonia.

4. *Method based upon the decomposition of the nitrates* (according to *Deville*).

This method presupposes that the bases are combined with nitric acid only.

Proceed first as directed § 124, A. 2. The escape of fumes of nitrous acid observed during the heating of the nitrates, is no sign of the total decomposition of the nitrates of sesquioxide of iron and alumina, as these vapors owe their formation to the conversion of the nitrate of protoxide of manganese into binoxide. Stop the application of heat when no more vapors are evolved, and the substance has acquired a uniform black color. After the treatment with nitrate of ammonia (§ 124, A. 2), the solution contains nitrate of lime, nitrate of magnesia, and nitrates of the alkalies, the residue, alumina, sesquioxide of iron, and binoxide of manganese. That, under certain circumstances, some manganese is dissolved, has been stated already in § 127, B. 4, γ.; the small quantity of manganese which has thus got into the solution, is found with the magnesia, and finally separated from the latter.

Deville recommends the following methods to effect the further separation of the bases:

a. Heat the residue with moderately strong nitric acid, until the alumina and sesquioxide of iron are dissolved, leaving the residuary binoxide of manganese of a pure black color. Ignite the residue, and weigh the protosesquioxide of manganese formed. Evaporate the solution in a platinum crucible, ignite, and weigh the mixture of sesquioxide of iron and alumina, and which may possibly also contain some protosesquioxide of manganese. Treat a portion of it as directed § 128, B. 3, *a.* β.; this

gives the weight of the alumina. If manganese was present the iron cannot be estimated from the difference. *Deville* therefore evaporates the solution of the protochlorides with sulphuric acid, ignites gently, and from the residue, which consists of sesquioxide of iron and some sulphate of protoxide of manganese, dissolves the latter with water. Should the heat applied have been too strong, which might possibly lead to the decomposition also of sulphate of protoxide of manganese, the residue is moistened with a mixture of oxalic acid and nitric acid, some sulphuric acid added, and the process repeated.

b. From the filtrate precipitate first the lime by oxalate of ammonia added in the least excess, filter, evaporate the filtrate to dryness, and separate the magnesia and the alkalies as directed § 121.

FIFTH GROUP.

OXIDE OF SILVER—SUBOXIDE OF MERCURY—OXIDE OF MERCURY—OXIDE OF LEAD—TEROXIDE OF BISMUTH—OXIDE OF COPPER—OXIDE OF CADMIUM.

I. SEPARATION OF THE OXIDES OF THE FIFTH GROUP FROM THOSE OF THE PRECEDING FOUR GROUPS.

§ 130.

Index: *Oxide of silver* from the oxides of groups 1—4: A.; B. 1.
Oxide of mercury from the oxides of groups 1—4: A.; B. 2.
Suboxide of mercury from the oxides of groups 1—4: A.; B. 2.
Oxide of lead from the oxides of groups 1—4: A.; B. 3;—from protoxide of manganese: B. 6.
Teroxide of bismuth from the oxides of groups 1—4: A;—from protoxide of manganese: B. 6.
Oxide of copper from the oxides of groups 1—4: A.;—from oxide of zinc: B. 4;—from protoxide of manganese: B. 6.
Oxide of cadmium from the oxides of groups 1—4: A;—from oxide of zinc and protoxide of nickel: B. 5;—from protoxide of manganese: B. 5 and 6.

A. *General method.*

SEPARATION OF ALL THE OXIDES OF THE FIFTH GROUP FROM THOSE OF THE PRECEDING FOUR GROUPS.

Principle: Sulphuretted hydrogen precipitates from acid solutions the metals of the fifth group, but not those of the first four groups.

The following points require especial attention in the execution of the process:

a. To effect the separation of the oxides of the fifth group from those of the first three groups, by means of sulphuretted hydrogen, it is neces-

sary simply that the reaction of the solution be acid, the nature of the acid to which the reaction is due being a matter of no consequence. But to effect the separation of the oxides of the fifth from those of the fourth group, the presence of a free mineral acid in the fluid is indispensable; otherwise zinc and, under certain circumstances, also cobalt and nickel, may fall down with the oxides of the fifth group.

β. But even the addition of a tolerably large quantity of hydrochloric acid to the fluid will not always prevent the precipitation of the zinc.* The precipitated sulphides of the metals of the fifth group must therefore in the ulterior analytical processes, always be treated so as to secure the separation of the zinc which they may possibly hold in admixture.

γ. Hydrochloric acid is used in preference as acidifying agent, except where it would produce a precipitate in the fluid, in which case nitric acid is employed, and the solution largely diluted.

δ. To effect the *complete* precipitation of the sulphides corresponding to the oxides of the fifth group, the solution must be diluted to a certain degree, even though no other acid besides hydrochloric be present.

B. *Special methods.*

SEPARATION OF INDIVIDUAL OXIDES OF THE FIFTH GROUP FROM SOME, OR FROM ALL OXIDES OF THE FIRST FOUR GROUPS.

1. SILVER is most simply and completely separated from the OXIDES OF THE FIRST FOUR GROUPS, by means of hydrochloric acid. The hydrochloric acid must not be used too largely in excess, and the solution must be sufficiently diluted; otherwise a portion of the silver will remain in solution. Care must be taken also not to forget the addition of nitric acid, which promotes the separation of the chloride of silver. The latter had, under these circumstances, better be collected and washed on a filter (§ 91, 1, *a*. β.), as washing by decantation would give too large a bulk of fluid.

2. The separation of MERCURY from the METALS OF THE FIRST FOUR GROUPS may be effected also by ignition, which will cause the volatilisation of the mercury or the mercurial compound, leaving the non-volatile bodies behind. The method is applicable to alloys as well as to oxides, chlorides, and sulphides. Which of these several methods may be the most appropriate depends upon the nature of the metals from which the mercury is to be separated, and the selection is accordingly guided by the deportment of the respective compounds. The quantity of mercury is estimated, in this method, either from the loss of weight suffered by the

* *Rivot* and *Bouquet* have pronounced a complete separation of copper from zinc, by means of sulphuretted hydrogen, to be altogether impracticable (Annal d. Chem. und Pharm. 80, 664); but *Spirgatis* (Journal f. prakt. Chem. 58, 351) has shown—what *Rose* also states with positive certainty—that complete separation is readily effected whenever a sufficient quantity of free acid is present, for instance, when the oxides are dissolved in a mixture of 100 parts of water and 30 of hydrochloric acid of 1·13 sp. gr.

ignited substance, in which case the operation is conducted in a crucible, or the sublimed mercury is collected and weighed as directed § 94, 1, *a*. The best way, where it is practicable, is to proceed in the manner described § 131, 6 (separation of mercury from silver, &c.).

MERCURY IN THE FORM OF SUBOXIDE may also be separated and determined by precipitating with hydrochloric acid.

3. FROM THOSE BASES WHICH FORM SOLUBLE SALTS WITH SULPHURIC ACID, OXIDE OF LEAD may be readily separated by that acid. The results are very satisfactory, if the rules given in § 92, 2, are strictly adhered to.

4. OXIDE OF COPPER FROM OXIDE OF ZINC.

a. Rivot and *Bouquet** have recommended the following process to effect the separation of these two oxides. Saturate the dilute nitric acid or hydrochloric acid solution with ammonia; add solid hydrate of potassa in slight excess, and heat gently in the sand-bath until the fluid has become colorless, and smells no longer of ammonia. Wash the precipitated oxide of copper with boiling water. Acidulate the alkaline filtrate with hydrochloric acid, and precipitate the zinc from it with carbonate of soda. *Spirgatis*† obtained unsatisfactory results by this method, finding about equal quantities of zinc and copper in the solution; and as this was found to be the case also in my own laboratory, I cannot recommend the process.

b. Bobierre employed the following method with satisfactory results in the analysis of many alloys of zinc and copper. The alloy is put into a small porcelain boat standing in a porcelain tube, and heated to redness for three quarters of an hour at the most, a rapid stream of hydrogen gas being conducted over it during the process. The zinc volatilises, the copper remains behind. Lead also (if that metal be present) is not volatilised in this process.

c. As in the separation of copper from zinc, by means of sulphuretted hydrogen, the oxide of copper obtained may, under certain circumstances, contain oxide of zinc, I recommend the following process to test the oxide of copper for oxide of zinc, and to remove the latter. When you have weighed the oxide of copper, reduce it as directed § 88, in the apparatus illustrated by Fig. 40; heat the metallic copper which has been cooled in the stream of hydrogen gas, for some time with water and hydrochloric acid, filter, wash, conduct a few bubbles of sulphuretted hydrogen into the fluid, to precipitate any traces of copper which might possibly have been dissolved, and determine the zinc as directed § 85, *a*.

5. OXIDE OF CADMIUM FROM OXIDE OF ZINC, PROTOXIDE OF MANGANESE, AND PROTOXIDE OF NICKEL.

* Ann. de Chim. et de Phys. 33, 24. Ann. der Chem. und Pharm. 80, 264.

† Journ. f. prakt. Chem. 57, 184.

Mix the solution with carbonate of baryta, and digest the mixture in the cold. Oxide of cadmium is completely precipitated, the other oxides remain in solution (compare § 128, A. 1).

6. PROTOXIDE OF MANGANESE FROM OXIDE OF LEAD, TEROXIDE OF BISMUTH, OXIDE OF CADMIUM, AND OXIDE OF COPPER.

If you have a solution containing protoxide of manganese and one of the other bases, precipitate the hot solution with carbonate of soda, wash the precipitate with boiling water, first by decantation, then on the filter, dry, ignite some time, weigh, and determine in a portion of the residue, the manganese by the volumetrical method (§ 112, appendix). If the oxide of lead, of copper, of cadmium, or the teroxide of bismuth is present in sufficient quantity, the residue has the formula

$$Mn_2O_3 + x\,MO.$$

Compare § 127, B. 4, *b*. N.B. (*Krieger*). You must never neglect adding some sulphide of ammonium to the filtrate to ascertain whether the oxides have been entirely precipitated by carbonate of soda, since oxide of copper, more especially, is not readily completely precipitated by carbonates of the alkalies.

II. SEPARATION OF THE OXIDES OF THE FIFTH GROUP FROM EACH OTHER.

§ 131.

Index : Oxide of silver from oxide of copper : 1, *a.* ; 3, *b. c.* and *d.* ; 5, *b.* ; 7 ;—from oxide of cadmium : 1, *a.* ; 3, *b.* and *d.* ;—from teroxide of bismuth : 1, *a.* ; 3, *a.* and *d.* ; 6, *b.* ;—from oxide of mercury : 1, *a.* ; 3, *b.* and *d.* ; 6, *a.* ;—from oxide of lead : 1, *a.* ; 2 ; 3, *a.* and *d.* ; 4, *c.* ; 5, *b.* ; 7.

Oxide of mercury from oxide of silver : 1, *a.* ; 3, *b.* and *d.* ; 6, *a.* ;—from suboxide of mercury : 1, *b.* ;—from oxide of lead : 1, *c.* ; 2 ; 3, *a.* and *d.* ; 6, *a.* ;—from teroxide of bismuth : 3, *a.* and *d.* ;—from oxide of copper : 3, *c.* and *d.* ; 5, *a.* ; 6, *a.* ;—from oxide of cadmium : 5, *a.*

Suboxide of mercury from oxide of mercury : 1, *b.* ;—from other metals : see *oxide of mercury*.

Oxide of lead from oxide of silver : 1, *a.* ; 2 ; 3, *a.* and *d.* ; 4, *c.* ; 5, *b.* ; 7 ;—from oxide of mercury : 1, *c.* ; 2 ; 3, *a.* and *d.* ; 6, *a.* ;—from oxide of copper : 1, *c.* ; 2 ; 3, *a.* and *d.* ;—from teroxide of bismuth : 1, *c.* ; 2 ; 6, *b.* ; 8 ;—from oxide of cadmium : 2 ; 3, *a.* and *d.*

Teroxide of bismuth from oxide of silver : 1, *a.* ; 3, *a.* and *d.* ; 6, *b* ;—from oxide of lead : 1, *c.* ; 2 ; 6, *b.* ; 8 ;—from oxide of copper : 3, *a.*

and *d.*; 4, *a.*; 6, *b.*;—from oxide of cadmium: 3, *a.* and *d.*;—from oxide of mercury: 3, *a.* and *d.*

Oxide of copper from oxide of silver: 1, *a.*; 3, *b. c.* and *d.*; 5, *b.*; 7;—from oxide of lead: 1, *c.*; 2; 3, *a.* and *d.*;—from teroxide of bismuth: 3, *a.* and *d.*; 4, *a.*; 6, *b.*;—from oxide of mercury: 3, *c.* and *d.*; 5, *a.*; 6, *a.*;—from oxide of cadmium: 3, *c.* and *d.*; 4, *b.*

Oxide of cadmium from oxide of silver: 1, *a.*; 3, *b.* and *d.*;—from oxide of lead: 2; 3, *a.* and *d.*;—from teroxide of bismuth: 3, *a.* and *d.*;—from oxide of copper: 3, *c.* and *d.*; 4, *b.*;—from oxide of mercury: 5, *a.*

1. *Methods based upon the insolubility of certain metallic chlorides in water or spirits of wine.*

a. OXIDE OF SILVER FROM OXIDE OF COPPER, OXIDE OF CADMIUM, TEROXIDE OF BISMUTH, OXIDE OF MERCURY, AND OXIDE OF LEAD.

α. To separate *oxide of silver* from *oxide of copper*, *oxide of cadmium*, and *teroxide of bismuth*, add to the nitric acid solution hydrochloric acid as long as a precipitate forms, and separate the precipitated chloride of silver from the other oxides in the solution, as directed § 91, 1.

β. The separation of *silver* from *oxide of mercury* is effected in the same way, with this modification, that the fluid is precipitated with solution of chloride of sodium, after previous addition of acetate of soda or acetate of ammonia. If this addition is neglected, the solution does not clear after the precipitation (*Levol*); moreover, some chloride of silver remains in solution, as that salt dissolves in notable quantity in solution of nitrate of oxide of mercury (*Wackenroder*, *Liebig*). Ann. der Chem. und Pharm. 81, 128.

γ. In the separation of *silver* from *lead*, the precipitation is also preceded by addition of acetate of soda. The fluid must be hot, and the hydrochloric acid rather dilute; no more must be added of the latter than is necessary. In this manner the separation may be readily effected, since chloride of lead dissolves in acetate of soda (*Anthon*). The lead is thrown down from the filtrate by sulphuretted hydrogen.

δ. The volumetrical method (§ 91, 5) is mostly had recourse to in the mint, to determine the *silver* in *alloys*. In presence of mercury acetate of soda is added to the fluid, immediately before the addition of the solution of chloride of sodium (see *β.*).

b. SUBOXIDE OF MERCURY FROM OXIDE OF MERCURY, OXIDE OF COPPER, OXIDE OF CADMIUM, AND OXIDE OF LEAD.

Mix the highly dilute cold solution with hydrochloric acid, as long as a precipitate (subchloride of mercury) continues to form; allow this to deposit, filter it on a tared filter, dry at 212°, and weigh. The filtrate contains the other oxides. If you have to analyse a solid compound of the

oxides, insoluble in water, you may either treat it directly, in the cold, with dilute hydrochloric acid, or you may dissolve in highly dilute nitric acid, and mix the solution with a large quantity of water before proceeding to precipitate. Care must always be taken to effect the solution in a manner excluding the chance of a conversion of the suboxide of mercury into oxide.

c. OXIDE OF LEAD FROM OXIDE OF MERCURY, OXIDE OF COPPER, AND TEROXIDE OF BISMUTH.

Mix the concentrated nitric acid solution with hydrochloric acid in excess, add a large quantity of strong alcohol and some ether, and proceed generally as directed § 92, 4. Heat the filtrate until the alcohol is expelled, and precipitate the metals by sulphuretted hydrogen.

2. *Methods based upon the insolubility of sulphate of oxide of lead.*

OXIDE OF LEAD FROM ALL OTHER OXIDES OF THE FIFTH GROUP.

Mix the nitric acid solution with pure sulphuric acid in excess, evaporate until the sulphuric acid begins to volatilise, allow the fluid to cool, add water (in which, if there is a sufficient quantity of free sulphuric acid present, even the sulphates of oxide of mercury and of teroxide of bismuth dissolve completely), and then filter the solution, which contains the other oxides, *without delay* from the undissolved sulphate of oxide of lead. Wash the latter with water containing sulphuric acid, lastly with alcohol, dry, and weigh (§ 92, 2). Precipitate the other oxides from the filtrate by sulphuretted hydrogen. Sulphate of oxide of silver being difficultly soluble; this method cannot be recommended in presence of oxide of silver in notable quantity.

3. *Methods based upon the different deportment of the several oxides and sulphides with cyanide of potassium* (according to *Fresenius* and *Haidlen*, Annal. der Chem. und Pharm. 43, 129).

a. OXIDE OF LEAD AND TEROXIDE OF BISMUTH FROM ALL OTHER OXIDES OF THE FIFTH GROUP.

Mix the *dilute* solution with carbonate of soda in *slight* excess, add solution of cyanide of potassium (free from sulphide of potassium), heat gently for some time, filter, and wash. On the filter you have carbonate of oxide of lead and of teroxide of bismuth, mixed with alkali; the filtrate contains the other metals as cyanides in combination with cyanide of potassium. The method of effecting their ulterior separation will be learnt from what follows.

b. OXIDE OF SILVER FROM OXIDE OF MERCURY, OXIDE OF COPPER, AND OXIDE OF CADMIUM.

Add to the solution, which, if it contain much free acid, must previously be neutralised with soda, cyanide of potassium, until the precipitate which forms at first is redissolved. The solution contains the cyanides of the metals in combination with cyanide of potassium as soluble double

salts. Add dilute nitric acid in excess, which effects the decomposition of the double cyanides; the insoluble cyanide of silver precipitates permanently, whilst the cyanide of mercury remains in solution, and the cyanides of copper and cadmium, which first fall down, redissolve in the excess of nitric acid. Treat the cyanide of silver as directed § 91, 3. If the filtrate contains only mercury and cadmium, precipitate at once with sulphuretted hydrogen, whereby the sulphides of the two metals are completely thrown down; but if it contains copper, you must first evaporate with sulphuric acid, until the odor of hydrocyanic acid is no longer perceptible, and then precipitate with sulphuretted hydrogen, or at once with solution of soda (§ 95, 1).

c. Oxide of copper from oxide of silver, oxide of mercury, and oxide of cadmium.

Mix the solution, as in *b.*, with cyanide of potassium, until the precipitate which is first thrown down redissolves; add some more cyanide of potassium, then sulphuretted hydrogen water, or sulphide of ammonium, as long as a precipitate continues to form. The sulphides of silver, cadmium, and mercury are completely thrown down, whilst the copper, as sulphide dissolved in cyanide of potassium, remains in solution. Allow the precipitate to subside, decant repeatedly, treat the precipitate, for security, once more with some solution of cyanide of potassium, heat gently, filter, and wash the sulphides of the metals. To determine the copper in the filtrate, evaporate the latter with addition of nitric acid and sulphuric acid, until there is no longer any odor of hydrocyanic acid perceptible, and then precipitate with solution of soda (§ 95, 1).

d. Metals of the fifth group from each other.

Mix the dilute solution with carbonate of soda, then with cyanide of potassium in excess, digest some time at a gentle heat, and filter. On the filter you have carbonate of lead and of teroxide of bismuth, mixed with alkali; separate the two metals by the proper method. Add to the filtrate dilute nitric acid in excess, and filter the fluid from the precipitated cyanide of silver, which determine as directed § 91, 3. Neutralise the filtrate with carbonate of soda, add cyanide of potassium, and conduct into the fluid sulphuretted hydrogen in excess. Add now some more cyanide of potassium, to redissolve the sulphide of copper which may have fallen down, and filter the fluid, which contains the whole of the copper, from the precipitated sulphide of mercury and sulphide of cadmium. Determine the copper as directed in *c.*, and separate the mercury and cadmium as directed § 131, 5, *a*.

4. *Methods based upon the solubility of some oxides in ammonia or carbonate of ammonia.*

a. Oxide of copper from teroxide of bismuth.

a. Mix the solution (in nitric acid) with carbonate of ammonia in ex-

cess. The bismuth separates as carbonate of teroxide, whilst the carbonate of copper is redissolved by the excess of carbonate of ammonia. Allow the fluid to digest for some time in a warm place, filter, and wash the precipitate, pouring over it during this operation from time to time some solution of carbonate of ammonia, to remove the last traces of copper. If the fluid was free from sulphuric acid and chlorine, the precipitate may be at once ignited and weighed; but in the contrary case, redissolve it in nitric acid, and precipitate once more with carbonate of ammonia (§ 96, *a.*). Apply heat to the filtrate that the carbonate of ammonia may volatilise (adding finally some ammonia), and determine the copper as directed § 95, 1, *a.* *β.* This process is more convenient than 3, *a.*, but the separation is less accurate.

β. Mix the solution with some chloride of ammonium, and drop it gradually into dilute solution of ammonia. The bismuth is precipitated as a basic salt, whilst the oxide of copper remains in solution as an ammoniacal double salt (*Berzelius*). Wash the precipitated salt of bismuth with dilute solution of ammonia, dissolve it in dilute nitric acid, and determine the bismuth as directed § 96. Determine the copper in the ammoniacal solution as directed § 95, 1, *a.* *β.*

b. Oxide of copper from oxide of cadmium.

Add carbonate of ammonia in excess. Carbonate of oxide of cadmium separates, whilst the oxide of copper remains in solution with some oxide of cadmium. Upon exposure to air, the latter separates, the former remaining in solution (*Stromeyer*). Treat the solution as in *a.* *α.* The process is more convenient than 3, *c.*, but the separation is less accurate than by the latter method.

c. Chloride of lead and chloride of silver may be separated also by solution of ammonia, which dissolves the latter, leaving the former undissolved as basic chloride of lead. Bear in mind that the chloride of silver must be recently precipitated, and the light carefully excluded during the process.

5. *Methods based upon the reduction of some oxides or chlorides by formiate of soda.*

a. Oxide of mercury from oxide of copper and oxide of cadmium.

Mix the solution with hydrochloric acid, if it does not already contain that acid, nearly saturate with soda, and precipitate the mercury with formiate of soda, as directed § 94, 2. The copper and cadmium in the fluid, filtered from the subchloride of mercury, are separated and determined by the proper method.

b. Oxide of silver from oxide of copper and oxide of lead.

Saturate the solution with soda, add formiate of an alkali, and apply heat until the evolution of carbonic acid ceases. The silver separates

completely in the metallic state, the oxide of copper and oxide of lead remain in solution (*H. Rose*).

6. *Methods based upon the volatility of some metals, oxides, or chlorides, at a high temperature.*

a. MERCURY FROM SILVER, LEAD, COPPER (in general from the metals forming non-volatile chlorides).

The process is conducted in the apparatus illustrated by Fig. 53.

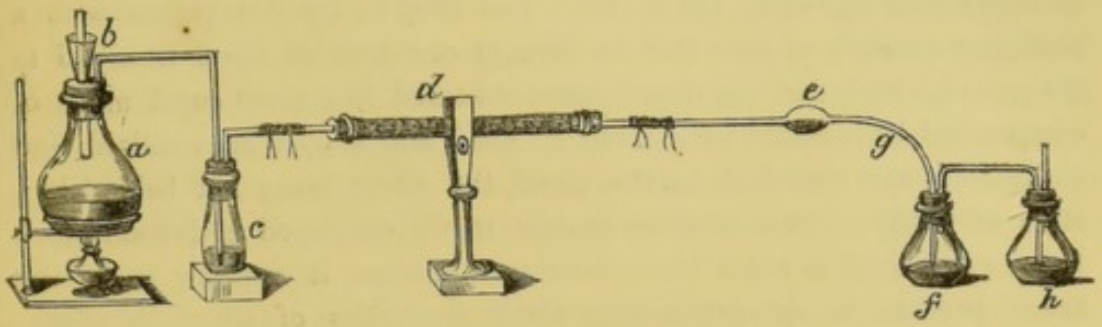


Fig. 53.

Precipitate with sulphuretted hydrogen, collect the precipitated sulphides on a weighed filter, dry at 212°, and weigh. Introduce a weighed portion of the dry precipitate into the bulb *e*; transmit a slow stream of chlorine gas through the tube, and apply a gentle heat to the bulb, increasing it gradually to faint redness. First chloride of sulphur distils over, which decomposes with the water in the flasks *f* and *h* (§ 116, II. *c.*), then the chloride of mercury formed volatilises, condensing partly in the flask *f*, partly in the hind part of the tube *g*. Cut off that part of the tube, rinse the sublimate with water into the flask *f*, and add to the contents of the latter also the water in *h*. Heat the solution until the smell of chlorine is gone off, and then determine in the fluid filtered from the sulphur which may still remain undissolved, the mercury as directed § 94. If the residue consists of silver only, or of lead only, you may weigh it at once; but if it contains several metals you must reduce the chlorides by ignition in a stream of hydrogen gas, and dissolve the reduced metals in nitric acid, for their ulterior separation. Bear in mind that, in presence of lead, the sulphides and the chlorides of the metals must be heated *gently*, the former in a stream of chlorine, the latter in a stream of hydrogen gas, otherwise some chloride of lead might volatilise. The mercury may also often be determined from the loss which the analysed substance has suffered by the process of ignition.

b. TEROXIDE OF BISMUTH FROM OXIDE OF SILVER, OXIDE OF LEAD, AND OXIDE OF COPPER.

The separation is effected exactly in the same way as that of mercury from the same metals. The method is more especially convenient for the

separation of the metals in alloys. Care must be taken not to heat too strongly, as otherwise chloride of lead might volatilise, nor to discontinue the application of heat too soon, as otherwise bismuth would remain in the residue. Water containing hydrochloric acid is poured into the flasks *f* and *h*, and the bismuth is then determined according to the direction of § 96.

7. *Separation of silver by cupellation.*

CUPELLATION was formerly the universal method to determine SILVER in alloys with COPPER, LEAD, &c. The alloy is fused together with a sufficient quantity of pure lead to give to one part of silver from 16 to 20 parts of lead, and the fused mass is heated in a small cupel made of compressed bone-earth, in a muffle. Lead and copper are oxidised, and the oxides are absorbed by the cupel, the silver being left behind in a state of purity. This method is only rarely employed in laboratories; I have given it a place here, however, because it appears to be the safest process to determine very small quantities of silver in alloys. (Compare *Malaguti* and *Durocher*, Comptes rendus, 29, 689. *Dingler*, 115, 276.)

8. *Precipitation of one metal by another in the metallic state.*

OXIDE OF LEAD FROM TEROXIDE OF BISMUTH.

Precipitate the solution with carbonate of ammonia, wash the precipitate and dissolve in acetic acid, in a stoppered flask; place a rod of pure lead upright in the solution and nearly fill up with water, so that the rod is entirely covered by the fluid; insert the stopper, and let the flask stand at rest for about twelve hours, with occasional shaking. Wash the precipitated bismuth off from the lead rod, collect it on a filter, wash, and dissolve in nitric acid; evaporate the solution, and determine the bismuth as directed § 96. Determine the lead in the filtrate as directed § 92. Dry the lead rod, and weigh it again; subtract the loss of weight which it has suffered in the process, from the amount of the lead produced from the filtrate (*Ullgren*).

SIXTH GROUP.

TEROXIDE OF GOLD—BINOXIDE OF PLATINUM—PROTOXIDE OF TIN—BINOXIDE OF TIN—TEROXIDE OF ANTIMONY—ARSENIOUS ACID—ARSENIC ACID.

I. SEPARATION OF THE OXIDES OF THE SIXTH GROUP FROM THE OXIDES OF THE FIRST FIVE GROUPS.

§ 132.

Index: Gold from the oxides of groups 1—3: A. 1; B. 2;—of group 4:

A. 1 ; B. 1, *a.*; 2 ;—from mercury, copper, and cadmium: B. 1, *a.* ; 2 ; —from bismuth: B. 1, *a.* ; 2 ; 13 ;—from lead : B. 1, *a.* ; 13 ;— from silver : B. 1, *a.* ; 10.

Platinum from the oxides of groups 1—3 : A. 1 ; B. 3 ;—of group 4 : A. 1 ; B. 1, *b.* ; 3 ;—from mercury, copper, cadmium, and bismuth : B. 1, *b.* ; 3 ;—from lead : B. 1, *b.* ;—from silver : B. 1, *b.* ; 10.

Protoxide and binoxide of tin from the oxides of groups 1 and 2 : A. 1 ; B. 4, *b.* ; 5, *b.* ;—of group 3 : A. 1 ; B. 4, *b.* ;—from sesquioxide of iron : A. 1 ; 2, *b.* ; B. 4, *a.* ;—from protoxide of manganese and oxide of zinc : A. 1 ; 2, *b.* ; B. 4, *a.* and *b.* ;—from protoxide of nickel and protoxide of cobalt : A. 1 ; 2, *b.* ; B. 4, *a.* and *b.* ; 5, *a.* ; —from oxide of mercury, oxide of cadmium, and teroxide of bismuth : A. 2, *a.* and *b.* ; B. 4, *a.* ;—from oxide of copper : A. 2, *a.* and *b.* ; B. 4, *a.* and *b.* ; 5, *a.* ;—from oxide of lead and oxide of silver : A. 2, *a.* and *b.* ; B. 4, *a.* ; 5, *a.*

Teroxide of antimony from the oxides of groups 1 and 2 : A. 1 ; 5, *b.* ;—of group 3 : A. 1 ;—from sesquioxide of iron, protoxide of manganese, and oxide of zinc : A. 1 ; 2, *b.* ; B. 4, *c.* ;—from protoxide of nickel and protoxide of cobalt : A. 1 ; 2, *b.* ; B. 4, *c.* ; 5, *a.* ;—from oxide of mercury, oxide of cadmium, and teroxide of bismuth : A. 2, *a.* and *b.* ; B. 4, *c.* ;—from oxides of copper, lead, and silver : A. 2, *a.* and *b.* ; B. 4, *c.* ; 5, *a.*

Arsenious and arsenic acids from the oxides of group 1 : A. 1 ; B. 5, *b.* ; 8 ; 12 ;—from magnesia : A. 1 ; B. 5, *b.* ; 7 ; 8 ; 12 ;—from baryta, strontia and lime : A. 1 ; B. 5, *b.* ; 7 ; 8 ; 11 ; 12 ;—from the oxides of group 3 : A. 1 ; B. 9 ;—from sesquioxide of iron : A. 1 ; 2, *b.* ; B. 7 ; 9 ;—from protoxide of manganese : A. 1 ; 2, *b.* ; B. 7 ; 9 ; 12 ; —from oxide of zinc : A. 1 ; 2, *b.* ; B. 7 ; 8 ; 9 ; 12 ;—from protoxide of nickel and protoxide of cobalt : A. 1 ; 2, *b.* ; B. 5, *a.* ; 7 ; 8 ; 9 ; 12 ;—from oxide of mercury and teroxide of bismuth : A. 2, *a.* and *b.* ; 7 ;—from oxide of copper : A. 2, *a.* and *b.* ; B. 5, *a.* ; 7 ; 8 ;—from oxide of cadmium : A. 2, *a.* and *b.* ; B. 7 ; 8 ;—from oxide of silver : A. 2, *a.* and *b.* ; B. 5, *a.* ; 7 ;—from oxide of lead : A. 2, *a.* and *b.* ; B. 5, *a.* ; 7 ; 8 ; 11.

A. *General methods.*

1. *Method based upon the precipitation of the oxides of the sixth group from acid solutions by sulphuretted hydrogen.*

ALL OXIDES OF THE SIXTH GROUP FROM THOSE OF THE FIRST FOUR GROUPS.

Conduct into the acid* solution sulphuretted hydrogen in excess, and

* Hydrochloric acid answers best as acidifying agent.

filter from the precipitated sulphides (corresponding to the oxides of the sixth group).

The points mentioned § 130, *a*. *β*. and *δ*. must also be attended to here. With respect to the exceptional conditions requisite to secure the complete precipitation of certain metals of the sixth group, I refer to Section IV. I have to remark in addition,

a. That sulphuretted hydrogen fails to separate arsenic acid from oxide of zinc, as even in presence of a large excess of acid, the whole or at least a portion of the zinc precipitates with the arsenic as ZnS, $As S_5$ (*Wöhler*). To secure the separation of the two bodies in a solution, the arsenic acid must first be converted into arsenious acid, by heating with sulphurous acid, before the sulphuretted hydrogen is conducted into the fluid.

β. That in presence of antimony, tartaric acid is judiciously added, when oxides of the fourth group alone are present, which may be thrown down from the filtrate, after addition of ammonia, by sulphide of ammonium; but that it had better be omitted in the analysis of compounds containing alumina, alkaline earths, and alkalies. In the case of such compounds, sulphuretted hydrogen is conducted into the clear hydrochloric acid solution, water is then added, sulphuretted hydrogen again conducted into the fluid, a further quantity of water added, and the precipitation completed by conducting a sufficient amount of sulphuretted hydrogen into the fluid.

2. *Methods based upon the solubility of the sulphides of the metals of the sixth group in sulphides of the alkali metals.*

a. THE OXIDES OF GROUP VI. (with the exception of gold and platinum) FROM THOSE OF GROUP V.

Precipitate the acid solution with sulphuretted hydrogen, paying due attention to the directions given in Section IV. under the heads of the several metals, and also to the remarks in 1. The precipitate consists of the sulphides of the metals of groups V. and VI. Wash, treat immediately with yellow sulphide of ammonium, and digest the mixture for some time at a gentle heat; filter off the clear fluid, treat the residue again with sulphide of ammonium, digest a short time, filter, and wash the residuary sulphides of group V. with water containing sulphuretted hydrogen. If protosulphide of tin is present, some sulphur in powder must be added to the sulphide of ammonium, except the latter be very yellow. In presence of copper, the sulphide of which is a little soluble in sulphide of ammonium, sulphide of sodium had better be used as precipitant, instead of sulphide of ammonium. However, this substitution can be made only in the absence of mercury, since the sulphides of that metal are soluble in sulphide of sodium.

To the alkaline filtrate, add, gradually, hydrochloric acid in small portions, until the acid predominates; allow it to deposit, and then filter the fluid from the sulphides of the metals of the sixth group which have been thrown down with some sulphur.

b. THE OXIDES OF GROUP VI. (with the exception of gold and platinum) FROM THOSE OF GROUPS IV. AND V.

a. Neutralise the solution with ammonia, and add yellow sulphide of ammonium in excess; cover the vessel, allow the mixture to digest some time at a moderate heat, and then proceed as in *a.* On the filter, you have the sulphides of the metals of groups IV. and V. Wash them with water containing sulphide of ammonium.

In presence of nickel this method offers peculiar difficulties. In presence of copper (and absence of mercury), soda and sulphide of sodium are substituted for ammonia and sulphide of ammonium).*

β. In the analysis of solid compounds (oxides or salts), it is in most cases preferable to fuse the substance with three parts of dry carbonate of soda, and three parts of sulphur, in a covered porcelain crucible, over a lamp. When the contents are completely fused, and the excess of sulphur is volatilised, the mass is allowed to cool, and then treated with water, which dissolves the sulpho-salts of the metals of the sixth group, leaving the sulphides of groups IV. and V. behind. By this means, even ignited binoxide of tin may be examined for iron, &c., and the admixture of oxides of groups IV. and V. removed from it (*H. Rose*). The solution is treated as in *a.*

B. *Special methods.*

1. *Methods based upon the insolubility of some metals of the sixth group in acids.*

a. GOLD FROM METALS OF GROUPS IV. AND V. IN ALLOYS.

a. Heat the alloy with dilute pure nitric acid or, according to circumstances, with hydrochloric acid. The other metals dissolve, leaving the gold behind. The alloy must be reduced to filings, or rolled out in thin sheets. Alloys of gold, containing silver or lead, or both, can be analysed by this method only if the quantity of the two latter metals or of either, amounts to more than 80 per cent, otherwise the silver and lead are not completely dissolved. Alloys of silver and gold, con-

* The hitherto universally admitted accuracy of this method has lately been called in question by *Bloxam* (Ann. d. Chem. und Pharm. 83, 204). That chemist found that sulphide of ammonium fails to separate small quantities of bisulphide of tin from large quantities of sulphide of mercury and sulphide of cadmium (1 : 100); and that more especially the separation of copper from tin and antimony (also from arsenic) by this method is a failure, as nearly the whole of the tin remains with the copper. For the present, I must confine myself to calling attention to these statements.

taining less than 80 per cent of silver, are therefore fused together with three parts of lead, before they are treated with nitric acid. The residuary gold is weighed; but its purity must be ascertained by dissolving it in nitrohydrochloric acid.

β. Heat the finely divided (filed or rolled) alloy in a capacious platinum dish with pure hydrate of sulphuric acid, until the evolution of gas has ceased, and the sulphuric acid begins to volatilise; or fuse the alloy with bisulphate of potassa (*H. Rose*). Separate the gold from the sulphates of the metals, by treating the mass first with cold, finally with boiling water. It is advisable to repeat the operation with the separated gold, and ultimately to test the purity of the latter.

b. PLATINUM FROM OTHER METALS OF GROUPS IV. AND V., IN ALLOYS.

The separation is effected by treating the substance with sulphuric acid, or, better still, with bisulphate of potassa (*a*. *β*.); but not with nitric acid, as platinum in alloys will, under certain circumstances, dissolve in that acid.

2. *Method based upon the separation of gold in the metallic state.*

GOLD FROM ALL OXIDES OF GROUPS I.—V., with the exception of OXIDE OF LEAD AND OXIDE OF SILVER.

Precipitate the hydrochloric acid solution with oxalic acid as directed § 98, *b*. *γ*., and filter off the gold when it has completely separated. Take care to add a sufficient quantity of hydrochloric acid to prevent oxalates insoluble in water precipitating in conjunction with the gold, for want of a solvent.

3. *Method based upon the precipitation of platinum as chloride of potassium, or chloride of ammonium, and bichloride of platinum.* (Potassio or ammonio-bichloride of platinum.)

PLATINUM FROM THE OXIDES OF GROUPS IV. AND V., with the exception of LEAD AND SILVER.

Precipitate the platinum with chloride of potassium or chloride of ammonium, as directed § 99, and wash the precipitate thoroughly with spirits of wine.

4. *Methods based upon the separation of oxides insoluble in nitric acid.*

a. TIN FROM METALS OF GROUPS IV. AND V. IN ALLOYS.

Treat the finely divided alloy with nitric acid as directed § 101, 1, *a*., and filter the solution from the undissolved binoxide of tin. The filtrate contains the other metals as nitrates. (In presence of bismuth, wash first with water containing nitric acid.) As binoxide of tin is liable to retain traces of copper, the safest way, in an accurate analysis, is to test it for such admixtures, and to determine the quantity of them as directed § 132, A. 2. *b*. *β*.

b. TIN FROM THE OXIDES OF GROUPS I., II., III., AND ALSO FROM PROTOXIDE OF MANGANESE, OXIDE OF ZINC, PROTOXIDE OF NICKEL, PROTOXIDE OF COBALT, OXIDE OF COPPER, and probably also from some other oxides (*Löwenthal*, Journal f. prakt. Chem. 60, 257).

Precipitate the hydrochloric acid solution, which must contain the tin entirely as binoxide (bichloride), as directed § 101, 1, *b.*; and separate the precipitated binoxide of tin from the fluid, which contains the other oxides. In the process attend to the following points:

a. Sulphate of soda is mostly to be preferred as precipitating agent, where the choice is permitted.

β. When the precipitate of binoxide of tin has subsided, decant the supernatant fluid, pass through a filter, repeat this decantation several times, and then treat the precipitate with a mixture of one part of nitric acid of 1·2 sp. gr., and nine parts of boiling water, before you transfer it to the filter for the purpose of completing the washing. The results are very satisfactory.

If the binoxide of tin is mixed with other oxides admitting of reduction by ignition in a stream of hydrogen, the oxides may also be reduced in this manner, and the metals then treated as in *a.*

c. ANTIMONY FROM THE METALS OF GROUPS IV. AND V. IN ALLOYS.

Proceed as in *a.*, filter from the precipitate, and convert it into antimonious acid by ignition (§ 100, 2). The results are only approximate, as some teroxide of antimony dissolves.

5. *Methods based upon the volatility of many chlorides or metals.*

a. TIN, ANTIMONY, ARSENIC FROM COPPER, SILVER, LEAD, COBALT, NICKEL.

Treat the sulphides of the metals in a stream of chlorine, proceeding exactly as directed § 131, 6, *a.* In presence of antimony fill the flasks *f* and *h* with a solution of tartaric acid in water, mixed with hydrochloric acid. In alloys also the metals may be separated by this method. The alloy must be very finely divided. Arsenical alloys are only very slowly decomposed in this way.

b. BINOXIDE OF TIN, TEROXIDE OF ANTIMONY (AND ALSO ANTIMONIC, ARSENIOUS, AND ARSENIC ACIDS), FROM ALKALIES AND ALKALINE EARTHS.

Mix the solid compound with five parts of pure chloride of ammonium in powder, in a porcelain crucible, cover this with a concave platinum lid, on which some chloride of ammonium is sprinkled, and ignite gently until all chloride of ammonium is expelled; add a fresh portion of that salt to the contents of the crucible, and repeat the operation until the weight of the latter remains constant. In this process the chlorides of the tin, antimony, and arsenic, escape, leaving the chlorides of the alkalies and

alkaline earths behind. The decomposition by this method proceeds most rapidly with arsenical compounds, less quickly with antimonial compounds, and least so with compounds of tin (*H. Rose*).

c. MERCURY FROM GOLD (in alloys, and also in other forms of combination).

The two metals are separated by ignition, and the mercury is either calculated from the loss or collected and weighed (§ 94).

6. *Method based upon the volatility of tersulphide of arsenic.*

THE ACIDS OF ARSENIC FROM SESQUIOXIDE OF IRON (probably also from protoxide of nickel, oxide of zinc, oxide of copper, oxide of lead, &c.), according to *Ebelmen*.

Heat the oxides in sulphuretted hydrogen, by which process they are completely converted into sulphides. The tersulphide of arsenic volatilises, leaving the sulphides of the other metals behind.

7. *Method based upon the conversion of arsenic into alkaline arseniate.*

ARSENIC FROM THE METALS AND OXIDES OF GROUPS II., IV., AND V.

If the substance contains the arsenic in the form of arsenites, or arseniates, it is fused with three parts of carbonate of soda and potassa and one part of nitrate of potassa; if it is an alloy, it is fused with three parts of carbonate of soda and one part of nitrate of potassa. In either case the residue is boiled with water, and the solution, which contains the arseniates of the alkalies, filtered from the undissolved oxides or carbonates. The arsenic acid is determined in the filtrate as directed § 102, 2. If the quantity of arsenic is small the fusion may be made in a platinum crucible; but if it is more considerable the process must be conducted in a porcelain crucible, as platinum would be injuriously affected by it. In the latter case bear in mind that the fused mass is contaminated with silicic acid and alumina.

8. *Method based upon the separation of arsenic as arseniate of suboxide of mercury.*

ARSENIC ACID FROM THE ALKALIES, ALKALINE EARTHS, OXIDE OF ZINC, PROTOXIDE OF COBALT, PROTOXIDE OF NICKEL, OXIDE OF LEAD, OXIDE OF COPPER, OXIDE OF CADMIUM.

Proceed exactly as in the separation of phosphoric acid by mercury (§ 106, I. *b.* γ.). The arsenic acid *cannot* be determined in the insoluble residue in the way in which the phosphoric acid is determined. Treat the filtrate as directed § 106, II. *k.* (*H. Rose*).

9. *Method based upon the separation of arsenic as arseniate of magnesia and ammonia.*

ARSENIC ACID FROM ALUMINA AND THE OXIDES OF GROUP IV.

Proceed as directed § 106, II. *f.* α. Treat the precipitate of arseniate of magnesia and ammonia as directed § 102, 2.

10. *Method based upon the insolubility of chloride of silver.*

SILVER FROM GOLD.

Treat the alloy with nitrohydrochloric acid, dilute, and filter the solution of the terchloride of gold from the precipitated chloride of silver. This method is applicable only if the alloy contains less than 15 per cent of silver; for if it contains a larger quantity the chloride of silver which forms protects the undecomposed portion from the action of the acid. In the same way silver may be separated also from *platinum*.

11. *Method based upon the insolubility of certain sulphates in water or spirits of wine,*

ARSENIC ACID FROM BARYTA, STRONTIA, LIME, AND OXIDE OF LEAD.

Proceed as in the separation of phosphoric acid from the same oxides (§ 106, II. *c.*). The compounds of these bases with arsenious acid are first converted into arseniates, before the sulphuric acid is added; this conversion is effected by heating the hydrochloric acid solution with chlorate of potassa, or by repeated evaporation with nitric acid.

12. *Method based upon the insolubility of arseniate of sesquioxide of iron.*

ARSENIC ACID FROM THE BASES OF GROUPS I. AND II., AND FROM OXIDE OF ZINC, AND THE PROTOXIDES OF MANGANESE, NICKEL, AND COBALT.

Precipitate the arsenic acid, according to circumstances, as directed § 102, 3, *a.* or *b.*, filter, and determine the bases in the filtrate.

13. *Method based upon the different deportment of the several metals with cyanide of potassium.*

GOLD FROM LEAD AND BISMUTH.

These metals may be separated in solution by cyanide of potassium, in the same way in which the separation of mercury from lead and bismuth is effected (§ 131, 3, *a.*). The solution of the double cyanide of gold and potassium is decomposed by boiling with hydrochloric acid, and, when the expulsion of the hydrocyanic acid is effected, the gold is determined by one of the methods given in § 98.

II. SEPARATION OF THE OXIDES OF THE SIXTH GROUP FROM EACH OTHER.

§ 133.

Index: Platinum from gold: 1;—from antimony, tin, and arsenic: 2.
Gold from platinum: 1;—from antimony, tin, and arsenic: 2.
Antimony from gold and platinum: 2;—from tin: 4, *a.*; 6, *a.*;
—from arsenic: 3, *b.*; 4, *a.* and *b.*; 5, *a.*

Tin from gold and platinum : 2 ;—from antimony : 4, *a.* ; 6, *a.* ;—from arsenic : 3, *a.* ; 6, *a.* ;—protoxide of tin from binoxide of tin : 7, *a.* ; 8, *a.*

Arsenic from gold and platinum : 2 ;—from antimony : 3, *b.* ; 4, *a.* and *b.* ; 5, *a.* ;—from tin : 3, *a.* ; 6, *a.* ;—arsenious acid from arsenic acid : 5, *b.* ; 7, *b.* ; 8, *b.*

1. *Method based upon the precipitation of platinum by chloride of potassium.*

PLATINUM FROM GOLD.

Precipitate from the solution of the chlorides of the metals the platinum as directed § 99, *b.*, and determine the gold in the filtrate as directed § 98, *b.*

2. *Method based upon the volatility of the chlorides of the inferior metals.*

PLATINUM AND GOLD FROM TIN, ANTIMONY, AND ARSENIC.

Heat the finely divided alloy or the sulphide in a stream of chlorine gas. Gold and platinum are left behind (compare § 132, B. 5, *a.*). The chlorides of the other metals volatilise.

3. *Methods based upon the volatility of arsenic and tersulphide of arsenic.*

a. ARSENIC FROM TIN (*H. Rose*).

Convert into sulphides or into oxides, dry at 212°, and heat a weighed portion of the dry mass in a bulb-tube, gently at first, but gradually more strongly, conducting a stream of dry sulphuretted hydrogen gas through the tube during the operation. Sulphur and tersulphide of arsenic volatilise, sulphide of tin is left behind. The tersulphide of arsenic is received in a small flask connected with the bulb-tube, in the manner described § 131, 6, *a.*, and which contains dilute solution of ammonia. When upon continued application of heat you observe no further sign of sublimation in the colder part of the tube, drive off the sublimate which has gathered inside the bulb on the glass, allow the tube to cool, and then cut it off above the coating. Divide the separated part in pieces, and heat these with some solution of soda until the sublimate is dissolved ; unite the solution with the ammoniacal fluid in the receiver, add hydrochloric acid, then, without filtering, chlorate of potassa, and heat gently until the tersulphide of arsenic is completely dissolved. Filter from the sulphur, and determine the arsenic acid as directed § 102, 2. The quantity of tin cannot be calculated at once from the blackish-brown sulphide of tin in the bulb, since this contains more sulphur than corresponds to the formula Sn S. It is therefore weighed, and the tin determined in a weighed portion of it, by converting it into binoxide, which is effected by moistening with nitric acid, and ignition (§ 101, 1, *c.*).

Tin and arsenic in alloys are more conveniently converted into oxides by cautious treatment with nitric acid. If, however, it is wished to convert

them into sulphides, this may readily be done by heating one part of the finely divided alloy with five parts of carbonate of soda and five parts of sulphur, in a covered porcelain crucible, until the mass is in calm fusion. It is then allowed to cool, dissolved in water, the solution filtered from the sulphide of iron, &c., which may possibly have formed, and the filtrate precipitated with hydrochloric acid.

b. Arsenic from antimony in alloys.

Heat a weighed portion of the finely divided alloy with two parts of carbonate of soda and two parts of cyanide of potassium in a bulb-tube, conducting through the tube dry carbonic acid; apply a gentle heat at first, but increase it gradually to a high degree of intensity, and continue heating until no more arsenic volatilises. Take care not to inhale the escaping fumes; the safest way is to put the hind part of the bulb-tube into a flask, in which the arsenic will sublime. Allow the tube to cool, treat the contents of the bulb first with a mixture of equal parts of spirits of wine and water, then with water, and weigh the residuary antimony. The quantity of the arsenic is calculated from the loss. This method gives only approximate results. The direct fusion of the alloy in a stream of carbonic acid, or hydrogen gas would give most inaccurate results, as a large quantity of antimony would volatilise under such circumstances.

4. *Methods based upon the insolubility of antimoniate of soda.*

a. Antimony from tin and arsenic in alloys (*H. Rose*).

Oxidise a weighed sample of the finely divided alloy in a porcelain crucible, with nitric acid of 1·4 specific gravity, adding the acid gradually. Dry the mass on the water-bath, transfer it to a silver crucible, rinsing the last particles adhering to the porcelain into the silver crucible, with solution of soda, dry again, add eight times the bulk of the mass of solid hydrate of soda, and fuse for some time. Allow the mass to cool, and then treat with hot water, until the undissolved residue presents the appearance of a fine powder; dilute with some water, and add alcohol of 0·83 sp. gr. in sufficient quantity to make the proportion of its volume to that of the water as 1 to 3. Allow the mixture to stand at rest for twenty-four hours, stirring it frequently, filter, transfer the last adhering particles from the crucible to the filter by rinsing with dilute spirits of wine (one volume of alcohol to three volumes of water), and wash the undissolved residue on the filter, first with spirits of wine containing one volume of alcohol to two volumes of water, then with a mixture of equal volumes of alcohol and water, and finally with a mixture of three volumes of alcohol and one of water. Add to each of the alcoholic fluids used for washing a few drops of solution of carbonate of soda. Continue the washing until the color of a portion of the fluid running off remains unaltered upon being acidified with hydrochloric acid and mixed with sulphuretted hydrogen water.

Rinse the antimoniate of soda from the filter, wash the latter with a mixture of hydrochloric acid and tartaric acid, dissolve the antimoniate in this mixture, precipitate with sulphuretted hydrogen, and determine the antimony as directed § 100, 1, *b*.

To the filtrate which contains the tin and arsenic, add hydrochloric acid, which produces a precipitate of arseniate of binoxide of tin; conduct now into the unfiltered fluid sulphuretted hydrogen for some time, allow the mixture to stand at rest until the odor of that gas is almost completely gone off, and then separate the weighed sulphides of the metals as in 3, *a*.

If the substance contains *antimony* and *arsenic* only, the alcoholic filtrate is heated, with repeated addition of water, until the fluid scarcely retains the odor of alcohol; hydrochloric acid is then added, and the arsenic acid determined as arseniate of magnesia and ammonia (§ 102, 2).

b. Determination of the sulphide of arsenic contained in the commercial sulphide of antimony (*Wackenroder*).

Deflagrate twenty grammes of the finely pulverised sulphide of antimony with forty grammes of nitrate of potassa and twenty grammes of carbonate of soda, by projecting the mixture gradually into a red hot hessian crucible; treat the strongly ignited mass repeatedly with water, filter the solution, acidify the filtrate with hydrochloric acid, treat it with sulphurous acid, and precipitate the arsenic with sulphuretted hydrogen. Digest the moist precipitate, which contains a small admixture of antimony, with carbonate of ammonia, filter, acidulate the filtrate, conduct sulphuretted hydrogen into the fluid, and determine the arsenic as tersulphide, as directed § 102, 4.

5. *Methods based upon the precipitation of arsenic as arseniate of magnesia and ammonia.*

a. Arsenic from antimony.

Oxidise the metals or sulphides with nitrohydrochloric acid or hydrochloric acid and chlorate of potassa, add tartaric acid, a large quantity of chloride of ammonium, and then ammonia in excess. Should the addition of the latter reagent produce a precipitate, this is a proof that an insufficient quantity of chloride of ammonium or of tartaric acid has been used, which error must be rectified before you proceed with the analysis. Then precipitate the arsenic acid as directed § 102, 2, and determine the antimony in the filtrate as directed § 100, 1, *b*.

b. Arsenious acid from arsenic acid.

Mix the solution with a large quantity of chloride of ammonium, precipitate the arsenic acid as directed § 102, 2, and determine the arsenious acid in the filtrate by precipitation with sulphuretted hydrogen (§ 102, 4).

6. *Methods based upon the precipitation of the metals in the metallic state.*

a. Tin from antimony (*Gay-Lussac*).

Heat a weighed portion of the finely divided alloy (or other form of combination) with hydrochloric acid, add chlorate of potassa in small portions until the mass is dissolved, and divide the fluid into two equal portions, *a.* and *b.* In *a.* precipitate both metals on a tin rod, rinse them off, and weigh; add to *b.* a tolerably large amount of hydrochloric acid, put in a clean slip of tin, and heat for some time. By this process the antimony is completely thrown down in form of a black powder, and the bichloride of tin reduced to protochloride. Wash the antimony from the slip of tin with water containing hydrochloric acid, collect it upon a weighed filter, dry, and weigh. The difference gives the quantity of the tin.

b. Determination of arsenic in metallic tin (*Gay-Lussac*).*

Dissolve with gentle heat the laminated or granulated† metal in a mixture of one equivalent of nitric acid and nine equivalents of hydrochloric acid. The solution ensues without evolution of gas; protochloride of tin and chloride of ammonium are formed, the arsenic remains behind as a powder. $NO_5 + 9\ HCl + 8\ Sn = 8\ SnCl + NH_4, Cl + 5\ HO$. The nitro-hydrochloric acid must therefore not be used in a much larger proportion than will give to eight equivalents of metal one equivalent of NO_5, and nine equivalents of HCl.

7. *Methods of analysis by measure.*

a. Protoxide of tin in presence of binoxide.

Dissolve in hydrochloric acid, carefully excluding the air during the operation, dilute the fluid with boiled water to a certain definite volume, measure off a portion of it, and determine in this the quantity of the protoxide of tin as directed § 101, 2. In another portion either determine the total quantity of the tin by analysis by measure, reducing the bichloride first to protochloride (§ 101, 2, *b.*), or oxidise the whole of the tin in it by heating with chlorate of potassa, and determine the tin according to § 101, 1, *b.*

b. Arsenious acid from arsenic acid.

If the substance to be analysed is solid determine in one portion the arsenious acid, by analysis by measure, according to the directions of § 102, 5; in another portion the total quantity of the arsenic, by one of the methods given in § 102.

If the acids are in solution the arsenious acid may be determined also by mixing a weighed portion of the fluid with hydrochloric acid and some solution of indigo, and adding solution of chloride of lime of known

* Ann. de Chim. et de Phys. 23, 128. *Liebig* and *Kopp's* Annual Report, 1847 and 1848, 2, 231.

† Prepared by pouring the fused metal into water.

strength, until the blue color of the indigo has disappeared. For the details of the process see the article on chlorimetry (§ 189, etc.).

8. *Indirect methods.*

a. PROTOXIDE OF TIN IN PRESENCE OF BINOXIDE.

Determine in a portion of the substance the total quantity of the tin; dissolve another portion in hydrochloric acid, taking care to exclude the air, and drop the solution into a large excess of solution of chloride of mercury, with stirring. Treat the precipitate of subchloride of mercury formed, as directed § 94, 2. One equivalent of it (Hg_2Cl) corresponds to one equivalent of protochloride of tin (SnCl). (*H. Rose.*)

b. ARSENIOUS ACID IN PRESENCE OF ARSENIC ACID.

Determine in a portion of the substance the total quantity of the arsenic; dissolve another portion in hydrochloric acid (of course no oxidising agents, such as nitrates, &c., must be present), and add an excess of solution of sodio- or ammonio-chloride of gold (terchloride of gold and chloride of sodium or ammonium). Let the mixture stand several days in the cold, or, in the case of dilute solutions, at a gentle heat, filter the fluid from the separated gold, and determine the latter as directed § 98, *b*. Keep the filtrate to make sure whether an additional quantity of gold may not separate, which is sometimes the case. Two equivalents of gold correspond to three equivalents of arsenious acid ($2\ AuCl_3 + 3\ AsCl_3 = 3\ AsCl_5 + 2\ Au$). (*H. Rose.*)

II. THE SEPARATION OF THE ACIDS FROM ONE ANOTHER.

I have again to remark that the methods of separation given in the following paragraphs, proceed generally upon the assumption that the acids exist either in the free state, or in combination with alkaline bases. Compare what is said on the subject, page 279.

FIRST GROUP.

ARSENIOUS ACID—ARSENIC ACID—CHROMIC ACID—SULPHURIC ACID—PHOSPHORIC ACID—BORACIC ACID—OXALIC ACID—HYDROFLUORIC ACID—SILICIC ACID—CARBONIC ACID.

§ 134.

1. ARSENIOUS ACID AND ARSENIC ACID FROM ALL OTHER ACIDS.

Precipitate the arsenic from the solution by means of sulphuretted hydrogen (§ 102, 4), filter, and determine the other acids in the filtrate. If chromic acid is present this is reduced, before the addition of the sulphuretted hydrogen, by one of the methods given in § 104; as sulphur would fall down with the tersulphide of arsenic if this precaution were neglected.

Arsenic acid must, wherever it is practicable, be reduced by sulphurous acid, before the addition of the sulphuretted hydrogen.

2. Sulphuric acid from the other acids.

a. From the acids of arsenic, from phosphoric, boracic, hydrofluoric, oxalic, silicic, and carbonic acids.

Make the dilute solution strongly acid with hydrochloric acid, mix with chloride of barium, and filter the sulphate of baryta from the solution, which contains all the other acids. Determine the sulphate of baryta as directed § 105.

b. From hydrofluoric acid in insoluble compounds.

A mixture of sulphate of baryta and fluoride of calcium cannot be decomposed by simple treatment with hydrochloric acid; the insoluble residue always containing besides sulphate of baryta, sulphate of lime and fluoride of barium. The end in view may be attained by the following process: fuse the substance with six parts of carbonate of soda and potassa, and two parts of silicic acid; allow the mass to cool, treat it with water, and the solution obtained with carbonate of ammonia; filter, wash the separated silicic acid with dilute solution of carbonate of ammonia, supersaturate the filtrate with hydrochloric acid, and precipitate with chloride of barium.

If you wish to determine the fluorine also, acidify with nitric acid, precipitate with nitrate of baryta, then saturate with carbonate of soda, and precipitate the fluoride of barium by spirits of wine. Wash a long time, first with spirits of wine of 50 per cent, then with strong alcohol; dry, ignite, and weigh (*H. Rose*).

c. If much chromic acid is present, the latter is reduced most conveniently by boiling the dry compound with concentrated hydrochloric acid (if this process is conducted according to the directions of § 104, I. *d.* β., the quantity of the chromic acid present is also ascertained); the solution is considerably diluted, and the sesquioxide of chromium precipitated by ammonia (§ 84); the fluid is filtered from the precipitate, hydrochloric acid added to the filtrate, and the sulphuric acid thrown down by chloride of barium.

3. Chromic acid from phosphoric acid.

Precipitate the phosphoric acid as phosphate of magnesia and ammonia (§ 106, I. *b.*). Determine the chromic acid in the filtrate by means of nitrate of suboxide of mercury; or, in another portion of the substance, by the volumetrical method, § 104.

4. Phosphoric acid from boracic acid.

Determine the phosphoric acid in the solution by means of sulphate of magnesia (§ 106, I. *b.*), the boracic acid in the filtrate by one of the methods given in § 107.

5. Phosphoric acid from oxalic acid.

a. If the two acids are to be determined in one and the same sample of the substance, the aqueous solution is mixed with sodio-chloride of gold in excess, heat applied, and the quantity of oxalic acid present calculated from that of the reduced gold (§ 108, *b.* *a.*). The gold added in excess is separated from the filtrate by means of oxalic acid, and the phosphoric acid then precipitated by sulphate of magnesia. If the compound does not dissolve in water, hydrochloric acid is used as solvent, and the process conducted as directed § 108, *b.* *β.* The gold is, in that case, precipitated from the filtrate by sulphuretted hydrogen, without applying heat.

b. If there is a sufficient quantity of disposable substance to allow it, the oxalic acid is determined in one portion according to the directions of § 108, *c.*, and the phosphoric acid in another portion. In cases where the substance is soluble in water, the phosphoric acid may—if the proportion of oxalic acid is not too considerable—be precipitated at once with sulphate of magnesia, in presence of chloride of ammonium and ammonia; in the contrary case, the substance is ignited with carbonate of soda and potassa, which destroys the oxalic acid, and the phosphoric acid determined in the residue.

6. METALLIC FLUORIDES FROM PHOSPHATES.

a. The substance is soluble in water.

a. If the substance contains a *relatively large* quantity of fluorine, which will permit its estimation from the difference, the solution is precipitated by chloride of calcium; and the precipitate washed, dried, ignited, and weighed. It consists of phosphate of lime and fluoride of calcium. It is heated in a platinum vessel, until all the fluorine has escaped as hydrofluoric acid, care being taken not to raise the heat to a degree at which sulphuric acid volatilises; the lime and the phosphoric acid are then determined according to the directions of § 106, II. *c.* If the phosphoric acid and lime are deducted from the total weight of the precipitate, the fluorine is found by the following calculation:—

The eq. of the fluorine less the eq. of the oxygen : the eq. of the fluorine

::

the ascertained loss of weight : the fluorine sought.

β. If the substance contains *relatively little* fluorine, the solution is mixed with basic nitrate of suboxide of mercury. A yellow precipitate of basic phosphate of suboxide of mercury is produced, the fluoride of mercury remaining in solution. The phosphoric acid in the precipitate is determined as directed § 106, I. *b.* *γ.* The filtrate is neutralised with carbonate of soda, sulphuretted hydrogen conducted into the unfiltered fluid, which is then filtered, and the fluorine determined as directed § 109, I. (*H. Rose*).

b. If the substance is not soluble in water, but yet decomposable by acids, the method *a.* *a.* may equally be applied. The substance is first

dissolved in hydrochloric acid, and the solution then evaporated with sulphuric acid.

b. If the substance is not decomposed by acids, it is fused with carbonate of soda and silicic acid (see § 134, 8).

7. Metallic fluorides from silicic acid and silicates.

A great many native silicates contain metallic fluorides; care therefore must always be taken in the analysis of minerals, not to overlook the latter.

If the silicates containing the metallic fluorides, are decomposable by acids (which is only rarely the case)—and the silicic acid is separated, in the usual way, by evaporation, the whole of the fluorine may volatilise.

a. Berzelius's method.

Fuse the finely pulverised and elutriated substance with four parts of carbonate of soda, for some time, at a strong red heat; digest the mass in water, boil, filter, and wash, first with boiling water, then with solution of carbonate of ammonia. The filtrate contains all the fluorine as fluoride of sodium, and, besides this, carbonate of soda, silicate of soda, and a mixture of soda and alumina. Mix the filtrate with carbonate of ammonia, and heat the mixture, replacing the carbonate of ammonia which evaporates. Filter off the precipitate of hydrate of silicic acid and hydrate of alumina, and wash with carbonate of ammonia. Heat the filtrate until the carbonate of ammonia is completely expelled, and determine the fluorine as directed § 109. To separate the silicic acid, the two precipitates are decomposed with hydrochloric acid, as directed § 111, II. *a.**

β. Wöhler's method (applicable only in the analysis of susbtances which contain a large proportion of fluorine, and are readily decomposed by sulphuric acid).

Reduce the compound under examination to the very finest powder, introduce this into a small flask, pour pure sulphuric acid over it, close the flask quickly with a perforated cork into which a small tube with chloride of calcium is fitted, weigh the apparatus with the greatest dispatch, and then apply heat until the evolution of fumes of fluoride of silicon cease; remove the last remaining traces of the gas from the flask, by an exhausting syringe, let the apparatus cool, and then weigh. The loss indicates the weight of the fluoride of silicon expelled in the process. Deduce from this the quantity both of the fluorine and of the silicon, calculate the latter as silicic acid, and add the quantity found to the weight of the silicic acid in the residue.

8. METALLIC FLUORIDES, SILICATES, AND PHOSPHATES, IN THE PRESENCE OF EACH OTHER.

* The whole of the silicic acid may be removed from the filtrate by the treatment with carbonate of ammonia; the addition of carbonate of zinc and ammonia, recommended by *Berzelius*, and afterwards by *Regnault*, appears therefore superfluous (*H. Rose*).

Native compounds of fluorides, silicates, and phosphates are not uncommon. They are decomposed as in 7, *a*. Complete decomposition of the phosphates is not always effected in this process, as, for instance, phosphate of lime is only partially decomposed by fusion with carbonate of soda. The solution remaining after the separation and removal of the silicic acid, and the volatilisation of the carbonate of ammonia, contains, in presence of phosphates, besides fluoride of sodium and carbonate of soda, also phosphate of soda.

Neutralise the fluid nearly with hydrochloric acid, precipitate with chloride of ~~barium~~ calcium, filter, dry, and ignite the precipitate, which consists of fluoride of calcium, phosphate of lime, and carbonate of lime; treat the residue with acetic acid in excess, and evaporate on the water-bath to dryness, and the acetic acid is completely expelled; dissolve the acetate of lime into which the carbonate has been converted by the last operation, with water, weigh the residue, which consists of phosphate of lime and fluoride of calcium, and effect its ulterior decomposition as directed in 6. In the original residue of the first operation and in the precipitate thrown down by carbonate of ammonia, determine the silicic acid, the rest of the phosphoric acid, and the bases.

9. SILICIC ACID FROM ALL OTHER ACIDS (except hydrofluoric acid).

a. In compounds decomposed by hydrochloric acid.

Decompose the substance by more or less protracted digestion with hydrochloric acid or nitric acid, evaporate on the water-bath * to dryness (§ 111, II. *a*.), treat the residue, according to circumstances, with water, hydrochloric acid, or nitric acid, filter the fluid from the residuary silicic acid, and determine the other acids in the filtrate. In presence of boracic acid, the evaporation is effected in a flask, and the escaping fumes are conducted into water, to avoid loss of substance. If carbonates are present, the carbonic acid is determined in a separate portion of the substance.

β. In compounds which are not decomposed by hydrochloric acid.

Decompose the substance by ignition with carbonate of soda and potassa (§ 111, II. *b*. *a*.), and either treat the residue at once cautiously with dilute hydrochloric acid or nitric acid, and the solution thus obtained as in *a*.; or treat the residue with water, precipitate the silicic acid by heating with bicarbonate of ammonia, filter, add the precipitate to the undissolved residue, and determine the silicic acid, in the united mass, by treating this with hydrochloric acid, and proceeding as directed § 111, II. *a*. Determine the other acids in the filtrate. Which of these two methods may be preferable in particular cases depends upon the nature of the bases, and upon the relative proportion of the silicic acid present.

* A higher temperature would not answer.

10. Carbonic acid from all other acids.

When carbonates are heated with stronger acids, the carbonic acid is expelled; the presence of carbonates, therefore, does not interfere with the quantitative estimation of most other acids. And as, on the other hand, the simplest and most ready way of determining the quantity of the carbonic acid present in a compound is to infer it from the loss of weight suffered by ignition, the presence of salts of non-volatile acids does not interfere with the determination of the carbonic acid. Accordingly, compounds containing carbonates, sulphates, phosphates, &c., are analysed in two separate portions, the carbonic acid being determined in one, the other acids in the other sample. In presence of fluorides, one of the *weak* non-volatile acids, such as tartaric acid or citric acid, must be employed to expel the carbonic acid; since, were sulphuric acid or hydrochloric acid used for the purpose, part of the liberated hydrofluoric acid would escape with the carbonic acid. If, as will occasionally happen in an analysis, a mixed precipitate of fluoride of calcium and carbonate of lime is thrown down from a solution, the two salts may be separated by evaporating the mixed precipitate with acetic acid to dryness, and treating the residue with water: the acetate of lime formed from the carbonate is dissolved, the fluoride of calcium is left undissolved.

SECOND GROUP.

HYDROCHLORIC ACID — HYDROBROMIC ACID — HYDRIODIC ACID — HYDROCYANIC ACID — HYDROSULPHURIC ACID (SULPHURETTED HYDROGEN).

I. Separation of the acids of the second group from those of the first.

§ 135.

a. Separation of all the acids of the second group from those of the first.

Mix the dilute solution of the compound under examination with nitric acid, add solution of nitrate of silver in excess, and filter the fluid from the insoluble chloride, bromide, iodide, &c., of silver. The filtrate contains the whole of the acids of the first group, the silver salts of these acids being soluble in water or in nitric acid. Carbonic acid must, under all circumstances, be determined in a separate portion. If this is done as § 110, II. *b.* β., chlorides being present, hydrochloric acid will escape with the carbonic acid. In an accurate analysis, the defect is avoided by adding a solution of sulphate of silver in slight excess, or, according to *Vohl*, by adding some finely triturated oxide of mercury; which addition will at the same time prevent the escape of sulphuretted hydrogen in presence of sulphides;

the latter object may be attained also by the addition of some neutral chromate of potassa.

b. Separation of some acids of the second group from acids of the first group.

As it is inconvenient for the ulterior separation of the acids of the second group to have them all in the form of insoluble silver compounds, the following methods are preferred to that described in *a.*, in cases where *several* acids of the second group have to be separated jointly from acids of the first group.

1. SULPHURIC ACID may be separated from the acids of the second group by the method described in § 134, 2, with this modification, that nitrate of baryta is substituted for chloride of barium.

2. PHOSPHORIC ACID may be precipitated by means of nitrate of magnesia in presence of ammonia and nitrate of ammonia (compare § 106, I. *b.*). The acids of the second group are determined in the filtrate.

3. OXALIC ACID may be readily removed by nitrate of lime.

4. SULPHURETTED HYDROGEN may be separated from the acids of the first group, by nitrate of copper, or of a solution of arsenious acid in water, to which some nitric acid is added.

5. CHLORINE IN SILICATES.

α. If the silicates dissolve in dilute nitric acid, precipitate the solution at once with nitrate of silver, without applying heat, remove the excess of silver from the filtrate by dilute hydrochloric acid, still without applying heat, and then separate the silicic acid in the usual way.

β. If the silicate forms a jelly upon its decomposition with nitric acid, dilute, allow it to deposit, filter, wash the silicic acid, and treat the filtrate as in *α.*

γ. If nitric acid fails to decompose the silicates, mix the substance with carbonate of soda and potassa, and moisten the mass with water ; dry in the crucible, fuse, boil with water, remove the silicic acid which may have dissolved, with carbonate of ammonia (§ 134, 7, *α.*), and then precipitate, after addition of nitric acid, with nitrate of silver (*H. Rose*).

6. CHLORIDES IN PRESENCE OF FLUORIDES.

If the substance is soluble in water, the separation may be effected as directed in *a.* ; but it is more convenient to precipitate the fluorine with nitrate of lime, and the chlorine in the filtrate with solution of nitrate of silver. Insoluble compounds are fused with carbonate of soda and silicic acid (see § 134, 7, *α.*).

7. CHLORINE IN PRESENCE OF FLUORINE, IN SILICATES.

Proceed as directed § 134, 7, *α.* Saturate the alkaline filtrate nearly with nitric acid, precipitate with nitrate of lime, separate the fluoride of calcium and the carbonate of lime as directed § 134, 10, and precipitate the chlorine in the filtrate by solution of nitrate of silver.

8. Sulphides from sulphates.

In solid compounds, sulphides of the alkali metals may be separated from sulphates of the alkalies by means of alcohol, in which the former are soluble, the latter insoluble (*H. Rose*); or the substance may be divided into two portions, and the quantity of the sulphide determined in one portion by analysis by measure, or by means of solution of copper (§ 116), the quantity of the sulphuric acid in the other portion, by precipitating with chloride of barium, decanting the fluid, and treating the precipitate with dilute hydrochloric acid before proceeding to filtration. The sulphur which may possibly have fallen down with the sulphate of baryta, is consumed upon the ignition of that salt, and does not interfere, therefore, with the quantitative estimation of the sulphate.

9. Metallic sulphides in silicates.

If the substance is decomposable by acids, reduce it to the very finest powder, and treat this with fuming nitric acid (§ 116, II. 2, *a.*). When the sulphur is completely oxidised, dilute, filter off the silicic acid, add carbonate of ammonia to the filtrate, to remove the portion of silicic acid which may possibly have dissolved, filter again, and determine in the filtrate the sulphuric acid formed.

Appendix: Analysis of compounds containing sulphides of the alkali metals, carbonates, sulphates, and hyposulphites.

§ 136.

The following method was first employed by *G. Werther*,* in the examination of gunpowder residues.

Put the substance into a flask, pour water over it, in which a sufficient quantity of carbonate of oxide of cadmium† is suspended, insert the cork, and shake the vessel frequently. The sulphide of the alkali metal decomposes completely with the carbonate of cadmium. Filter the yellow precipitate off, and treat it with dilute acetic acid (not with hydrochloric acid); the carbonate of cadmium dissolves, the sulphide of cadmium is left undissolved. Oxidise the latter with chlorate of potassa and nitric acid (§ 116, II. 2, *a.* *β.*), and precipitate with chloride of barium the sulphuric acid formed from the sulphide.

Heat the fluid filtered from the yellow precipitate, and mix with solution of nitrate of silver. The precipitate thrown down by that reagent consists of carbonate of silver and sulphide of silver ($KO, S_2O_2 + AgO, NO_5 = KO, SO_3 + AgS + NO_5$). Remove the former salt by means of ammonia, and precipitate from the ammoniacal solution the silver—

* Journ. f. prakt. Chem. 55, 22.

† To obtain the carbonate of oxide of cadmium free from alkali, carbonate of ammonia must be used as precipitant.

after acidifying with nitric acid—by means of chloride of barium. Every equivalent of chloride of silver so obtained corresponds to an equivalent of carbonate.* Dissolve the sulphide of silver in dilute boiling nitric acid, determine the silver in the solution as chloride of silver, and calculate from the resulting number the quantity of the hyposulphite; one equivalent of AgCl corresponds to two equivalents of sulphur in hyposulphurous acid, and accordingly to one equivalent of hyposulphite (KO, S_2O_2).

From the fluid filtered from the sulphide and carbonate of silver, remove first the excess of silver, by means of hydrochloric acid, and then precipitate the sulphuric acid by a salt of baryta. From the weight of the sulphuric acid found you have, of course, to deduct an amount corresponding to the quantity of that acid resulting from the decomposition of the hyposulphurous acid, and accordingly for one equivalent of chloride of silver formed from the sulphide, 0·28 equivalent of sulphuric acid. The balance gives the amount of sulphuric acid originally present in the analysed compound. As a control for the accuracy of your analysis you may determine, in the fluid filtered off from the sulphate of baryta, the alkali as sulphate, as directed in § 76 or § 77.

II. Separation of the acids of the second group from each other.

§ 137.

1. Chlorine from bromine.

All the methods of direct analysis hitherto proposed, to effect the separation of chlorine from bromine, are defective. The bromine is therefore usually determined in a more indirect way.

a. Precipitate with nitrate of silver, wash the precipitate, dry, fuse, and weigh. Transfer a portion of the mixed chloride and bromide of silver to the bulb of a weighed bulb-tube,† fuse in the bulb, let the mass cool, and weigh. This operation gives both the total weight of the tube with its contents, and the weight of the portion of mixed chloride and bromide of silver in the bulb. The greatest accuracy in the several weighings is indispensable. Transmit through the tube a slow stream of dry pure chlorine gas, heat the contents of the bulb to fusion, and shake the fused mass occasionally about in the bulb. After the lapse of about twenty minutes, take off the tube, allow it to cool, hold it in an oblique position, that the chlorine gas may be replaced by atmospheric air, and then weigh. Heat once more, for about ten minutes, in a stream of chlorine gas, and

* A quantity equivalent to the sulphide found has to be deducted from this (KS+CdO, CO_2=CdS+KO, CO_2).

† The best way of effecting the transfer of this portion from the crucible to the tube is to fuse the mass in the crucible again, and then let a portion of it run from the latter into the tube.

weigh again. If the two last weighings agree, the experiment is terminated; if not, the operation must be repeated once more. The loss of weight suffered, multiplied by 4·223 gives the quantity of the bromide of silver decomposed by the chlorine. For the mode of calculating the results, see § 168.

This method gives very accurate results, if the proportion of bromine present is rather large; but uncertain ones in cases where mere traces of bromine have to be determined in presence of large quantities of chlorides, as, for instance, in saline springs. To render the method available in such cases, the great point is to produce a silver compound which contains all the bromine present, and only a small part of the chlorine. This end may be attained in several ways.

a. According to *Fehling*. Mix the solution *cold* with a quantity of solution of nitrate of silver very insufficient to effect complete precipitation, and shake the mixture vigorously. If the amount of the precipitate produced corresponds at all to the quantity of bromine present, the whole of the latter substance is obtained in the precipitate.

Fehling recommends the following proportions:—

To 0·001 of bromine use one-fifth or one-sixth the quantity of solution of nitrate of silver that would be required to effect complete precipitation; —to 0·0001 of bromine, one-tenth;—to 0·00002 of bromine, one-thirtieth; —to 0·00001 of bromine, one-sixtieth.

Wash the mixed precipitate of chloride and bromide of siver *thoroughly*, dry, ignite, weigh, and treat with chlorine, as above. To find the quantity of the chlorine, precipitate another weighed portion of the original solution completely with solution of nitrate of silver, and deduct from the weight of the precipitate the quantity of bromide of silver found.

β. *Marchand* * has slightly modified *Fehling's* method. He reduces with zinc the mixed precipitate of chloride and bromide of silver obtained by *Fehling's* fractional precipitation, decomposes the solution of chloride and bromide of zinc with carbonate of soda, evaporates to dryness, and treats the residue with absolute alcohol, which dissolves all the bromide of sodium with only a little of the chloride of sodium; he then evaporates the solution to dryness, treats the residue with water, precipitates again with solution of nitrate of silver, and subjects a part of the weighed precipitate to the treatment with chlorine.

b. Determine in a portion of the solution the chlorine + bromine (by precipitation with solution of nitrate of silver), either by analysis by weight or by analysis by measure; and in another portion the bromine, either by the colorimetrical method (§ 113, I. *b*.), or by the volumetrical method (§ 113, I. *c*.); calculate the chlorine from the difference. This method is well adapted for an expeditious analysis of mother liquors.

* Journ. f. prakt. Chem. 47, 363.

2. Chlorine from iodine.

a. Mix the solution with nitrate of protoxide of palladium, and determine the precipitated protiodide of palladium as directed § 114, I. *b.* Conduct sulphuretted hydrogen into the filtrate, to remove the excess of the palladium, destroy the excess of the sulphuretted hydrogen by solution of sulphate of sesquioxide of iron, and precipitate the chlorine ultimately with solution of nitrate of silver. It is generally found more simple and convenient to divide the solution of the substance to be analysed, into two parts, and to precipitate from one portion the iodine, by means of protochloride of palladium, as directed § 114, I. *b.*, from the other portion, the chlorine and iodine jointly with solution of nitrate of silver (§§ 112 and 114), and to calculate the chlorine from the difference. The results are very accurate.

In the case of fluids containing a large proportion of chlorides of the alkali metals, to a small quantity of iodides of the alkali metals, the iodide is concentrated by adding carbonate of ammonia to the fluid, evaporating to dryness, treating the residue with alcohol, evaporating the alcoholic solution, and treating the residue with water.

b. Precipitate a portion of the fluid with solution of nitrate of silver, and determine the chlorine + iodine; in another portion, determine the quantity of the iodine separately by the volumetrical method (§ 114, I. *c.*), and calculate the chlorine from the difference.

c. Proceed exactly as in the indirect determination of bromine in presence of chlorine (§ 137, 1, *a.*). The loss of weight suffered by the silver precipitate in the fusion in chlorine gas, multiplied by 2·569, gives the quantity of the iodide of silver decomposed by chlorine.

d. According to *Moride* (Comp. rend. 35, 789.—Journ. f. prakt. Chem. 58. 317). Free iodine dissolves in benzole, imparting a red color to the fluid; this color is the darker, the greater the quantity of iodine dissolved; upon exposure to the air the iodine volatilises, and the fluid loses its color. If, therefore, a fluid containing an iodide of an alkali metal, is mixed with a few drops of yellow fuming nitric acid and from 2 to 3 grammes of benzol, and the mixture is vigorously shaken; the benzole ascends to the surface, and exhibits a magnificent color, which will indicate even as little as 0·001 grm. of iodine in 4 litres of water. To determine the quantity of the iodine, the iodised benzole is washed with water, shaken with a few drops of solution of nitrate of silver, the iodide of silver formed washed with alcohol of 33 degrees, and determined in the usual way;* chlorine and bromine impart no color to benzole, and remain dissolved in the water with which the benzole is washed. They are precipitated with solution of nitrate of silver.

* It is probable that the iodine may be determined in the benzole solution, approximately by the colorimetrical method, and accurately by *Bunsen's* method (page 261).

3. CHLORINE, BROMINE, AND IODINE FROM EACH OTHER.

a. The three metalloids are determined jointly in a portion of the fluid, by precipitating with solution of nitrate of silver. To determine the iodine, another portion is precipitated with protochloride of palladium in the least possible excess. The fluid filtered from the precipitate is freed from palladium, by means of sulphuretted hydrogen, and the excess of the latter removed by means of sulphate of sesquioxide of iron; the chlorine and bromine are then precipitated jointly, either completely or partially, with solution of nitrate of silver, and the bromine is ultimately determined as directed § 137, 1, *a.*

b. If the compound contains a large proportion of chlorine to a small proportion of bromine, the iodine may be precipitated also by nitrate of protoxide of palladium, as there is no danger in that case of protobromide of palladium being thrown down with the precipitate. The filtrate is treated as in *a.*

Both methods give very accurate results.

c. Separate the iodine by means of benzole (2, *d.*), and determine in the aqueous fluid the bromine and chlorine as in *a.*

d. According to *Grange* (Compt. rend. 33, 627.—Journal f. prakt. Chem. 55, 167). Hyponitric acid (free from nitric acid),* conducted into a pure solution, of bromide of potassium causes no alteration; but if the solution contains an iodide, the iodine separates and imparts a color to the fluid. If chloroform is now added, and the mixture shaken, the iodine dissolves in the chloroform. In the fluid separated from the latter, the bromine is thrown down by means of nitric acid and sulphuric acid added slightly in excess; and the separated bromine is then also removed by chloroform; the chlorine is ultimately determined by means of solution of nitrate of silver.

The quantities of the dissolved iodine (and probably also of the bromine) in the iodised and bromised chloroform may be estimated, according to *Rabourdin*,† by the colorimetrical method; but they may, undoubtedly also be accurately determined by *Bunsen's* methods (§ 113, Appendix, and § 114, Appendix).

4. CYANOGEN FROM CHLORINE, BROMINE, OR IODINE.

a. Precipitate with solution of nitrate of silver, collect the precipitate upon a tared filter, and dry in the water-bath until the weight remains constant; determine the quantity of the cyanogen in it, by the methods of organic elementary analysis. The difference gives the quantity of chlorine, bromine, or iodine.

b. Hydrocyanic acid in presence of hydrochloric acid, in aqueous solu-

* This may be obtained by a more intense ignition of feebly ignited nitrate of oxide of lead.

† Compt. rend. 31, 784. Ann. d. Chem. u. Pharm. 76, 375.

tion. Divide the solution into two portions, determine in one the two acids jointly, by precipitating with solution of nitrate of silver (§ 115). Add to the other portion solution of biborate of soda, evaporate to dryness, heat the residue, but not to fusion, and determine the hydrochloric acid in it. The hydrocyanic acid has been completely volatilised in the process of evaporation with biborate of soda (*Wackenroder*).

c. Determine the elements jointly in a portion of the solution, by precipitating with solution of nitrate of silver, and the cyanogen in another portion, by the volumetrical method (§ 115, I. *b.* and *c.*).

5. SULPHURETTED HYDROGEN FROM HYDROCHLORIC ACID.

The usual method of separating the two acids by means of a metallic salt is liable to give false results, as part of the chloride of the metal may fall down with the sulphide. The safest way therefore, is to precipitate both as silver compounds, dry the precipitate at 212°, and determine the sulphur in a weighed portion. To remove sulphuretted hydrogen from an acid solution in order that chlorine may be determined in the latter by means of nitrate of silver, *H. Rose* recommends to add solution of sulphate of sesquioxide of iron, which will effect the separation of sulphur alone; the separated sulphur is allowed to deposit, and then filtered off. The sulphuretted hydrogen may be determined in another portion, by the volumetrical method (§ 116).

6. A perfectly new method of determining ferrocyanides and ferricyanides in presence of each other will be found in § 198.

THIRD GROUP.

NITRIC ACID—CHLORIC ACID.

I. SEPARATION OF THE ACIDS OF THE THIRD GROUP FROM THOSE OF THE TWO FIRST GROUPS.

§ 138.

a. If you have a mixture of nitric acid or chloric acid with another free acid in a fluid containing no bases, determine in one portion the joint amount of the free acid, by the acidimetrical method, in another portion the acid mixed with the chloric or nitric acid, and calculate the amount of either of the latter from the difference.

b. If you have to analyse a mixture of a nitrate or chlorate with some other salt, determine in one portion the nitric acid or chloric acid, by the volumetrical method (§ 117, II. *a.* and § 118), or, the nitric acid, by means of arsenious acid (§ 117, II. *b.*); and in another portion the other acid. I think I need hardly remark that no substances must be present which would interfere with the application of these methods.

c. From the chlorides of those metals which form with phosphoric acid insoluble tribasic phosphates, the salts of the acids of the third group may be separated also by digesting the solution with freshly precipitated thoroughly washed tribasic phosphate of silver, and boiling the mixture. In this process the chlorides transpose with the phosphate—chloride of silver and phosphate of the metal with which the chlorine was originally combined, being formed, which both separate, together with the excess of the phosphate of silver, whilst the chlorates and nitrates remain in solution (*Chevenix, Lassaigne*).

d. The estimation of the chloric acid in a compound of a chlorate of an alkali and a metallic chloride, may be effected also in the following manner: A weighed portion of the compound is precipitated from the aqueous solution with nitrate of silver, and the precipitated chloride of silver accurately weighed; an equal portion of the substance is cautiously ignited, the residue dissolved in water, nitrate of silver added in excess to the solution, and the precipitated chloride of silver weighed. The quantity of the chloric acid is then calculated from the difference between the respective weights of the two precipitates.

II. Separation of the acids of the third group from each other.

We have as yet no method to effect the direct separation of nitric acid from chloric acid; some indirect method must therefore be employed to determine either of the two acids in presence of the other. No general rules can be given as to which of the indirect methods may be best adapted in particular cases.

SECTION VI.

ORGANIC ELEMENTARY ANALYSIS.

§ 139.

Organic compounds contain only comparatively few of the elements which constitute the material world. A small number of them consist simply of two elements, viz.,

C and H,

The greater number contain three elements, viz., usually,

C, H, and O.

Most of the rest contain four elements, viz., generally,

C, H, O, and N;

A small number contain five elements, viz.,

C, H, O, N, and S,

And a few contain six elements, viz.,

C, H, O, N, S, and P.

This applies to all the natural organic compounds which have as yet come under our notice. But we may *artificially* prepare organic compounds containing other elements besides those enumerated; thus we know many organic substances, the radicals of which contain chlorine, iodine, or bromine; or arsenic, platinum, iron, cobalt, &c., &c.; and it is quite impossible to say which of the other elements may not be similarly capable of forming constituents of organic compounds (constituents of organic radicals).

With these compounds we must not confound those that are to be looked upon as compounds of a higher order, such as tartrate of lead, for instance, silicate of oxide of ethyle, borate of morphia, &c.; since in this class of compounds, of course, all and every one of the elements may happen to be present.

Organic compounds may be analysed either with a view simply to resolve them into their proximate constituents; thus, for instance, a gum resin is resolved into resin, gum, and ethereal oil;—or the analysis may have for its object the determination of the absolute and relative weight of the ultimate constituents (the elements) of the analysed compound. The simple resolution of organic compounds into their proximate constituents, is effected by methods perfectly similar to those used in the analysis of inorganic compounds; that is, the operator endeavors to separate (by solvents, application of heat, &c. &c.) the individual constituents from one another, either *directly*, or after having previously converted them into appropriate forms. We disregard here altogether this branch of organic analysis—of which the methods must be nearly as numerous and varied as the cases which require their application, and proceed at once to treat of the second branch, which, to distinguish it from the other, is called Organic Elementary Analysis.

Organic elementary analysis, as I have already stated, has for its object the determination of the absolute and proportional weight of the individual elements of organic compounds. It teaches us how to convert these elements into compounds of known composition, to separate the new compounds formed from one another, to weigh these, and to calculate from their weight the quantities of the separate elements. Organic elementary analysis, therefore, is based upon the same principle upon which rest most of the methods of separating and determining inorganic compounds.

The decomposition of most organic substances into distinctly characterised and readily separable products which will permit an accurate determination of their weight, offers no great difficulties, and organic elementary analysis is therefore usually one of the more easy tasks of analytical chemistry;—and as the limited number of the elements which constitute organic bodies leads to a great sameness in the products of their decomposition, the analytical process is always very similar, and a few methods suffice for all cases. It is principally ascribable to this latter circumstance that organic elementary analysis has so speedily attained its present high degree of perfection:—the constant examination and improvement of a *few* methods by a *great number* of chemists, could not fail to produce this result.

Organic elementary analysis may have for its object either simply to ascertain the *relative* proportion of the constituent elements of a substance —thus, for instance, woods are analysed to ascertain their value as fuel, fats to ascertain their capacity of furnishing light—or to determine not only the *relative proportions* of the constituent elementary atoms, but likewise their *absolute quantity*, that is, to determine the exact number of atoms of carbon, hydrogen, oxygen, &c. &c., which constitute one atom of the analysed compound. In scientific investigations we have invariably the latter object in view, although we are not yet able to achieve it in all cases. These two distinct objects cannot well be attained by one and the same operation; each requires a different and distinct process.

The methods by which we ascertain the relative proportions of the constituent elements of organic compounds, may be called collectively, "*organic elementary analysis*" in a more restricted sense; whilst the methods which reveal to us the *absolute number* of elementary atoms constituting the complex atom of the analysed compound, may be styled "*determination of the atomic weight of organic bodies.*"

The success of an elementary analysis depends upon two conditions; viz., 1, upon the selection of the proper method; and 2, upon the correct performance of the necessary operations and processes: expertness in this branch may be readily acquired by any one endowed with some patience, clearness of perception, and skill in chemical manipulation. The selection of the method depends upon the knowledge of the constituents of the compound under examination, and the method selected will always require certain modifications, according to the different properties and state of aggregation of these constituents. Before we can proceed, therefore, to describe the various methods applicable in the different cases that may occur, we have first to occupy ourselves here with the means of ascertaining the constituent elements of some one organic substance.

I. Qualitative examination of organic bodies.

§ 140.

It is not necessary for the correct selection of the proper method, to know all and every one of the elements of an organic compound, since the presence or absence of some of them—of oxygen, for instance, has not the slightest modifying influence upon the manner of proceeding with the analysis. But with regard to other elements, such as nitrogen, sulphur, phosphorus, chlorine, iodine, bromine, &c. &c., and also the various metals, it is absolutely indispensable that the operator should know positively whether either of them is present. This may be ascertained in the following manner:—

1. *Testing for nitrogen.*

Substances which contain a tolerably large amount of nitrogen, exhale upon combustion, or when intensely heated, the well-known smell of singed hair or feathers. No further test is required, if this smell is distinctly perceptible; otherwise the following experiments are resorted to:

a. The substance under examination is mixed with caustic potassa in powder, or with *soda-lime* (§ 45, 4) and the mixture heated in a test-tube. If the examined substance contains nitrogen, ammonia will be evolved, which may be readily detected by its peculiar odor, by its reaction upon vegetable colors, and by the formation of white fumes when it is brought into contact with volatile acids. Should these reactions fail to afford positive proof of the presence of nitrogen, every doubt may be removed by the following experiment:—Heat a somewhat larger portion of the substance in a short tube, with an excess of *soda-lime*, and conduct the products of the combustion into dilute hydrochloric acid; evaporate the acid in the water-bath, dissolve the residue in a little water, and mix the solution with bichloride of platinum and alcohol. Should no precipitate form, even after the lapse of some time, the examined substance may be considered free from nitrogen.

b. Lassaigne has recently proposed another method, which is based upon the property of potassium to form cyanide of potassium when ignited with a nitrogenous organic substance. The following is the best mode of performing the experiment:

Heat the substance under examination in a test-tube, with a small lump of potassium, and after the complete combustion of the whole of the potassium, treat the residue with a little water (cautiously); filter the solution, add two drops of solution of sulphate of protoxide of iron containing some sesquioxide, digest the mixture slightly, and add hydrochloric acid in excess. The formation of a blue or blueish-green precipitate or coloration proves the presence of nitrogen.

Both methods are delicate; the latter admits less readily of a mistake than the former.

c. In organic substances containing oxides of nitrogen, the presence of nitrogen cannot be shown by either *a.* or *b.*, but it may be readily detected from the red acid fumes which such substances evolve when heated in a tube.

2. *Testing for sulphur.*

a. Solid substances are fused with about 12 parts of pure hydrate of potassa, and 6 parts of nitrate of potassa; or they are intimately mixed with some nitrate of potassa and carbonate of soda; nitrate of potassa is then heated to fusion in a porcelain crucible, and the mixture gradually added to the fusing mass. The mass is allowed to cool, then dissolved in water, and the solution tested with baryta, after previous acidulation with hydrochloric acid.

b. Fluids are treated with fuming nitric acid, or with a mixture of nitric acid and chlorate of potassa, at first in the cold, ultimately with application of heat; the solution is tested as in *a.*

c. As the methods *a.* and *b.* serve simply to indicate the presence of sulphur in a general way, but afford no information regarding the state or form in which that element may be present, I add here another method, which serves to reveal the presence of that sulphur alone which is contained in the non-oxidised state in organic compounds.

Boil the substance with strong solution of potassa, and evaporate nearly to dryness. Dissolve the residue in a little water, pour the solution into the flask *A* (Fig. 54), and slowly add dilute sulphuric acid through the funnel-tube *c*; if sulphur is present, the slip of paper *b*, which has been thoroughly moistened with solution of acetate of lead, and then touched with a few drops of solution of carbonate of ammonia, will turn brown. I need hardly mention that the cork must not fit air-tight into the mouth of *A*. Instead of in the manner described, the sulphide of potassium formed may be detected also by means of nitroprusside of sodium, or by just acidifying the dilute solution with hydrochloric acid, and adding a few drops of a mixture of sesquichloride of iron, and ferricyanide of potassium. The presence of the smallest amount of sulphuretted hydrogen is at once indicated by a blue coloration of the fluid (*Löwenthal*).



Fig. 54.

3. *Testing for phosphorus.*

The methods described in 2, *a.* and *b.* may likewise serve for phosphorus. The solutions obtained are tested for phosphoric acid with sulphate of magnesia, or with sesquichloride of iron with addition of acetate of soda,

or with molybdate of ammonia (Compare Qualit. Analysis). In method *b.* the greater part of the excess of nitric acid must be removed by evaporation.

4. *Testing for inorganic substances.*

A portion of the substance under examination is heated on platinum foil, to see whether or not a residue remains. When acting upon difficultly combustible substances, the process may be accelerated by heating the spot which the substance under examination occupies on the platinum foil, to the most intense redness, directing the flame of the blow-pipe upon the corresponding point of the lower surface of the foil. The residue is then examined by the usual methods.

These preliminary experiments should never be omitted, since neglect in this respect may give rise to very great errors. Thus, for instance, *taurine*, a substance in which a large proportion of sulphur was afterwards found to exist, had originally the formula $C_4\,N\,H_7\,O_{10}$ assigned for its composition. The preliminary examination of organic substances for chlorine, bromine, and iodine, is generally unnecessary, as these elements do not occur in natural organic compounds; and as their presence in compounds artificially produced by the action of the salt-radicals, requires generally no further proof. Should it, however, be desirable to ascertain positively whether a substance does or does not contain chlorine, iodine, or bromine, this may be done by the same methods which we shall have occasion to describe in the quantitative determination of organic compounds.

II. Organic elementary analysis.

It is not my intention to give an account of the rise and progress of the science of organic elementary analysis; I shall therefore confine myself to the description of the most simple, precise, and universally applicable methods, omitting all the rest.

The accuracy of the results depends both upon the appropriate construction and arrangement of the apparatus required for the various analytical processes, and upon the proper execution of these processes. I am anxious, therefore, to impress upon the student the necessity of bestowing equal attention and diligence upon both; the rules which I have laid down are the fruits of long experience and of innumerable experiments.

A. Analysis of compounds which consist simply of carbon and hydrogen, or of carbon; hydrogen, and oxygen.

§ 141.

The principle of the method which serves to effect the quantitative

analysis of such compounds, and which owes its present perfection to Professor Liebig, is exceedingly simple. The substance under examination is burned, and is thus converted into carbonic acid and water; these products are then separated from each other and weighed, and the carbon of the analysed substance is calculated from the weight of the carbonic acid, the hydrogen from that of the water. If the sum of the calculated weight of the carbon and hydrogen is equal to the original weight of the substance, the absence of oxygen is at once satisfactorily proved; should the sum, on the other hand, be less than the original weight of the substance, the difference will at once indicate the amount of oxygen originally present in the analysed compound.

The combustion is effected either by igniting the organic substance in conjunction with oxygenised bodies which readily yield up their oxygen, (oxide of copper, chromate of lead, &c. &c,); or directly, by means of free oxygen gas; or, finally, at the expense both of free and combined oxygen.

a. SOLID BODIES.*

a. Readily combustible, non-volatile substances. (*Ex. gr.* sugar, starch, tartaric acid, in short, most solid organic substances.)

1. *Liebig's Method.*

I. APPARATUS AND PREPARATIONS NECESSARY FOR ORGANIC ELEMENTARY ANALYSIS.

§ 142.

The following is a complete list of every thing requisite for the performance of an organic elementary analysis:

1. THE SUBSTANCE INTENDED FOR ANALYSIS.—This must be most finely pulverised, and perfectly pure and dry;—for the method of drying organic substances, I refer to § 15.

2. A TUBE IN WHICH TO WEIGH THE SUBSTANCE.—A small perfectly dry glass tube, about 4 or 5 centimeters long, and about 1 centimeter wide, is used for this purpose; the weight of this tube must be accurately determined to within a centigramme. It is advisable to put the tube into the drying apparatus together with the substance intended for analysis. On the balance the tube is appropriately placed in a little foot made of tin.



Fig. 55.

3. THE COMBUSTION TUBE.—A tube of difficultly fusible glass (po-

* For the analysis of fats, waxy bodies, &c., which cannot be reduced to powder, I refer to § 150.

tassa glass), about 2 millimeters thick, 90 centimeters in length, and from 12 to 41 millimeters inner diameter, is softened in the middle before a glassblower's lamp, drawn out as represented in Fig. 56, and finally cut

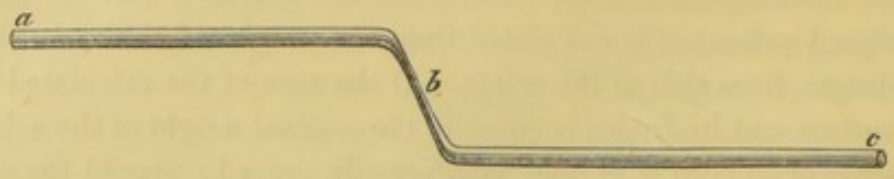


Fig. 56.

in two at *b*. The fine points of the two pieces are then thickened a little and perfectly closed in the flame, and the sharp edges of the open ends *a* and *c*, are slightly rounded by fusion, care being taken to leave the aperture perfectly round; and also to have the pointed end of the tube shaped as shown in Fig. 57, and not as in Fig. 58.



Fig. 57.



Fig. 58.

Two perfect combustion tubes are thus produced. The one intended for immediate use, is cleaned with a linen or paper-wiper attached to a piece of wire, and then thoroughly dried. This is effected either by laying the tube, with a piece of paper twisted over its mouth, for some time on the plate of a common stove, or on a sand-bath; or, in cases where it is desirable to accomplish the end in view in a more expeditious manner, by introducing a small glass tube into it, and moving it backwards and forwards over the flame of a spirit-lamp, continually removing the hot air by suction. (Fig. 59.)

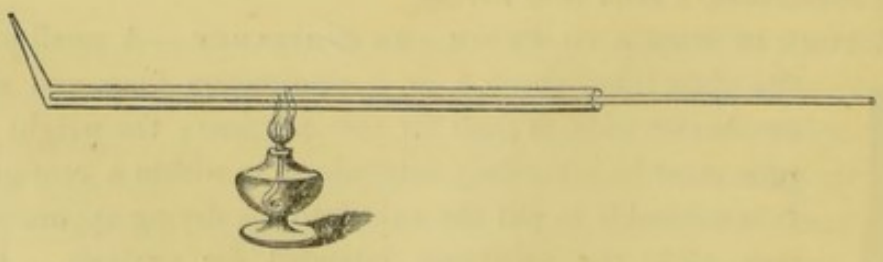


Fig. 59.

The tube, when perfectly dry, is closed air-tight with a perfectly dry cork, and kept in a warm place until required for use.

In default of glass tubes possessed of the proper degree of infusibility, a thin sheet of copper is rolled round the tube, and iron wire coiled round it.

4. A (LIEBIG'S) POTASS-APPARATUS (illustrated by Fig. 60), which may be readily procured from any maker of chemical instruments, or glass-blower. This apparatus is filled to the extent indicated in the engraving, with a clear solution of caustic potassa of 1·27 sp. gr., and which should be as free as possible from carbonate of potassa (§ 45, 7). The introduction of the solution of potassa into the apparatus, is effected by plunging the end *a* (but on no account the other end) into the vessel which contains the solution of potassa, and applying suction to *b*, either by means of a perforated cork, or, and this is the safest way, with the aid of a small suction tube (Fig. 61). The two ends are then wiped perfectly dry with twisted paper slips, and the outside of the apparatus with a clean cloth.

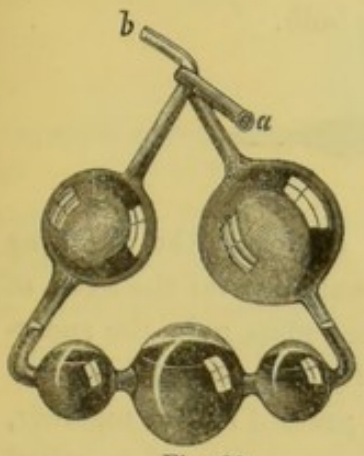


Fig. 60.

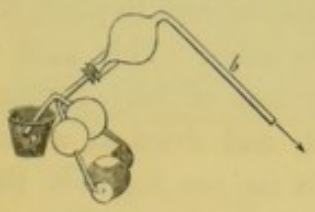


Fig. 61.

5. THE CHLORIDE OF CALCIUM TUBE (Fig. 62) may also be purchased. This tube is prepared for use in the following manner:— In the first place, the aperture *a* of the tube *b a* is loosely stopped with a small cotton plug, reaching about one centimeter into the tube; this is effected by introducing a very loose cotton plug into *c*, and applying a sudden and energetic suction at *b*. The bulb of the tube is then filled with small lumps of chloride of calcium (§ 45, 8, *b*.), and the tube *c d* up to *e* with smaller fragments, intermixed with coarse powder of the same substance; a loose cotton plug is then inserted, and the tube finally closed with a perforated cork, into which a small glass tube is fitted; the protruding part of the cork is cut off, and the cut surface covered over with sealing-wax; the edge of the little tube *f g* is slightly rounded at *g* by fusion (see Fig. 63).



Fig. 62.



Fig. 63.

The tube illustrated by Fig. 64, is still better adapted for the purpose —at least in most cases (for substances containing no sulphur)—as its construction enables the operator to test after the experiment, the reaction,

&c., of the water condensed in the empty bulb *a*. It affords also the advantage that it may be much more frequently used without requiring a new filling than a tube not provided with an empty bulb.



Fig. 64.

6. A SMALL CAOUTCHOUC TUBE.—This is made in the following manner: a piece of sheet india-rubber is slightly warmed over the flame of a spirit-lamp, stretched, and bent round a moistened glass rod; the superfluous portion is removed, with sharp and *perfectly clean* scissors, at one cut, when the fresh cut edges of the caoutchouc, pressed closely together, will completely cohere, provided they have not been moistened or soiled by contact with the fingers. Another piece of india-rubber is then stretched round the first piece, and cut in the same manner, taking care to place the cut edges of the inner and outer tube on opposite sides. This kind of double caoutchouc tube will stand the wear and tear of fifty or more analyses. It is carefully drawn off the glass rod, and dried at a very gentle heat (the temperature of the water bath is far too high for this purpose). The diameter of this little connecting tube must be sufficiently wide to permit the ready introduction of the end *a* of the potassa apparatus, and of the end *f g* of the chloride of calcium tube. (Fig. 63.)

7. SILK CORD.—A strong twisted silk cord is selected; two pieces about ten inches long, are cut off, and each of them tied into a knot at both ends.

N. B.—The introduction of vulcanised india-rubber tubes, has now relieved the analytical chemist from the necessity of making his own caoutchouc tubes; these vulcanised tubes close tight round the glass, without binding.

8. CORK STOPPERS.—Soft and smooth corks, as free as possible from visible pores, are best adapted for the purpose; a cork should be selected which fits perfectly tight, and screws with some difficulty, at the most, to one-third of its length, into the mouth of the combustion tube; a perfectly smooth and round hole, of the same diameter as the end *b a* of the chloride of calcium tube, is then carefully made through the axis of the cork by means of a fine round file; into this perforation the end *b a* of the chloride of calcium tube must fit perfectly air-tight. The cork is then dried in the water-bath. It is advisable always to have two corks of this description ready.

9. A MORTAR FOR MIXING.—A porcelain mortar, of greater width than depth, should be selected; it must be provided with a lip, and free from indentations and fissures, and should not be glazed inside. Before use it is washed with water, allowed to dry in a warm place, and left there till required.

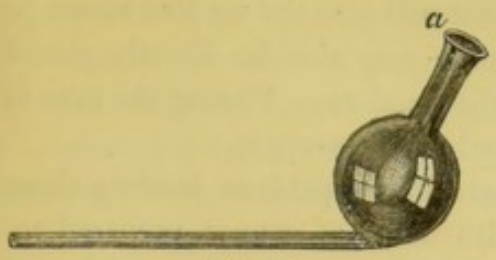


Fig. 65.

10. A SUCTION TUBE.—Fig. 65 illustrates the most appropriate form of a suction tube.

The aperture *a* is closed with a perforated cork, into which the tube *b* of the potass-apparatus is fitted.

11. A GLASS TUBE open at both ends, about 60 centimeters long, and of sufficient width to admit being pushed over the pointed end of the combustion tube; where it is kept in position by making it lean against a filtering stand (see Fig. 26).

12. A sheet of GLAZED PAPER, with cut edges.

13. A LIEBIG'S COMBUSTION FURNACE of sheet iron, with a single and a double screen. This has the form of a long box open at the top and behind. Fig. 66, represents the furnace as seen from the top.

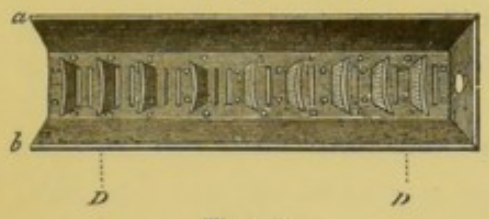


Fig. 66.

It is from 50 to 60 centimeters long, and from 7 to 8 deep, and the bottom, which by cutting small slits in the sheet iron, is converted into a grating, has a width of about 7 centimeters. The side walls are inclined slightly outward, so that at the top they stand about 12 centimeters apart. The furnace is provided with a series of upright pieces of strong sheet iron of the form shown in the cut (*D*), and which are fastened upon the bottom of the furnace, at intervals of about 5 centimeters. These pieces serve to support the combustion tube. They must be of exactly corresponding height, with the round aperture in the front piece of the furnace (Fig. 67, *A*).

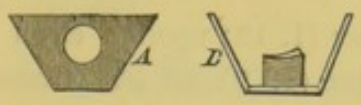


Fig. 67.



Fig. 68.

This aperture must be sufficiently large to admit the combustion tube easily. Of the two screens, the one has the form shown in Fig. 68, the other that shown in Fig. 67, *A*, with the border turned down at the upper edge. The openings cut into the screens must be sufficiently large to receive the combustion tube without difficulty. The furnace is placed upon flat bricks resting upon wood, and is slightly raised at the farther end, by inserting a piece of wood between the supports (see Fig. 71). The apertures of the grating at the anterior end of the furnace must not be blocked up by the supporting brick. In cases where the combustion tubes are of a good quality, the furnace may be raised more advantageously by introducing a little iron rod or a piece of a tile between the furnace

and the supporting brick; this arrangement will give the air free access to all the holes of the grating; or the furnace may also be directly placed upon a tripod, and which, in fact, is now the usual way. Placing the tube in a gutter of very thin sheet iron tends greatly to preserve it.

14. Oxide of copper.—A hessian crucible, capable of holding about three ounces of water, is nearly filled with oxide of copper prepared according to § 45, 1; the crucible is covered with a properly fitting lid, and heated to dull redness; it is then allowed to cool so that, by the time the oxide of copper is required for use, the hand can only just bear contact with it.

15. An exhausting syringe, with chloride of calcium tube. —See Fig. 70. For the manner of performing an organic elementary analysis without the aid of this apparatus, I refer to § 144.

16. Hot sand.—The temperature of this should exceed 212°, but must not be sufficiently high to singe paper.

17. A wooden trough for the sand.—See Fig. 70.

II. Performance of the analytical process.

§ 143.

a. Weigh first the potass-apparatus, then the chloride of calcium tube. Put from 0·350 to 0·600 grm. (more or less according as the substance under examination is rich or poor in oxygen) into the little tube* (I. 2), which must be no longer warm, and weigh the latter accurately with its contents. The weight of the empty tube being known, it is easy to judge of the right quantity of substance required for the analysis. The tube is then closed with a smooth cork, covered on the bottom and sides with tin foil.

b. Spread the sheet of glazed paper (I. 12) upon a clean table, and place the still moderately warm mortar (I. 9) on it. Rinse both the mortar and the still warm combustion tube with a little of the hot oxide of copper;† then fill the combustion tube up to *b*. (see Fig. 69) with

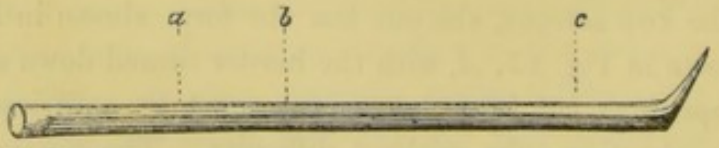


Fig. 69.

oxide of copper, either using the tube itself by way of a ladle to take up the oxide with, or transferring the latter from the crucible to the tube by

* Care must be taken that no substance adheres to the sides of the tube, at least not at the top.

† The oxide which has served for this purpose is put by.

the aid of a small warm funnel and a teaspoon of German silver. Transfer a portion of the oxide of copper from the tube to the mortar, add the substance intended for analysis from the small tube in which it has been weighed, taking care to shake out, as far as practicable, the last adhering traces of the substance; put by the empty tube in a safe place, as you will have to re-weigh it. Mix the substance and the oxide in the mortar most intimately together, taking care to avoid a too energetic pressure upon the pestle; add to the mixture nearly all the oxide of copper still in the tube, leaving only a layer of about three or four centimeters in the latter; and mix the whole most intimately together. Take the pestle out of the mortar, shaking off as clean as possible the minute particles of the mixture adhering to it; transfer the greatest part of the contents of the mortar to the tube, by making use of the latter itself by way of a ladle to take up the mixture with; place the rest of the mixture on a smooth card, and pass it into the tube; rinse the mortar with a little more oxide of copper from the crucible, and put this also into the tube, which will now be full to about the point *a*; fill up to within three or four centimeters from the mouth with pure oxide of copper from the crucible, and close the tube temporarily with a dry cork. The reason why the operation of filling the tube is conducted over the sheet of glazed paper

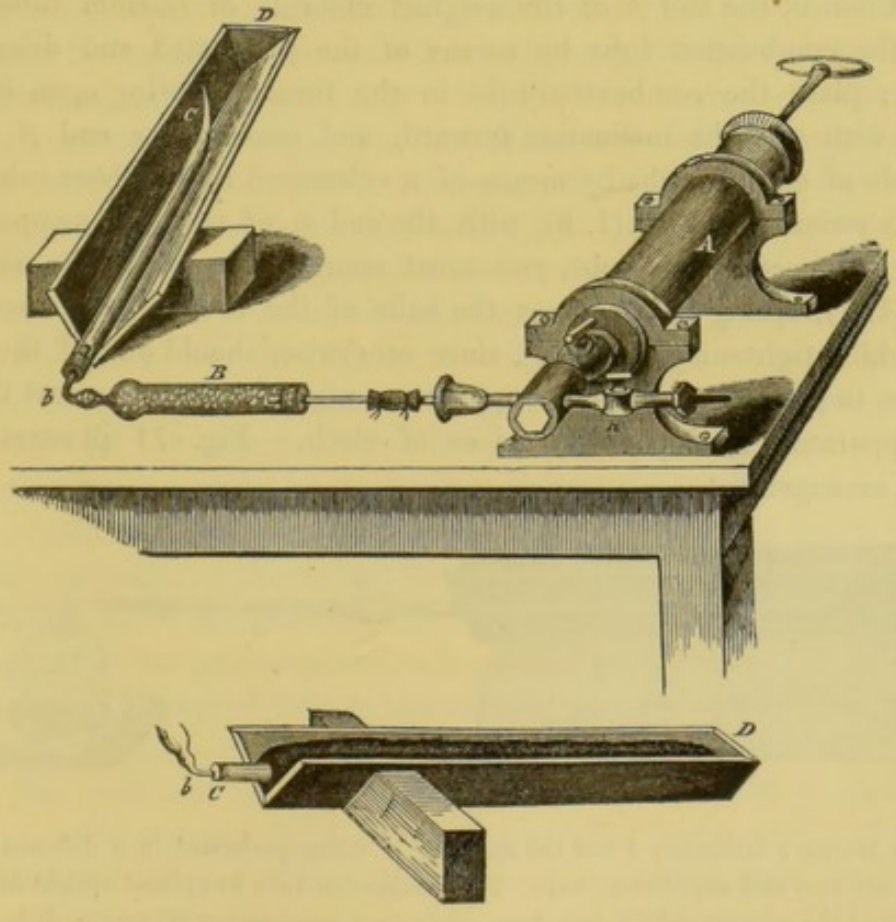


Fig. 70.

is that, should any of the mixture be spilled, this may be readily recovered.*

c. A few gentle taps on the table suffice generally to shake together the contents of the tube, so as to clear the pointed end perfectly from oxide of copper, and leave a free passage above the mixture, from end to end, as shown by the shading in the figure. Should a few gentle taps not suffice to effect this, as will sometimes happen, owing to malformation of the beak, the object in view may be attained by striking the mouth of the tube several times against the side of a table, the tube being all the while held in an horizontal position. Place the tube now into the wooden trough *D*, (Fig. 70), connect it by means of a cork with the chloride of calcium tube *B*, and the latter again with an exhausting syringe. Surround the combustion tube in its whole length with the hot sand (I. 16), and pump out the air *slowly* (quick and incautious pumping might cause a portion of the mixture to pass into the chloride of calcium tube). Open the stopcock *a* to admit a fresh supply of air, which is completely dried in its passage through the chloride of calcium tube; exhaust again, re-admit fresh air, and repeat this process of alternate exhaustion and re-admission of air ten or twelve times, which will ensure the perfect removal of the moisture which the oxide of copper may have absorbed during the operation of mixing.

d. Connect the end *b* of the weighed chloride of calcium tube (I. 5) with the combustion tube by means of the perforated and dried cork (I. 8); place the combustion tube in the furnace, resting upon its supports, with a slight inclination forward, and connect the end β. of the chloride of calcium tube by means of a vulcanised india-rubber tube or of a little caoutchouc tube (I. 6), with the end *m* of the potass-apparatus; if you use a caoutchouc tube, you must secure it on both sides with silk cord (I. 7), taking care to press the balls of the two thumbs close together whilst tightening the cords, since otherwise, should one of the cords happen to give way, the whole apparatus might be broken; rest the potass-apparatus upon a folded piece of cloth. Fig. 71 illustrates the whole arrangement.

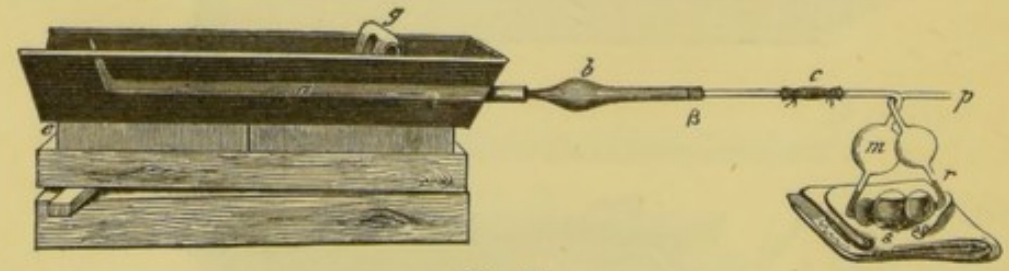


Fig. 71.

* In *Mulder's* laboratory I saw the operation of filling performed in a different but certainly very easy and expeditious way. The combustion tube was placed upright in a retort holder, and the mixture, which had been made in a small copper triturating dish, filled in through a smooth, warm copper funnel.

e. To ascertain whether the joinings of the apparatus fit air-tight, put a piece of wood of the size of a finger (*s*), or a cork or other body of the kind, under the bulb *r* of the potass-apparatus, so as to raise that bulb slightly (see Fig. 71). Heat the bulb *m*, by holding red-hot charcoal near it, until a certain portion of air is expelled through the apparatus; then remove the piece of wood (*s*), and allow the bulb *m* to cool. The solution of potassa will now rise into the bulb *m* and fill it more or less; if the liquid in *m* preserves, for the space of a few minutes, the same level which it has assumed after the perfect cooling of the bulb, the joinings may be considered perfect; should the fluid, on the other hand, gradually regain its original level in both limbs of the apparatus, this is a positive proof that the joinings are not air-tight. The few minutes which elapse between the two observations you may advantageously employ in re-weighing the little tube in which the substance intended for analysis was originally weighed.

f. Arrange the position of the combustion tube in the furnace, in a manner to make the tube project a full inch beyond the latter; suspend the single screen over the exterior border of the furnace, as a protection to the cork; put the double screen over the combustion tube about two inches farther on (see Fig. 71), replace the little piece of wood (*s*) under *r*, and put small pieces of red-hot charcoal first under that portion of the tube which is separated by the screen; surround this portion gradually altogether with ignited charcoal, and let it get red hot; then shift the screen an inch further back, surround the newly exposed portion of the tube also with ignited charcoal, and let it get red hot; shift the screen another inch farther back, surround with ignited charcoal, and proceed in this manner slowly and gradually extending the application of heat to the pointed end of the tube, taking care to wait always until the last exposed portion is red hot, before shifting the screen, and also to maintain the whole of the exposed portion of the tube before the screen in a state of ignition, and the projecting part of it so hot that the fingers can hardly bear the shortest contact with it. The whole process requires generally from three-quarters to one hour. It is quite superfluous, and even injudicious, to keep on fanning the charcoal during the operation;—this should be done only when the process is drawing to an end, as we shall immediately have occasion to see.

The liquid in the potass-apparatus is gradually displaced from the bulb *m* upon the application of heat to the anterior portions of the combustion tube, owing simply to the expansion of the heated air. When the heat reaches that portion of oxide of copper which has been used to rinse the mortar, a little carbonic acid and aqueous vapor begin to be evolved, which drive the whole of the air in the apparatus before them, and force it in large bubbles through the potass-apparatus. The evolution of carbonic acid and aqueous vapor proceeds with greater briskness when

the heat begins to reach the actual mixture; the first bubbles are only partly absorbed in the potassa apparatus, as the carbonic acid contains still an admixture of air; but those which follow are so completely absorbed by the potassa, that a solitary air-bubble only escapes from time to time through the liquid. The process should be conducted in a manner to make the gas-bubbles follow each other at intervals of from half to one second. Fig. 72 shows the usual level of the solution of potassa, during the operation.

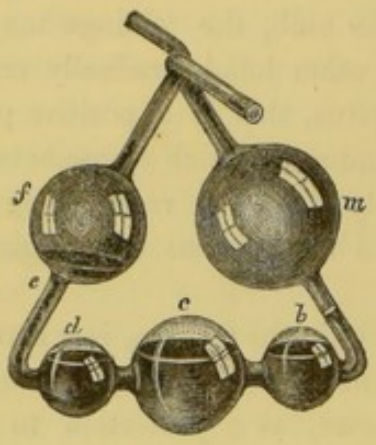


Fig. 72.

It will be seen from this that an air-bubble entering at *a* passes first into the bulb *b*, thence to *c*, from *c* to *d*, and passing over the solution in the latter, escapes finally into the bulb *f*, through the fluid which just covers the mouth of the tube *e*.

g. When the tube is in its whole length surrounded with red hot charcoal, and the evolution of gas has relaxed, fan the burning charcoal gently with a piece of pasteboard. When the evolution of gas has entirely ceased adjust the position of the potass-apparatus to a level, remove the charcoal from the farther end of the tube, and place the screen before the point. The ensuing refrigeration of the tube on the one hand, and the absorption of the carbonic acid in the potass-apparatus on the other, cause the solution of potassa in the latter to recede, slowly at first, but with increased rapidity from the moment the liquid reaches the bulb *m*. If you have taken care to adjust the position of the potass-apparatus correctly, you need not fear that the contents of the latter will recede to the chloride of calcium tube. When the bulb *m* is about half filled with solution of potassa break off the point of the combustion tube with a pair of pliers or scissors, whereupon the fluid in the potass-apparatus will immediately resume its level. Restore the potass-apparatus now again to its original oblique position, invert the glass tube described § 142, 11, over the pointed end, leaning it against the arm of a filtering stand; join the suction tube (§ 142, 10) to the potass-apparatus, and apply suction until the last bubbles no longer diminish in size in passing through the latter.

The analysis is now concluded. Disconnect the potass-apparatus and remove the chloride of calcium tube, together with the cork, which must not be charred, from the combustion tube; remove the cork also from the chloride of calcium tube, and place the latter upright, with the bulb upwards. After the lapse of half an hour weigh the potass-apparatus and the chloride of calcium tube, and then calculate the results obtained. They are generally very satisfactory;—as regards the carbon, they are

nearly *absolutely* accurate, rather somewhat too low (about 0·1 per cent) than too high. The method, indeed, is not altogether free from sources of error; but none of them interfere materially with the accuracy of the results, and the deficiency arising from the one is partially balanced by the excess arising from the other. In the first place, the air which passes through the solution of potassa during the combustion, and finally during the process of suction, carries with it a minute amount of moisture. The loss arising from this cause is increased if the evolution of gas proceeds very briskly, since this tends to heat the solution of potassa; and also if nitrogen gas or oxygen gas pass through the potass-apparatus (compare § 147 and § 151);—this may be remedied, however, by fixing to the exit end of the latter a weighed tube with solid hydrate of potassa or with chloride of calcium. In the second place, traces of carbonic acid from the atmosphere are carried into the potass-apparatus, in the final process of suction; this may be remedied by connecting the pointed end of the combustion tube with a potassa tube by means of a perforated cork. In the third place, it happens frequently, in the analysis of substances containing a considerable proportion of water or of hydrogen, that the carbonic acid is not absolutely dried in passing through the chloride of calcium tube; this also may be remedied by fixing behind the chloride of calcium tube a tube filled with asbestos moistened with sulphuric acid.

As regards the hydrogen, the results are somewhat too high, on an average about 0·1 to 0·15 per cent; this arises principally from the circumstance that the air passing through the apparatus during the final process of suction, conveys a little moisture into the chloride of calcium tube; but this may be readily remedied by connecting the pointed end of the combustion tube with a potassa tube.

I must, however, expressly remark that, in most cases, it is perfectly superfluous to make the operation more complicated for the purpose simply of correcting these defects, more particularly as we know from innumerable experiments the exact limits of the influence which they may exercise upon the accuracy of the results.

2. *Bunsen's modification of Liebig's method* (*Kolbe*, "Handwörterbuch der Chemie," Supplemente, 186).

§ 144.

The essential points of this modification are, that the oxide of copper is allowed to cool in a closed tube, and that instead of being mixed with the substance in a triturating dish, it is transferred at once to the combustion tube, and the operation of mixing effected in the latter; by which means the absorption of moisture from the air is effectually guarded against, and the application of the exhausting syringe dispensed with.

The dried substance is weighed in a tube of thin glass, about 20 centimeters long, and of about 7 centimeters inner diameter; one end of this tube is closed by fusion, the other, during the operation of weighing, with a small smooth cork.

Besides this weighing tube, *Bunsen's* method requires, like *Liebig's*, a combustion tube, potass-apparatus, chloride of calcium tube, connecting tube of vulcanised india-rubber, perforated cork, suction tube, furnace, and oxide of copper (see § 142); and in addition to these, a so-called *filling-tube*, to let the freshly ignited oxide of copper cool in, and to transfer it to the combustion tube, secure from the possible absorption of moisture from the air. A glass tube, 45 centimeters long, and from 2·5 to 3 centimeters wide, closed by fusion at one end, and drawn out at the other to the extent that the opening is reduced to 1 centimeter, is used for this purpose (see Fig. 73).



Fig. 73.

With this tube carefully cleaned and dried inside, the freshly ignited still hot oxide of copper is taken up direct from the crucible, by laying hold of the tube at the lower end with one hand, with a piece of cloth, and plunging the open end repeatedly into the oxide with a rapid turning motion, holding the crucible with the other hand, with the aid of a pair of pincers, in an inclined, almost horizontal, position. When the tube is nearly full it is closed with a small smooth cork. It saves time to fill in at once a sufficient quantity of oxide to last for several analyses. If the cork fits tight, the contents will remain several days fit for use, even though a portion has been taken out, and the tube repeatedly opened.

The filling of the combustion tube is effected as follows: the perfectly dry tube is rinsed with some oxide of copper; the pointed end of the filling tube is inserted into the mouth of the combustion tube, and the two tubes so united are inverted and repeatedly moved up and down, until a layer of from 7 to 10 centimeters long of oxide of copper is transferred to the closed end of the combustion tube; care must be taken in this manipulation to hold the filling tube throughout in a straight line with the combustion tube, as the point of the former is liable to break off if this precaution is neglected.

The tube with the substance intended for analysis has been accurately weighed shortly before, together with the cork. After removing the cork cautiously to prevent the slightest loss of substance, the open end of the

tube is inserted as deep as possible into the combustion tube, and the requisite quantity of substance poured from it, by giving it a few turns, pressing it all the while gently against the upper side of the combustion tube, to prevent its coming into contact with the powder already poured out; the combustion tube is kept, in this manipulation, inclined a little downwards (see Fig. 74).



Fig. 74.

When a sufficient quantity of the substance intended for analysis has been thus transferred from the weighing to the combustion tube, the latter is again brought into a position, which gives to the former a gentle inclination with the closed end downwards. If the little tube is now slowly withdrawn, with a few turns, the powder near the border of the opening falls back into it, leaving the opening free for the cork. The moment it is withdrawn it is corked and weighed, the combustion tube also being meanwhile kept closed with a cork. The difference between the two weighings shows the quantity of substance transferred from the weighing to the combustion tube. The latter is then again opened, and a quantity of oxide of copper, equal to the first, transferred to it from the filling tube, taking care to rinse down with this also the particles of the substance still adhering to the sides of the tube. There are now in the hind part of the tube two layers of oxide of copper, each about ten centimeters long, and with the substance intended for analysis between them.

The next operation is the mixing; this is performed with the aid of a long clean iron wire, with a ring for a handle at one end, and pointed and twisted corkscrew fashion (with one twist only) at the other (see Fig. 75).

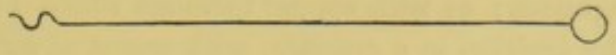


Fig 75.

The wire is pushed down to the end, and rapidly moved about in all directions in the pulverulent mass. A few minutes suffice to achieve perfect intermixture, so perfect indeed, in the case of pulverulent substances which do not cake, that the minutest particles cannot be distinguished with the naked eye. The combustion is effected as in § 143.

β. Difficultly combustible, non-volatile substances, as, for instance, many resinous and extractive matters, coal, &c.

If substances of the kind are analysed by the methods given in §§ 143 and 144, minute particles of carbon are liable to escape combustion. To prevent this, one of the following methods is resorted to.

1. Combustion with chromate of lead.

§ 145.

Of the apparatus, &c., enumerated in § 142, only those marked from 1 to 13 are required, and in addition to these some chromate of lead (§ 45, 2). A narrow combustion tube may be selected, as chromate of lead contains a much larger amount of available oxygen in an equal volume than oxide of copper. A quantity of the chromate more than sufficient to fill the combustion tube is heated in a platinum or porcelain dish over a lamp, until it begins to turn brown; before filling it into the tube, it is allowed to cool down to 212°, and even lower. The process is conducted as the one described in § 143, with the single difference that the application of the exhausting syringe is omitted, as chromate of lead is not hygroscopic like oxide of copper.

One of the principal advantages which chromate of lead has over oxide of copper as an oxidising agent, being its property of fusing at an intense heat, the temperature must, in the last stage of the process of combustion, be raised (by fanning the charcoal, &c.) sufficiently high to fuse the contents of the tube completely as far as the layer of the substance extends. To heat the *anterior* end of the tube to the same degree of intensity, would be injudicious, since the chromate of lead in that part would thereby lose all porosity, and thus also the power of effecting the combustion of the products of decomposition which may have escaped oxidation in the other parts of the tube. As the chromate of lead, even in powder, is, on account of its heaviness, by no means all that could be desired in this latter respect, it is preferable to fill the *anterior* part of the tube, instead of with chromate of lead, with coarsely pulverised oxide of copper deprived of its hygroscopic properties by very intense ignition; or with copper turnings which have been superficially oxidised by ignition in a crucible, with access of air.

In the case of very difficultly combustible substances it is desirable that the mass should not alone readily cake, but also, in the last stage of the process give out a little more oxygen than is given out by chromate of lead. It is, therefore, advisable in such cases to add to the latter one-tenth of its weight of bichromate of potassa in powder (pulverised after previous fusion). With the aid of this addition, complete oxidation of even very difficultly combustible bodies may be effected. (*Liebig.*)

2. Combustion with oxide of copper and chlorate or perchlorate of potassa.

§ 146.

This method requires the whole of the apparatus, &c., enumerated in § 142 or § 144, and in addition a small quantity of chlorate of potassa. The latter substance is freed from water by heating it to the point of fusion, allowing it to cool, and then reducing it to coarse powder, which is kept in a warm place until required for use.

The process is conducted as in § 143 or § 144, with this difference that the layer of oxide of copper in the posterior end of the tube is made about 5 centimeters long, instead of 3 or 4, and is mixed with about one-eighth (from 3 to 4 grms.) of chlorate of potassa; a layer of 2 centimeters of pure oxide of copper is placed between this mixture, and that which contains the substance to be analysed. When in the subsequent heating of the tube, you approach the part occupied by the mixture containing the chlorate of potassa, do not fail to place the hot charcoal with the greatest caution, so as to ensure the very gradual decomposition of the chlorate; since, if you neglect this precaution, the impetuous rush of the gas will eject a small portion of the solution of potassa, thus vitiating the analysis altogether.

The oxygen liberated from the chlorate of potassa drives the carbonic acid which fills the tube before it, effects the combustion of the unconsumed particles of carbon, and oxidises the reduced copper. Oxygen gas can therefore escape through the potass-apparatus only when all that is oxidisable in the tube has been oxidised.

If in the last stage of the process of combustion, a large quantity of gas has in this way passed unabsorbed through the potass-apparatus, it is unnecessary to break off the point, and draw air through the combustion tube, as the latter contains now only oxygen, but no carbonic acid nor aqueous vapour. But through the chloride of calcium tube and the potass-apparatus, air* must be drawn, as they would otherwise be weighed filled with oxygen.

Chlorate of potassa decomposes with a certain degree of violence which does not occur in the decomposition of *perchlorate of potassa*. The latter, prepared by heating the former, may therefore be used instead of it, in the process of combustion, as *Bunsen* has proposed. The fused and still hot perchlorate is introduced into the farther end of the tube, a loose plug of recently ignited asbestos is inserted, and the tube then

* Air dried and freed from carbonic acid answers the purpose best.

filled in the usual way. If *Bunsen's* mode of mixing (§ 144) is adopted, the perchlorate must always be used in this method instead of the chlorate of potassa.

As the dry oxygen gas passing through the potass-apparatus carries away a little aqueous vapor from the solution of potassa, it is advisable to connect the exit tube of the apparatus by a cork, or a tube of vulcanised india-rubber, with a small tube filled with hydrate of potassa, which is afterwards weighed together with the potass-apparatus; the increase of weight of the two is equal to the quantity of the carbonic acid absorbed.

3. Combustion with oxide of copper and oxygen gas.

§ 147.

Many chemists deviate, in the analysis of organic bodies, from the methods described in the preceding paragraphs, and effect the combustion with oxide of copper and oxygen gas, supplied by a gasometer. *Hess*, *Dumas* and *Stass*, *Erdmann* and *Marchand*, *Wöhler*, and others, have proposed methods which are based upon this principle, and which they apply not only in the analysis of difficultly combustible bodies, but also to effect the determination of the carbon and hydrogen in organic substances in general.

As these methods require a gasometer filled with oxygen, also certain arrangements to dry the oxygen completely, and to free it from carbonic acid, it is evident that their apparatus must be more complicated than that of *Liebig*, or *Bunsen*. The application of these new methods is therefore generally resorted to in cases where a number of elementary analyses have to be made in succession; and also more particularly in the analysis of substances which cannot be reduced to powder, and do not admit therefore of intimate mixture with the oxide of copper.

Hess, and *Erdmann* and *Marchand*, use spirits of wine to heat the combustion tube. In English laboratories gas is sometimes employed for the purpose; or red-hot charcoal may be used. Fig. 76 shows an apparatus with charcoal fire.

A is a gasometer with oxygen; the cock *i* is connected by a brass tube with the bulb apparatus *h*, which contains concentrated sulphuric acid. The brass tube is laterally connected, by means of a tube of vulcanised india-rubber, with a gasometer containing atmospheric air; this part of the apparatus is omitted in the engraving. The tube *g* contains solid hydrate of potassa; *a b* represents the combustion tube, which is about 60 centimeters long, and open at both ends. This is connected, by means of perforated corks, at the end *a* with the potassa tube *g*, at the

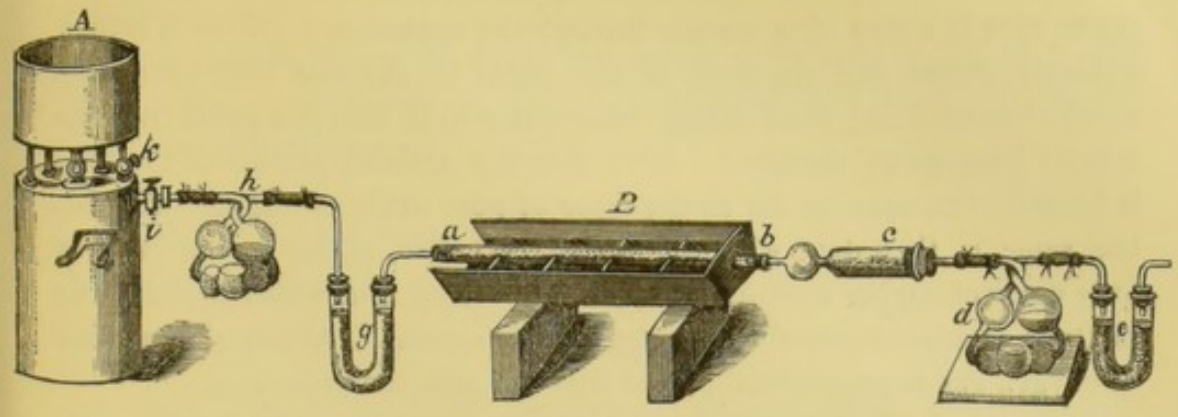


Fig. 76.

end *b* with the chloride of calcium tube *c*; *d* is a potass-apparatus;* *e* contains solid hydrate of potassa.

The ignition of the oxide of copper is effected in the tube itself. To accomplish this a tolerably dense stopper of copper turnings is inserted into *b*, the tube then filled from *a* to two-thirds of its length with oxide of copper; *a* is then joined to *g* and *h*, as shown in the cut, and the tube gently ignited in its whole length, whilst a slow stream of atmospheric air is conducted through it. At the end of this operation the charcoal is removed, the end *b*, which has up to this time remained open, is connected with a small chloride of calcium tube, and the ignited oxide allowed to cool in a slow stream of atmospheric air. When the tube is cold it is opened at the end *a*, the substance introduced with the aid of a tube (compare § 144), and quickly mixed with the oxide by means of the iron wire illustrated by Fig. 75; the hind part of the tube is filled to within a few inches with ignited oxide of copper, cooled in the tube illustrated by Fig. 73; a few gentle taps on the table will suffice to shake the contents down a little, leaving a clear passage above. The connection of *a* with *g* is again made, and the chloride of calcium tube, affixed to *b* during refrigeration of the combustion tube, exchanged for the one marked *c*,† which is accurately weighed first, and to which the weighed apparatus marked *d* and *e* are also joined.

* As the solution of potassa cannot possibly recede with this arrangement of the apparatus, it is preferable to connect the small bulb with the chloride of calcium tube, instead of the large one, as in § 143.

† Instead of drying the cork which connects *c* with the combustion tube, *Erdmann* and *Marchand* cover it with lead foil, in the following manner: the bottom of the cork is covered with a round piece of lead foil of the requisite size, and the projecting border part turned over and pressed firmly against the sides of the cork. The foil is then pierced at the part where it covers the perforation of the cork, by turning the narrow tube of the chloride of calcium apparatus cautiously into the latter from the bottom, then withdrawing it again, and turning it in from the top. In this way the tube is passed through, in most cases, without forcing off the lead foil.

The cock *i*, of the oxygen gasometer is now opened a little,* to allow the gas to pass in a very slow stream through the apparatus ; the cock is then suddenly closed, and the level of the fluids in the two bulb apparatus watched some time ; if no change takes place in it, this is a proof that the several joinings fit air-tight. After this the anterior portion of the tube is heated to redness, as far as the layer of pure oxide of copper extends ; the same is then done with the farther part also, as far as the layer of pure oxide of copper extends, the part intervening, and which contains the mixture, is advantageously protected by two screens. A very slow stream of oxygen gas is transmitted all the time through the apparatus.

The part of the tube containing the mixture is then also heated, proceeding slowly from the anterior to the posterior part. The stream of oxygen gas is gradually somewhat increased, but never so much that oxygen gas escapes through the potass-apparatus *d*. When the tube in its whole length is at a red heat, and the evolution of gas in it has ceased, the cock is opened a little wider, and the transmission of oxygen continued, until at last, when the reduced oxide of copper is completely re-oxidised, the gas begins to escape unabsorbed through the potass-apparatus. The cock of the oxygen gasometer is now shut, whilst that of the air gasometer is opened a little ; the ignited charcoal is removed as far as practicable, and the combustion tube, &c., allowed to cool in a slow stream of atmospheric air. The chloride of calcium tube and the potass-apparatus, with the potassa tube joined to it, are then weighed.

A very great advantage of this method consists in this, that the combustion tube, after the termination of the first, is quite ready for a second analysis.

γ. Volatile substances or bodies suffering alteration at 212° (*losing water, for instance*).

§ 148.

If substances of this kind were analysed as directed § 143, a portion of the substance or some water would escape upon mixing with hot oxide of copper and the application of the exhausting syringe to the tube, surrounded as it is with hot sand ; the results, therefore, could not possibly be accurate. And if, on the other hand, the mixing were effected in the

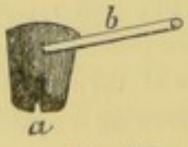


Fig. 77.

* To enable the operator to do this at pleasure, an arm is fixed to the turning part (*Erdmann* and *Marchand*). *H. Rose* has proposed the following simple contrivance instead (Fig. 77) : *a* is a cork to be placed on the cock ; *b*, a thick wire or rod, serves as lever.

same way with *cold* oxide of copper, the mixture would absorb a notable quantity of water.

The process is, therefore, conducted either as directed § 144, or § 147. Ignited chromate of potassa, cooled in a closed tube, may also be employed as oxidising agent.

b. Fluid substances.

a. *Volatile fluids* (*e. g.* ethereal oils, alcohol, &c.).

§ 149.

1. The analysis of organic volatile fluids requires all the objects enumerated in § 142, with the exception of the exhausting syringe and the apparatus for weighing and mixing; it requires besides a glass tube, such as that described in § 144, for the temporary reception of the oxide of copper, and also several small glass bulbs for the reception of the fluid to be analysed. These bulbs are made in the following manner:

A quill tube, made of moderately thick readily fusible glass, is drawn out as shown in

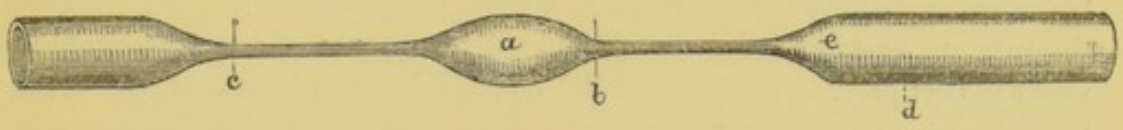


Fig. 78.

(Let the reader imagine that the two ends of the tube are each a foot longer than represented in the engraving.) The bulb *a* is severed by fusion at *b*, and, if necessary, the thickened part slightly expanded; the tube is then again cut at *c*. In this manner 2 or 3 bulbs are made of the shape illustrated by Fig. 79. The length of the ends of the tube is intended to prevent the bulbs getting moist inside whilst being expanded. Two of these bulbs are accurately weighed; they are then filled with the fluid to be analysed, closed by fusion, and weighed again. The filling is effected by slightly heating the bulb over a spirit-lamp and immersing the pointed end into the fluid to be analysed, part of which will now, upon cooling, enter the bulb. If the fluid is highly volatile the portion entering the still warm bulb is converted into vapor, which expels the fluid again; but the moment the vapor is recondensed, the bulb fills the more completely. If the fluid is of a less volatile nature, a small portion only will enter at first; in such cases, the bulb is heated again to convert what has ascended, into vapor, and the point is then again immersed into the fluid, which will now readily enter and fill the bulb. The excess



Fig. 79.

of fluid is ejected from the neck of the little tube by a sudden jerk; the point is then closed by fusion. The combustion tube is now prepared for the process by introducing into it from the filling tube (§ 144), a layer of oxide of copper occupying about 6 centimeters in length. The middle of the neck of one of the bulbs is slightly scratched with a file, the point is quickly broken off, and the bulb and point are dropt into the combustion tube. Another layer of oxide of copper, from about 6 to 9 centimeters long, is then filled in, and a second bulb introduced in the same manner as the first. The tube is ultimately nearly filled with oxide of copper. A few gentle taps upon the table suffice to make a free passage for the gases evolved. It is advisable to place in the anterior part of the combustion tube small fragments of oxide of copper (compare § 45, 1), or superficially oxidised copper turnings, which will permit the free passage of the gases, even with a narrow channel; since with a wide channel there is the risk of vapors passing unconsumed through the tube.

The combustion of highly volatile substances demands great care, and requires certain modifications of the common method. The operation commences by heating to redness the smaller anterior half of the tube, which is separated from the rest by a screen (in the case of highly volatile substances two screens are used instead of one); ignited charcoal is then placed behind the tube, to heat the pointed end, and thus to prevent the condensation of vapor in that part. A piece of red-hot charcoal is now put to that part of the tube which is occupied by the first bulb; this causes the efflux and evaporation of the contents of the latter; the vapor passing over the surface of the oxide of copper suffers combustion, and thus the evolution of gas commences, which is then maintained by heating very gradually the first and after this the second bulb; it is better to conduct the operation too slowly than too quickly. Sudden heating of the bulbs would at once cause such an impetuous rush of gas as to eject the fluid from the potass-apparatus. The tube is finally in its entire length surrounded with ignited charcoal, and the rest of the operation conducted in the usual way. If the air drawn through the apparatus tastes of the analysed substance, this is a sure sign that complete combustion has not been effected. In the combustion of fluids of high boiling point and abounding in carbon, *e. g.* ethereal oils, unconsumed carbon is apt to deposit on the completely reduced copper near the substance; it is therefore advisable to distribute the quantity intended for analysis (about 0·4 grm.) in three bulbs, separated from each other in the tube, by interposed layers of oxide of copper.

2. If there is reason to apprehend that the oxygen supplied by the oxide of copper may not suffice to effect the complete combustion of the carbon, the process is terminated in a stream of oxygen gas evolved from a layer of chlorate or perchlorate of potassa in the posterior part of the tube (compare § 146).

3. If it is intended to effect the combustion in the apparatus described, § 147, in a stream of oxygen gas, the bulbs must be drawn out into a fine long point, and filled almost completely with the fluid. The point is then closed by fusion, and the bulbs are transferred in that state to the combustion tube. When the anterior and the farther end of the tube are red hot, a piece of ignited charcoal is put to the part occupied by the first bulb when the expansion of the fluid in the latter will cause it to burst. When the contents of the first bulb are consumed, the second, and afterwards the third, are treated in the same way. This method will not answer, however, for very volatile fluids, as ether, for instance, on account of the explosion inseparable from it.

β. Fluid non-volatile bodies (*e. g.* fixed oils).

§ 150.

The combustion of non-volatile fluids is effected either, 1, with chromate of lead or with oxide of copper, combined with chlorate, or, as the case may be, perchlorate of potassa; or, 2, in the apparatus described § 147.

The substance to be examined is weighed in a small tube, and the process of mixing is then accomplished in the following manner:—

1. The general operation is conducted as directed § 145 or § 146. The substance is weighed in a small tube, and the mixing effected as follows: first, a layer, about 6 centimeters long, of chromate of lead, or of oxide of copper and chlorate of potassa, is introduced into the combustion tube; the small cylinder with the substance is then dropt in, and the oil allowed completely to run out into the tube, when it is made to spread about in various directions, taking care, however, to leave the upper side (intended for the channel) and the forepart, to the extent of one-fourth or one-third of the length of the tube, entirely clean. The tube is now nearly filled up with chromate of lead or oxide of copper—which has previously been cooled in a tube—taking care that the little cylinder which contained the oil intended for analysis, be completely filled with the oxidising agent. The tube is then placed in hot sand, which imparting to the oil a high degree of fluidity leads to its perfect absorption by the oxidising agent; the exhausting syringe is now applied, if necessary, and the combustion proceeded with in the usual way. It is advisable to select a tolerably long tube. Chromate of lead is usually preferable as oxidising agent to the mixture of oxide of copper and chlorate of potassa. When the former agent is used, a very intense heat, sufficiently strong to fuse the contents of the tube, is cautiously applied in the last stage of the process.

Solid fats or waxy substances which, not being reduceable to powder, cannot be mixed with the oxidising agent in the usual way, are treated in

a similar manner to fixed oils. They are fused in a small weighed glass-boat (Fig. 80), made of a tube divided lengthwise, when cold the little boat with its contents is weighed, and then dropped into the combustion tube, which has been previously filled to the extent of about six centimeters with chromate of lead, or with a mixture of oxide of copper and chlorate of potassa. The substance is then fused by the application of heat, and made to spread about in the tube in the same manner as is done with fixed oils; the rest of the operation also being conducted exactly as in the latter case.



Fig. 80.

2. If it is intended to effect the combustion of fatty substances or other bodies of the kind, in a stream of oxygen gas, in the apparatus described in § 147, the substance is weighed in a glass or porcelain-boat, which is then inserted into the tube, and the posterior part of the latter filled with oxide of copper as directed above. The combustion must be conducted with great care. As soon as the oxide of copper in the anterior, and the posterior parts of the tube is red hot, a piece of red-hot charcoal is put to the part holding the substance. The volatile products generated by the dry distillation of the substance, burn at the expense of the oxygen of the oxide of copper.

When it is perceived that the surface layer of the oxide of copper is reduced to the metallic state, the application of heat is suspended for a time, and resumed only when the reduced copper is re-oxidised in the stream of oxygen gas. Care is finally taken to insure the complete combustion of the carbon remaining in the boat.

B. Analysis of compounds consisting of carbon, hydrogen, oxygen, and nitrogen.

The principle of the analysis of such compounds is in general this: the substance is divided into two portions, and the carbon determined as carbonic acid, the hydrogen as water, in the *one* portion; the nitrogen in the *other* portion, either in the gaseous form or as chloride of ammonium and bichloride of platinum, or, by neutralising the ammonia formed by the liberated nitrogen; the oxygen is calculated from the loss.

As the presence of nitrogen exercises a certain influence upon the quantitative estimation of carbon and hydrogen, we have to consider here not only the method of determining the nitrogen in organic compounds, but also the modifications which the presence of the nitrogen renders necessary in the usual method of determining the carbon and hydrogen.

a. Determination of the carbon and hydrogen in nitrogenous substances.

§ 151.

1. When nitrogenous substances are ignited with oxide of copper or with chromate of lead, a portion of the nitrogen present escapes in the gaseous form, together with the carbonic acid and aqueous vapor, whilst another portion, minute indeed, still, in bodies abounding in oxygen, not quite insignificant, is converted into nitric oxide gas, which is subsequently transformed wholly or partially into nitrous acid by the air in the apparatus. The application of the methods described in § 143, &c., in the analysis of nitrogenous substances would accordingly give a higher number for the carbon than corresponds to the actual amount of that element present in the analysed substance; since the solution of potassa in the apparatus would retain, besides the carbonic acid, also the nitrous acid formed and a portion of the nitric oxide (which in the presence of potassa decomposes slowly into nitrous acid and nitrous oxide). This defect may be remedied, on the one hand, by the exclusive use of oxide of copper as oxidising agent, the most intimate mixture of the substance with the oxide, and slow combustion; as brisk combustion, and the use of chromate of lead, or the addition of chlorate of potassa to the oxide of copper, tend greatly to promote the evolution of nitric oxide; and, on the other hand, by selecting a combustion tube from about 12 to 15 centimeters longer than those commonly employed, filling this in the usual way, but finishing with a loose layer, from about 9 to 12 centimeters long, of clean fine copper turnings (§ 45, 6). The process is commenced by heating these copper turnings to redness, in which state they are maintained during the whole course of the operation. These are the only modifications required to adapt the methods given in § 143, &c., to the analysis of nitrogenous substances. The action of the copper turnings in the process rests upon the property of metallic copper in a state of intense ignition to decompose all the oxides of nitrogen into oxygen, with which the metal combines forming oxide, and into pure nitrogen gas. As the metal exercises this action only when in a state of intense ignition, care must be taken to maintain the anterior part of the tube in that state throughout the process. As metallic copper recently reduced retains hydrogen gas, and, after being kept for a time, aqueous vapor condensed on the surface, the copper turnings intended for the process must be introduced into the tube hot as they come from the drying case (which is heated to 212°). *Liebig* recommends to compress the hot turnings in a tube into a cylindrical form, to facilitate their introduction into the combustion tube.

2. If it is intended to burn nitrogenous bodies in the apparatus de-

scribed in § 147, a tube of a length of about 75 centimeters is used, and the anterior part of the same filled with a layer from 9 to 12 centimeters long of clean copper turnings. Care must be taken to keep at least the anterior portion of the turnings from oxidising both during the ignition in the stream of air and during the actual process of combustion. When the operation is terminated, and the oxidation of the metallic copper is visibly progressing, the oxygen is turned off, and the cock of the air gasometer opened a little instead, to let the tube cool in a slow stream of atmospheric air.

b. DETERMINATION OF THE NITROGEN IN ORGANIC COMPOUNDS.— It has already been stated above, that two essentially different methods are pursued to effect the determination of the nitrogen in organic compounds; viz., the nitrogen is either separated in the gaseous form and determined by measuring the volume of the isolated gas; or it is converted into ammonia, which again is then determined either as bichloride of platinum and chloride of ammonium, or by neutralisation.

a. Determination of the nitrogen from the volume.

The many methods that have been recommended to effect this purpose, may all be brought under two general heads; viz., 1st., methods having for their object the collection of the whole of the nitrogen contained in a weighed portion of the substance; and 2nd, methods determining simply the relative proportion between the carbonic acid and the nitrogen gas evolved, from which the quantity of the nitrogen is then calculated; these latter methods require therefore, of course, that the amount of carbon contained in the substance should be previously known. The methods based upon the the former principle are denominated *quantitative*, those based upon the latter are called *qualitative*. I will describe here one of each, selecting those which are most readily performed and give the most accurate results.

I. QUALITATIVE METHOD (LIEBIG'S).

§ 152.

This method is applicable only in the analysis of substances containing a notable amount of nitrogen in proportion to that of the carbon. See also the end of the paragraph.

The performance of this method requires the following:

1. Six to eight accurately graduated tubes of strong glass, each about 30 centimeters long and 15 millimeters in diameter.

2. A tall cylinder of strong glass widened at the top (See Fig. 82).

3. A pipette with the lower orifice bent upwards (See Fig. 82).

4. A quantity of mercury more than sufficient to fill the glass cylinder.

5. A mercurial trough.

6. Solution of potassa.

7. A straight combustion tube 60 centimeters long, and closed by fusion at one end; with gas-conducting tube (see Fig. 81); also a long combustion furnace.

8. Oxide of copper; this need not have been ignited recently.

9. Pure and clean copper turnings.

The process is conducted in the following manner: A quantity of oxide of copper sufficient to form a layer of 6 centimeters in length, is introduced into the farther end of the combustion tube; a quantity of about 0·5 grm. of the very finely pulverised substance* intended for analysis is then most intimately mixed with a portion of oxide of copper sufficient to fill the combustion tube about half. This mixture is introduced into the tube and followed by another layer of oxide of copper; the rest of the tube—a part at least 12 centimeters long—is then filled with copper turnings. The combustion tube so prepared is connected with the bent delivery tube, and placed in the furnace; the anterior part of the tube is then surrounded with red-hot charcoal, the part holding the mixture being protected by a screen which is shifted back 3 centimeters each time as the application of heat is gradually advanced in the usual way to the part occupied by the mixture. When about one-fourth part of this is decomposed, and the atmospheric air is thus almost completely expelled from the tube by the products of the combustion, one of the graduated tubes, filled with mercury,† is inverted over the mouth of the bent delivery tube, which opens under mercury, and allowed to fill with gas to about three-fourths; it is then lifted out of the mercurial trough, so that the rest of the mercury flows out; if, upon looking through the tube lengthways, the operator perceives not the slightest red coloration of the gaseous contents, he may feel convinced that the gases contain no admixture of nitric oxide. To acquire the positive certainty that there is no nitric oxide in any of

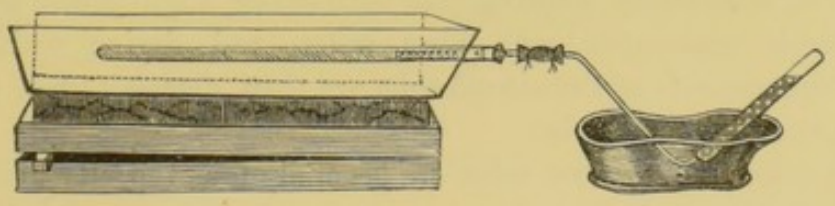


Fig. 81.

* The weight need not be more accurately known in this process.

† The best way of filling a tube completely with mercury, so as to prevent any air-bubbles remaining in it, is to fill the tube nearly with mercury, to close the aperture with the finger, to invert the tube, and to make the minute bubbles of air adhering to the sides gradually unite with the large bubble at the top. The tube is then turned upright and slowly filled up with mercury.

the tubes, this must be repeated in the middle and towards the end of the operation. After this preliminary operation, the graduated tubes are filled one after another in the same way (see Fig. 81), whilst the heating is continued slowly and uniformly. This operation requires a stand with places for six or eight tubes.* In default of an apparatus of the kind, an assistant must hold the filled tubes until they are required for measuring; care must be taken to mark the order in which they were filled.

When all the tubes are filled, the gas is measured successively in them in the following manner. The tube is completely immersed for some time in the mercury with which the cylinder, illustrated by Fig. 82, is filled; by this means perfect uniformity of temperature between the gas and the mercury is established. After this, the tube is raised until the mercury is on an exact level inside and outside; the volume is then read off and noted (see § 11). A small quantity of solution of potassa is now made to pass into the tube from the pipette β., which is nearly filled with this liquid; this is effected by blowing cautiously into the pipette. The latter is then withdrawn, and the absorption of the carbonic acid by the solution of potassa is promoted by moving the firmly held tube up and down in the mercury, pressing its mouth firmly against the side of the cylinder; the tube is ultimately once more completely immersed, raised again until the mercury is inside and outside on an exact level, and the volume then accurately read off. The pressure which the small column of solution of potassa exercises, may be altogether disregarded. The volume of the carbonic acid is determined by subtracting the quantity found in the second measuring (the nitrogen gas), from that noted in the first (nitrogen gas + carbonic acid gas).

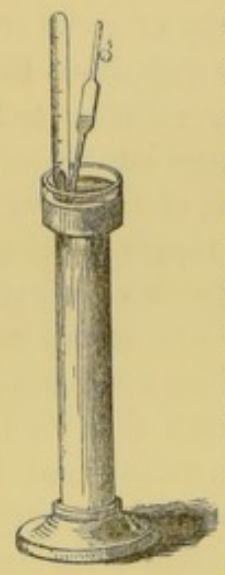


Fig. 82.

When the contents of the first tube have thus been determined, the mercury is cleaned by washing first with water slightly acidulated with hydrochloric acid, then with pure water, and drying with blotting paper; the contents of the second tube are then determined in the same manner, and so on to the last.

The results of the several tubes are generally found pretty uniform; in many cases, however, where the nitrogenous substance, previously to complete combustion, is resolved into products of different degrees of volatility, the several tubes show notable differences in the respective results. As a general rule, the arithmetical mean is taken as correct, and this may be considered the more accurate and reliable, the less the respective results of the several tubes diverge from it. If, however,

* Compare "Das chemische Laboratorium zu Giessen," von *J. P. Hoffmann*, Heidelberg, 1842.

the tubes first filled give a considerably larger proportion of nitrogen than those filled after, it may be safely assumed that the air was not completely expelled when the first tubes were filled; and in that case their contents are not taken into account.

The relative proportion of the carbonic acid to the nitrogen gas expresses directly, and without further calculation, the proportion which the equivalents of the carbon bear to those of the nitrogen: since one equivalent of carbon combines with two equivalents of oxygen, leaving the volume of the latter element unaltered, and giving accordingly, two volumes of carbonic acid;—and one equivalent of nitrogen gives equally two volumes of nitrogen gas.

Suppose we have found the proportion which the carbonic acid bears to the nitrogen gas as like 4 : 1, the analysed compound contains in that case, to four equivalents of carbon $=4\times75=300$, one equivalent of nitrogen $=175$. If, therefore, we have found, 26 parts of carbon in 100 parts of the analysed substance, the latter contains 15·17 of nitrogen; since $300 : 175 : : 26 : x$; $x=15{\cdot}17$.

There is one irremediable source of error inherent in this method, viz., it is impossible to remove the air completely from the tube, and thus the resulting number for the nitrogen is somewhat too high. This defect, however, does not materially interfere with the correctness of the results, if the substance contains a relatively large amount of nitrogen; thus, for instance, if the proportion be found as 1 : 4·1, it is at once evident that 1 : 4 is the correct number. But if the relative proportion of the nitrogen is inconsiderable, this defect vitiates the results; and experience has proved that the method is no longer applicable in the analysis of substances containing less than one equivalent of nitrogen to eight equivalents of carbon.

Bunsen has modified this method so as to attain still greater accuracy. However, his process is less simple and requires greater dexterity and expertness. A description of it is given in the "Handwörterbuch der Chemie" Supplemente, 200, *Kolbe;* and also in *Liebeg's* "Anleitung zur Analyse, organischer Körper," II Auflage, S. 72.

2. Quantitative method. (Dumas.)

§ 153.

This method may be employed in the analysis of all organic compounds containing nitrogen. It requires, besides the objects enumerated in § 152, from 4 to 9, and in § 142, 2, 9, and 12, a barometer and a thermometer, and a graduated glass cylinder of a capacity of about 200 cubic centimeters; and finally a ground-glass plate to cover the latter.

The combustion tube should be about 70 or 80 centimeters long, and closed at one end by fusion, in the manner of a test tube: a layer of dry bicarbonate of soda, from 12 to 15 centimeters long, is introduced into it; this is followed by a layer of oxide of copper, 4 centimeters long, and this again by an accurately weighed portion of the substance (from 0·300 to 0·600 grm., or, in the case of compounds poor in nitrogen, a somewhat larger quantity), most intimately mixed with oxide of copper. After this comes the oxide which has served to rinse the mortar, and then a layer of pure oxide, and the tube is then ultimately filled up with a layer of copper turnings, about 15 centimeters long. The tube so prepared is connected with the bent delivery tube, *a* (see below, Fig. 83), and placed in the furnace. The posterior end of the tube (to the extent of about 6 centimeters) is then gradually heated to redness, the other parts being protected from the heat by a screen. The bicarbonate of soda is decomposed by the heat, and the carbonic acid evolved drives the air in the tube before it, and thus effects its expulsion. When the evolution of gas has proceeded for some time, the end of the bent delivery tube is immersed under mercury, and a test cylinder, filled with solution of potassa, inverted over it; the red-hot pieces of charcoal are then slightly advanced towards the anterior part of the tube. If the gas bubbles entering the cylinder are completely absorbed by the solution of potassa, this is a proof that the air is thoroughly expelled from the tube; the actual combustion may therefore now be at once commenced; but should this not be the case, the evolution of carbonic acid must be continued until the desired point is attained. The gas evolved is then made to enter the graduated cylinder, which is filled to two-thirds with mercury, and one-third with strong solution of potassa, and inverted in the mercurial trough, over the opening of the bent delivery tube,* as Fig. 83 shows.

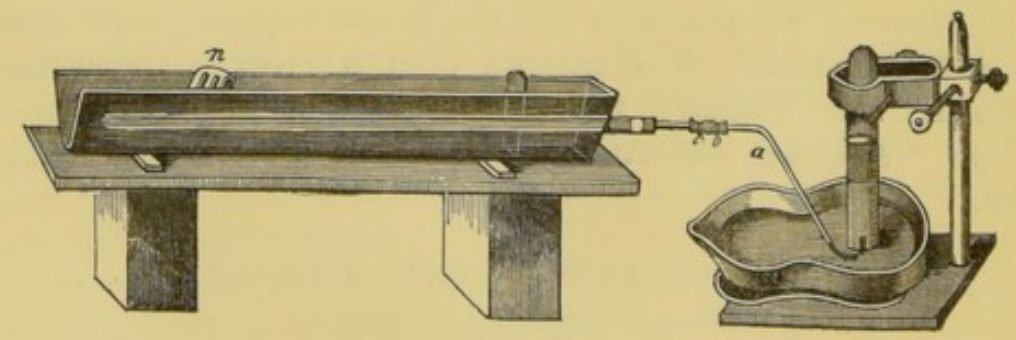


Fig. 83.

* The following is the best way of filling the cylinder and inverting it over the opening of the bent delivery tube. The mercury is introduced first, and the air-bubbles which adhere to the walls of the vessel are removed in the usual way. The solution of potassa is then poured in, leaving the top of the cylinder free, to the extent of about two lines; this is cautiously filled up to the brim with pure water, and the ground-glass plate placed over it.

The actual combustion is then proceeded with in the usual way, by heating first the anterior part of the tube to redness, and advancing gradually towards the farther end. In the last stage of the process, the other half of the bicarbonate of soda is decomposed, and thus the whole of the nitrogen gas which still remains in the tube is forced into the cylinder. The operator must now wait until the volume of the gas in the cylinder decreases no longer, even upon agitating the latter (consequently, until the whole of the carbonic acid has been absorbed). The cylinder is then placed in a large and deep glass vessel, filled with water, the safe transport from the mercurial trough to this vessel being effected by keeping the aperture closed with a small dish filled with mercury. The mercury and the solution of potassa sink to the bottom, and are replaced by water. The cylinder is totally immersed, and then raised again until the water is inside and outside on an exact level; the volume of the gas is now accurately read off, and the temperature of the water, and the height at which the barometer stands, are carefully marked; the weight of the nitrogen gas is finally calculated from its volume, after previous reduction to 32° of the thermometer, and 29·8 of the barometer, and with due regard to the tension of the aqueous vapor (compare "Calculation of Analysis"). The results are generally somewhat too high, viz., by about 0·2 to 0·5 per cent; this is owing to the circumstance that even protracted transmission of carbonic acid through the tube fails to expel every trace of atmospheric air adhering to the oxide of copper.

β. Determination of nitrogen by weight. (Varrentrapp and Will.)

§ 154.

This method may be employed in the analysis of all nitrogenous compounds, with the exception of those which contain the nitrogen in the form of nitric acid, hyponitric acid, &c. It is based upon the same principle as the method of examining organic compounds for nitrogen (§ 140, 1, *a.*), viz., upon the circumstance that, when nitrogenous bodies are ignited with the hydrate of an alkali metal, the hydration water of the latter is decomposed, its oxygen forming with the carbon of the organic body carbonic acid, which then combines with the alkali, whilst the hydrogen at the moment of its liberation combines with the whole of the nitrogen present, forming ammonia.

In the analysis of substances abounding in nitrogen, such as uric acid, mellone, &c., the whole of the nitrogen is not at once converted into am-

The cylinder is now inverted, and the opening placed under the mercury in the trough; the glass plate is then withdrawn from under the cylinder. In this manner the operation may be performed easily and without soiling the hands with the solution of potassa.

monia at the beginning of the decomposition; a portion of it enters into combination with part of the carbon, forming cyanogen, which then combines, either as such, with the alkali metal, or in form of cyanic acid, with the alkali. Direct experiments have proved, however, that even in such cases the whole of the nitrogen is ultimately obtained as ammonia, if the hydrated alkali is present in excess, and the heat applied sufficiently intense.

As in all organic nitrogenous compounds, the carbon preponderates over the nitrogen, the oxidation of the former, at the expense of the water, will invariably liberate a quantity of hydrogen more than sufficient to convert the whole of the nitrogen present into ammonia; for instance,

$$C_2N + 4\,HO = 2\,CO_2 + NH_3 + H.$$

The excess of the liberated hydrogen escapes either in the free state, or in combination with the not yet oxidised carbon, according to the relative proportions of the two elements and the temperature, as marsh gas or olefiant gas, or as vapor of readily condensable carbides of hydrogen, which gases serve in a certain measure to dilute the ammonia. As a certain dilution of that product is necessary for the success of the operation, I will here at once state that it may be produced at pleasure by adding to substances abounding in nitrogen, a greater or less proportion of a non-nitrogenous body, as sugar, for instance. The ammonia is determined, by receiving it in hydrochloric acid, converting the chloride of ammonium formed into bichloride of platinum and chloride of ammonium, which is then either weighed at once, or ignited, and its quantity, respectively that of the ammonia and of the nitrogen, calculated from the residuary metallic platinum. Many nitrogenous organic compounds give upon ignition with soda-lime no ammonia, but yield other nitrogenous volatile bases free from oxygen; thus indigo blue yields aniline; narcotine, morphia, quinine, and cinchona yield new volatile bases. All these volatile bases have, like ammonia, the property of forming double salts with hydrochloric acid and bichloride of platinum. Now, it would be committing a serious blunder to take these double salts for ammonio-bichloride of platinum, weigh them as such, and calculate the nitrogen from the weight found. By igniting them, and calculating the nitrogen from the residuary metallic platinum, all error is avoided, as these bases, like ammonia, contain in the double salts which they form with bichloride of platinum, to every one equivalent of platinum one equivalent of nitrogen.—(*Liebig.*) The other parts of the practical process (the collection and determination of the ammonia) require no theoretical explanation.

aa. Apparatus and other objects required for the process.

1. The objects enumerated § 142, 2, 9, and 12.

2. A COMBUSTION TUBE of the kind described § 142, 3 (with point at the farther end, and rounded edges at the mouth); length about 40 cen-

timeters, with about 12 millimeters. The combustion is effected in a common combustion furnace (§ 142, 13).

3. SODA-LIME. A mixture of caustic lime with hydrate of soda, § 45, 4. It is advisable to heat a sufficient quantity of the soda-lime to fill the combustion tube, gently in a platinum—or porcelain—dish, in order to obtain it perfectly dry for the process of combustion. In the analysis of non-volatile substances, the best way is to use the soda-lime while still warm.

4. ASBESTOS. A small portion of this substance is ignited in a platinum crucible previously to use.

5. A VARRENTRAPP AND WILL'S BULB APPARATUS, as illustrated in Fig. 84.

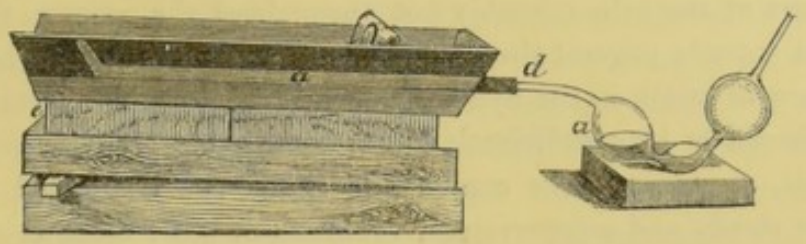


Fig. 84.

This may be procured at any chemical apparatus and instrument warehouse. It is filled with hydrochloric acid of 1·13 specific gravity to the extent indicated in the engraving, either by dipping the point into the acid, and sucking at *d*, or by means of a pipette.

6. A soft, well-perforated CORK, which fits the combustion tube airtight, and in which the tube *d* of the bulb apparatus fits closely.

7. A SUCTION TUBE filled with hydrate of potassa, and closed at the anterior end with a perforated cork, through which the point of the bulb apparatus passes.

The reagents, &c., required for the ulterior treatment of the fluid obtained in the process of combustion, are omitted here, as it is not necessary to have them ready at the beginning of the operation.

bb. THE PROCESS.

The combustion tube is half filled with soda-lime, which is then gradually transferred to the perfectly dry, and, if the nature of the substance permits, still warm mortar, where it is most intimately mixed with the weighed substance (compare § 143), forcible pressure being carefully avoided; a layer of soda-lime, about 3 centimeters in length, is now introduced into the posterior part of the combustion tube, and the mixture filled in after; the latter, which will occupy about 20 centimeters of the length of the tube, is followed by a layer of abour 4 or 5 centimeters of soda-lime, which has been used to rinse the mortar, and this again by a layer of about 10 or 12 centimeters of pure soda-lime, leaving about

3 centimeters unoccupied. The tube is closed with a plug of loose asbestos, and a canal for the free passage of the evolved gases formed by a few gentle taps; it is then connected with the bulb apparatus by means of the perforated cork, and ultimately placed in the combustion furnace (see Fig. 84).

To ascertain whether the apparatus closes air tight, some air is expelled by holding a piece of red-hot charcoal to the bulb *a*, and watching whether the liquid, upon cooling, assumes permanently a higher position in *a* than in the other limb. This being satisfactorily done, the tube is gradually surrounded with ignited charcoal, commencing at the anterior part, and progressing slowly to the pointed end, the operation being conducted exactly as in a common combustion (§ 143). Care must be taken to keep the anterior part of the tube tolerably hot throughout the process, since this will almost entirely prevent the formation of liquid carbides of hydrogen, the presence of which in the hydrochloric acid would be inconvenient. The asbestos should be kept sufficiently hot to guard against its retaining water, and with it, ammonia. The combustion should be conducted so as to maintain a steady and uninterrupted evolution of gas; there is no fear of any ammonia escaping unabsorbed, even if the evolution is rather brisk; whilst the analysis runs some risk from the receding of the hydrochloric acid which inevitably takes place the very moment the gas evolution stops, and this in some instances with such impetuosity as to force the acid into the combustion tube, which of course spoils the whole analysis. When operating upon compounds abounding in nitrogen, even the greatest care in conducting the combustion process will prove unavailing against the powerful affinity of the hydrochloric acid for the ammoniacal gas in the tube. This may be readily prevented, however, by mixing with the substance an equal amount of sugar, which will give rise to the evolution of other and more permanent gases diluting the ammonia.

When the tube is ignited in its whole length, and the evolution of gas has *totally* ceased,* the point of the combustion tube is broken off, and a certain volume of air (three or four times the capacity of the tube) is drawn through the apparatus, to force the last traces of ammonia into the hydrochloric acid; to guard against the inhalation of acid fumes, the suction tube filled with hydrate of potassa or a small aspirator is used.

Fluid nitrogenous compounds are weighed in small sealed glass bulbs, and the process is conducted as directed § 149 (determination of carbon), with this difference, that soda-lime is substituted for oxide of copper. It is advisable to employ tubes of greater length for the combustion of fluids than are required for solid nitrogenous bodies. The best method of

* This is indicated by the white color which the mixture re-assumes when the carbon deposited on the surface is completely oxidised.

conducting the operation is, in the first place, to heat about one-third of the tube at the anterior end, and then to force the liquid from the bulbs into the tube by heating the posterior end of the latter; the expelled liquid will thus become diffused in the central part of the tube without being decomposed. By a progressive application of heat, proceeding slowly from the anterior to the posterior end, a steady and uniform evolution of gas may be easily maintained.

When the combustion is terminated, the bulb apparatus is emptied through the aperture at the point, into a small porcelain dish, and then rinsed with water until the rinsings cease to manifest acid reaction. If liquid carbides of hydrogen have been formed, the fluid is passed through a moistened filter to separate them. Solution of *pure* bichloride of platinum* in excess, is added to the filtrate, and the mixture evaporated to dryness on a water-bath (§ 24, Fig. 20); the residue is treated with a mixture of two volumes of strong alcohol and one volume of ether. If the fluid acquires a bright yellow color, this may be taken as a proof that the quantity of bichloride of platinum added was sufficient for the intended purpose; if not, a fresh portion of that substance (best in alcoholic solution) must be added.† The residuary double salt of bichloride of platinum and chloride of ammonium is finally collected upon a tared filter, which has been dried at 212°, washed with the above-mentioned mixture of alcohol and ether, dried, and weighed (compare § 78). The dried filter is weighed best between two close-fitting watch-glasses held together by a clasp (Fig. 85). The bichloride of platinum and chloride of ammonium so obtained is not invariably of a pure bright yellow color, but sometimes of a darker or brownish yellow. This is the case more especially with difficultly combustible substances

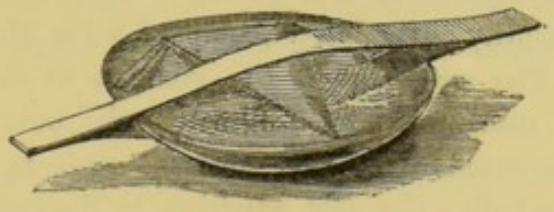


Fig. 85.

* If the bichloride of platinum contains an admixture of chloride of potassium or chloride of ammonium, an excess of nitrogen is the result; if it contains an admixture of nitric acid, this will, during the evaporation, cause the formation of chlorine and the consequent destruction of a portion of the ammonia, and accordingly too little nitrogen will be obtained. It is therefore always necessary to ascertain the purity of the bichloride of platinum used.

† As the double salts of platinum with some of the volatile bases produced in the decomposition of many nitrogenous organic substances (see above), are more readily soluble in alcohol than ammonio-bichloride of platinum (bichloride of platinum and chloride of ammonium), ether mixed with a few drops of alcohol is used as washing fluid, instead of the mixture of alcohol and ether, if there is reason to suppose that such double salts of platinum are present.

abounding in carbon, as in such cases it is less easy to avoid the formation of fluid carbides of hydrogen, which blacken during the evaporation of the hydrochloric acid. Direct experiments have proved, however, that this coloration does not perceptibly impair the accuracy of the results. The purity of the bichloride of platinum and chloride of ammonium may be ascertained by reducing it to metallic platinum, according to the directions given in § 78.

The results are very accurate; usually somewhat too low rather than too high (about from 0·1 to 0·2 per cent.), which is owing to traces of chloride of ammonium escaping condensation in the absorption apparatus, and being carried off with the permanent gases, as is observed in every analysis of the kind. If, as is sometimes the case, the results are too high, this is principally owing to the impurity of the bichloride of platinum used.

γ. Peligot's modification of Varrentrapp and Will's Method.

§ 155.

The essential part of this modification consists in this, that the ammonia generated in the process of combustion with soda-lime, instead of being conducted into hydrochloric acid, is received in a measured quantity of sulphuric acid of known strength; the amount of free acid remaining is then determined, by neutralising with an alkaline fluid (solution of lime in sugar water, or dilute solution of soda); from this is calculated the amount of acid saturated by the ammonia, and accordingly also the quantity of the latter (compare § 78, 3).

The apparatus is the same as in *β.* (Fig. 84). The sulphuric acid is measured into a beaker; the point of the bulb apparatus is then immersed in the acid, and as much as possible of the latter drawn into the bulb; the acid adhering to the point is rinsed off. When the combustion is completed the bulb-apparatus is emptied into the same beaker and properly rinsed; the fluid is then neutralised. The sulphuric acid intended for the process is prepared by adding 66 grammes of sulphuric acid to 1000 c. c. of water; 20 c. c. of the mixture, which is about the quantity required, contains about one gramme of sulphuric acid. The exact strength of the mixture is determined by precipitation with chloride of barium. The dilute solution of soda is best prepared of the strength that five degrees of it neutralise one degree of the acid. Solution of potassa may be used instead of soda.

This method gives very satisfactory results, though not quite so accurate as *β.*; but it takes much less time, and is particularly well adapted for commercial investigations.

C. Analysis of organic compounds containing sulphur.

§ 156.

The usual method of determining the carbon in organic bodies, viz., by combustion with oxide of copper or chromate of lead, would give results too high in the analysis of compounds containing sulphur; since—more especially if oxide of copper is used as oxidising agent—a portion of the sulphur would be converted in the process into sulphurous acid, which would be absorbed with the carbonic acid in the potass-apparatus. To remedy this defect a tube from ten to twelve centimeters long, filled with perfectly dry binoxide of lead, is placed between the chloride of calcium tube and the potass-apparatus. The binoxide of lead absorbs the sulphurous acid, and, transposing with it, is converted into sulphate of lead ($PbO_2 + SO_2 = PbO, SO_3$); and thus the carbonic acid alone finds its way to the potass-apparatus. No sulphurous acid remains in the chloride of calcium tube, if the latter is left undisturbed until the water combining with it, has formed crystallised chloride of calcium. It is advisable after this to draw some dried air through the tube. The presence of sulphur exercises no modifying influence upon the methods described §§ 153, 154, and 155, for the determination of nitrogen. As regards the quantitative estimation of the sulphur in organic compounds, that element is invariably weighed in the form of sulphate of baryta, into which it may be converted either in the dry or in the moist way; the former, however, is preferable to the latter. If besides sulphur the substance also contains oxygen, the quantity of the latter element is calculated from the loss.

a. Methods in the dry way.

1. *Method applicable, more particularly, to determine the sulphur in non-volatile substances poor in sulphur, e. g. in the so-called Proteïne compounds (Liebig).*

Put some lumps of hydrate of potassa (free from sulphuric acid)* into a capacious silver dish, add one-eighth part of pure nitrate of potassa, and fuse the mixture, with addition of a few drops of water. When the mass is cold, add to it a weighed quantity of the finely pulverised substance, fuse, stir with a silver spatula, and increase the heat, continuing the operation until the white color of the mass shows that the carbon separated at first has been completely consumed. Should this occupy too much time, you may accelerate it by the addition of nitrate of potassa in small portions. When the mass is cold dissolve it in water, super-

* This is prepared by treating the common hydrate of potassa with alcohol, evaporating the upper stratum of the fluid—the alcoholic solution of hydrate of potassa—in a silver dish to dryness, and fusing.

saturate the solution with hydrochloric acid in a capacious beaker covered with a glass dish, and precipitate with chloride of barium. Wash the precipitate well with boiling water, first by decantation, then on the filter. Dry and ignite. Treat the ignited sulphate of baryta as directed page 223, from line 1 at the top; if this latter operation is neglected the result is almost always too high.

2. *Method adapted more particularly for the analysis of non-volatile or difficultly volatile substances containing more than 5 per cent of sulphur* (*Kolbe*—Supplemente zum Handwörterbuch, S. 205).

Introduce into the posterior part of a straight combustion tube,* from 40 to 45 centimeters long, a layer, 7 to 8 centimeters long, of an intimate mixture of eight parts of pure anhydrous carbonate of soda and one part of pure chlorate of potassa; after this introduce the weighed substance to be analysed, and then another layer 7 or 8 centimeters long of the same mixture; mix the organic compound intimately with the carbonate of soda and chlorate of potassa, by means of the mixing wire (Fig. 75), to ensure its equal distribution through the entire mass; fill up the still vacant part of the tube with anhydrous carbonate of soda or potassa mixed with a little chlorate of potassa. Free a *wide* passage above the mixture by a few gentle taps, place the tube in a combustion furnace, heat the anterior part to redness, and then, progressing slowly towards the pointed end, proceed to surround with red-hot charcoal the part also which contains the organic compound. In the analysis of substances abounding in carbon it is advisable to introduce into the posterior part of the tube a few lumps of pure chlorate of potassa, to ensure the complete combustion of the carbon, and the perfect conversion into sulphates of the compounds of potassa with the lower oxides of sulphur that may have formed. The sulphuric acid in the contents of the tube is determined as in 1.

3. *Method adapted for the analysis both of non-volatile and volatile substances, but more especially the latter* (*Debus*—Annal. d. Chem. und Pharm. 76, 90).

Dissolve one equivalent (149 parts) of bichromate of potassa purified by recrystallisation, and two equivalents of carbonate of soda (106 parts), in water, evaporate the solution to dryness, reduce the lemon-colored saline mass ($KO, CrO_3 + NaO, CrO_3 + NaO, CO_2$) to powder, heat to intense redness in a hessian crucible, and transfer it still hot to a filling tube† (Fig. 73). When the powder is cold introduce a layer of it, from 7 to 10 centimeters long, into a common combustion tube; introduce the sub-

* Sealed and rounded at the end like a test tube.

† The saline mass must always first be tested whether it is quite free from sulphur. For this purpose a small portion of it is reduced with hydrochloric acid and alcohol, chloride of barium added, and the mixture allowed to stand twelve hours at rest; it is then carefully examined to ascertain whether or not traces of a precipitate are visible.

stance, and then another layer from 7 to 10 centimeters long of the powder. Mix the substance intimately with the latter by means of the mixing wire (Fig. 75); fill the empty part of the tube with the powder of carbonate of soda and the chromates of soda and potassa; heat as in a common elementary analysis. When the entire mass is heated to redness, conduct a slow stream of dry oxygen gas over it for from half an hour to one hour. When cold brush the ashes off the tube, cut it into several pieces over a sheet of paper, place in a beaker, and pour over them a sufficient quantity of water to dissolve the saline mass. Add hydrochloric acid in tolerable excess, then some alcohol, and apply a gentle heat until the solution shows a beautiful green color; filter the fluid from the sesquioxide of chromium produced by the combustion (which contains sulphuric acid), wash with water containing hydrochloric acid, then with alcohol, dry, and transfer the dry sesquioxide of chromium to a platinum crucible; add the filter ash, mix with one part of chlorate and two parts of carbonate of potassa (or soda), and ignite until the sesquioxide of chromium is completely converted into chromate of potassa. Dissolve the fused mass in dilute hydrochloric acid, and reduce by heating with alcohol; add the solution to the fluid filtered from the sesquioxide of chromium, heat the mixture to boiling, and precipitate the sulphuric acid with chloride of barium. *Debus* obtained by this method very satisfactory results (99·76 and 99·50 instead of 100 of sulphur) in the experimental analysis of substances of known composition; thus he obtained 30·2 of sulphur in the *Xanthogenamide*, instead of 30·4, &c.

4. *Heinz* burns substances poor in sulphur with oxide of copper in excess, conducts the gases evolved through solution of potassa, and after the combustion, treats both the oxide of copper and the solution of potassa with hydrochloric acid and chlorate of potassa, and precipitates with chloride of barium. I do not think this process possesses any advantage over *Debus's* method. A description of it, and also of another method which *Heinz* employs in the analysis of substances rich in sulphur, will be found in *Poggend.* Annal. 85, 424; also in the Pharm. Centralblatt, 1852, 536.

b. Method in the moist way.

1. Treat the substance under examination with red fuming nitric acid, or with a mixture of nitric acid and chlorate of potassa, until the whole of the substance is oxidised; towards the end of the process the action of the oxidising agents may, if necessary, be aided by the application of heat. Volatile organic compounds containing sulphur are weighed in a small glass bulb (§ 149), the point of the latter is broken off and, together with the bulb, dropped into a tall narrow-necked flask containing the strongest red fuming nitric acid. The action of the acid proceeds slowly

since it is compelled to force its way through the narrow aperture at the point of the bulb; by placing the flask in an oblique position, and taking care to keep the neck cool, the operation may be performed without suffering the slightest loss of substance. The nitric acid which now contains the sulphuric acid formed in the process, is treated according to the directions given in § 105, 1. The application of this method requires the greatest care, as, in the analysis of many organic substances, complete oxidation of the sulphur is not attained by this process. *Sorby* has determined the sulphur in many plants and parts of plants by boiling with nitric acid.

2. According to *Beudant*, *Daguin* and *Rivot*, the sulphur in organic compounds may be readily determined, by heating with solution of potassa, and conducting chlorine into the fluid. When the oxidation is effected, the acidified solution is freed from the excess of chlorine by heat, then filtered, and the filtrate precipitated with chloride of barium (Pharm. Centralblatt, 1854, 41). I have not yet tried this method.

*** Substances leaving ashes on incineration, and which may therefore be presumed to contain sulphates, are boiled with hydrochloric acid; the solution obtained is filtered, and the filtrate tested with chloride of barium.

If a precipitate of sulphate of baryta forms, the sulphur contained in it is deducted from the quantity found by one of the methods described above; the difference gives the quantity of the sulphur which the analysed substance contains in organic combination.

D. Determination of phosphorus in organic compounds.

§ 157.

Mulder, who has occupied himself more than any other chemist with the determination of phosphorus in organic substances, recommends the following method:

Dissolve a weighed portion of the substance by boiling with hydrochloric acid; filter, if necessary, and determine the phosphoric acid which the fluid may contain by *Berthier's* method (§ 106, I. *c.*). Boil another weighed portion of the substance with nitric acid, and treat the fluid in the same way as the hydrochloric acid solution. If you find in both the same percentage amount of phosphoric acid, the analysed substance contains the phosphorus only in the form of phosphoric acid; but if you obtain a larger proportion of acid in the second experiment than in the first, the difference indicates the quantity of phosphoric acid formed by the action of the nitric acid upon phosphorus contained in the analysed compound in the non-oxidised state. Thus, *e. g. Mulder* found in caseine in both experiments 3·5 per cent of phosphoric acid, whilst in the case of

albumen the hydrochloric acid solution gave 0·35 per cent, the nitric acid solution 0·78 per cent of that acid.

The phosphorus cannot be determined by incineration of the substance and examination of the ashes. Vitellin, which when treated with nitric acid gives three per cent of phosphoric acid, yields barely 0·3 per cent of ash (*Baumhauer*).

The methods described in § 156, *a*. 1 and 2, may also be employed to determine the total quantity of phosphorus in organic compounds.

E. Analysis of organic compounds containing chlorine.

§ 158.

The combustion of organic compounds containing chlorine, with oxide of copper gives rise to the formation of subchloride of copper, which, were the process conducted in the usual manner, would condense in the chloride of calcium tube, and would thus vitiate the determination of the hydrogen. This, and every other defect may be readily remedied, however, by substituting chromate of lead for oxide of copper, and conducting the process exactly as directed § 145. The chlorine is, in that case, converted into chloride of lead, and remains in that form in the combustion tube.

If the combustion is effected with oxide of copper in a stream of oxygen gas, the subchloride of copper formed is decomposed by the oxygen into oxide of copper and free chlorine, which latter element is retained partly in the chloride of calcium tube, partly in the potass-apparatus. To remedy this defect, *Städeler** proposes to retain the chlorine in the tube, by filling the anterior part of the latter with clean copper turnings, to be kept red hot during the process of combustion, and arresting the stream of oxygen the moment the copper turnings begin to oxidise. According to *A. Völcker*,† the evolution of chlorine may be avoided, by adding to the oxide of copper one-fifth part of oxide of lead.

As regards the determination of the chlorine in organic compounds containing that element, this is invariably effected by igniting the substance with alkalies, or alkaline earths, by which process all the chlorine is obtained as metallic chloride.

Lime free from chlorine (which is easily obtained by the calcination of marble) is usually employed as a decomposing agent; the lime used must always be carefully tested, to make quite sure that it contains no chlorine.

Introduce into a combustion tube, about 40 centimeters long, the posterior end of which is rounded like a test tube, a layer of lime, 6 centimeters long, then introduce the substance, then another layer of lime, 6 centimeters long, and mix intimately with the wire (Fig. 75); fill the tube

* Annal. der Chem. und Pharm. 69, 335. † Chem. Gaz. 1849, 245.

almost to the mouth with lime, open a free passage above the contents, by a few gentle taps, and apply heat in the usual way. If you have to operate upon volatile fluids, introduce them into the tube in small glass bulbs. When the decomposition is terminated, dissolve in dilute nitric acid, and precipitate with solution of nitrate of silver (§ 112). *Kolbe* recommends the following process to obtain the contents of the combustion tube: when the decomposition is completed, remove the charcoal, insert a cork into the open end of the tube, brush away every particle of ash, and immerse the tube still hot, with the sealed end downwards, into a beaker filled two-thirds with distilled water; the tube breaks into many pieces, and the contents are then more readily acted upon.

In the analysis of acid organic compounds containing chlorine (*e. g.* chlorospiroylic acid), the chlorine may often be determined in a simpler manner, viz., by dissolving the substance under examination in an excess of dilute solution of potassa, evaporating to dryness, and igniting the residue, by which means the whole of the chlorine present is converted into a soluble chloride. (*Löwig.*)

Organic compounds containing bromine are analysed in the same manner as those containing chlorine.

F. Analysis of organic compounds containing inorganic bodies.

§ 159.

In the analysis of organic compounds containing inorganic bodies, it is, of course, necessary first to ascertain the weight of the latter before proceeding to the determination of the carbon, &c., as otherwise the amount of the organic substance, whose constituents have furnished the carbonic acid, water, &c., not being known, it would be impossible to estimate the quantity of the oxygen from the loss.

If the organic bodies in question are salts or similar compounds, their bases are determined by the methods given in the fourth section; but in cases where the inorganic admixtures are of a nature to be regarded more or less as impurities (*e. g.* lime in gum arabic), they may usually be determined with sufficient accuracy by the combustion of a weighed portion of the substance in an obliquely placed platinum crucible. In the analysis of substances containing fusible salts, even long continued ignition will often fail to effect complete combustion, as the carbon is protected by the fused salt from the action of the oxygen. In such cases, the best way to effect the purpose is to carbonise the substance, treat the mass with water, and incinerate the undissolved residue; the aqueous solution is, of course, likewise evaporated to dryness, and the weight of the residue added to that of the ashes. (Compare Special Part "Analysis of Ashes.")

If organic compounds containing potassa, soda, baryta, lime, or strontia, are burnt with oxide of copper, part of the carbonic acid evolved remains combined with the alkalies or earths. As, in many cases, the amount of carbonic acid thus retained is not constant, and the results are, at all events, more accurate, if the whole amount of the carbon is expelled and determined as carbonic acid, the oxide of copper is mixed with substances which will effect the decomposition of the carbonates at a high temperature, *e. g.* with teroxide of antimony, phosphate of copper, boracic acid (*Fremy*), &c.; or the combustion is effected with chromate of lead according to the directions given in § 145; the latter method deserves the preference. Accurate experiments have shown that in a combustion effected with chromate of lead, not a trace of carbonic acid remains with the bases, since, if carbonate of an alkali (or of an alkaline earth) is fused with neutral chromate of lead—basic chromate of lead, and a neutral chromate of the alkali (or earth) is formed, and the carbonic acid escapes [$2(PbO, CrO_3) + BaO,CO_2 = 2\ PbO, Cr\ O_3 + BaO, Cr\ O_3 + CO_2$.]

If, as is always done by *Wöhler*, the organic substance containing such fixed constituents, is weighed in a small platinum boat (Fig. 86), the ashes, the carbon, and the hydrogen, may be determined in one and the same portion; the apparatus described in § 147 may be employed. The combustion tube is two-thirds filled with ignited oxide of copper; a layer of freshly ignited asbestos is introduced, then the small boat with the substance, then another layer or plug of asbestos, and the remainder of the tube filled with oxide of copper. When the entire anterior part of the tube is red hot (but not before), the part holding the boat is very cautiously heated. The amount of carbonic acid contained in the ashes, is added to that found by the process of combustion; if the carbonic acid in the ashes cannot be calculated, as with carbonates of the alkalies, it may be determined by means of fused biborate of soda (§ 110). Many chemists leave the space behind the boat empty.



Fig. 86.

III. Determination of the atomic weight of organic compounds.

The methods of determining the atomic weight of organic compounds differ essentially according to the nature and properties of the various compounds. There are three general methods in use for this purpose, viz.:—

§ 160.

1. *We take a substance of known atomic weight and determine the*

exact proportional amount of it which forms a definite and well characterised compound with the body whose atomic weight we wish to determine.

This method is pursued in determining the atomic weight of the organic acids and organic bases, and of many indifferent bodies possessed of the property of combining with bases. We occupy ourselves here simply with the analytical process; the mode of calculating the atomic weight from the results obtained, will be found in the chapter on the calculation of analyses.

a. The atomic weight of *organic acids* is in most cases determined from their respective silver salts, because the analysis of these salts is very simple, and there is almost always the positive certainty that the analysed salt is not a basic or hydrated compound. Other salts also are, however, frequently used for the same purpose, particularly the lead, baryta, and lime salts of organic acids. In the analysis of the lead salts of organic acids, especial care must be taken not to mistake basic for neutral, nor in the analysis of the baryta and lime salts, hydrated for anhydrous salts. For the manner in which the quantitative determination of the bases in question is effected, I refer to Section IV.

b. The atomic weight of *alkaloids*, forming crystallisable salts with sulphuric acid, hydrochloric acid, or any other easily determined acid, is best ascertained by estimating the proportion of the acid contained in a weighed amount of the salt.

If the salts do not crystallise, a known quantity of the dried alkaloid is introduced into a drying tube (Fig. 87), which is then accurately weighed with its contents; a slow stream of dry hydrochloric acid gas is transmitted through the apparatus for some time (Fig. 87); the tube is ultimately heated to 212° (see page 36, Fig. 13), and a stream of atmospheric air transmitted through it; the quantity of the hydrocholoric acid absorbed is found from the increase in the weight of the tube. The accuracy of the results may be controlled by dissolving the hydrochlorate in water, and precipitating the chlorine from the solution, by nitrate of silver (*Liebig*). The atomic weight of the alkaloids may be determined also from the insoluble double salts produced by precipitating the solutions of their hydrochlorates with bichloride of platinum; the double chlorides thus produced are cautiously ignited (§ 99), and the residuary platinum accurately weighed.

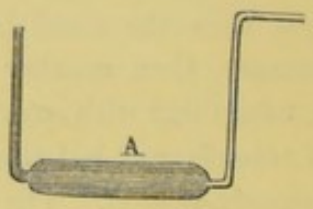


Fig. 87.

c. In the case of *indifferent bodies*, such as gum, starch, extractive matter, &c., there is usually no other choice left than to determine the atomic weight from the lead compound; since these substances either altogether refuse to enter into combination with other bases besides lead,

or form with them compounds only which it is impossible to obtain in a state of purity.

§ 161.

2. *The density of the vapor of the compound is determined* (*Dumas*).

The following are the outlines of *Dumas's* method, which I shall immediately after proceed to describe more in detail. A light glass globe filled with dry air, and the exact capacity of which is afterwards ascertained, is accurately weighed; the weight of the air which the globe contains at the temperature, and atmospheric pressure, noted during the process, is calculated and subtracted from the first weight: the difference expresses the weight of the exhausted vessel. A more than sufficient quantity of the substance, the density of the vapor of which it is intended to determine, is then introduced into the globe, and exposed to a uniform temperature exceeding the boiling point of the substance, until the latter is completely converted into vapor, and the excess expelled together with the atmospheric air originally contained in the globe; it is then sealed air-tight, and accurately weighed. The difference between the weight found and that of the exhausted globe, expresses the exact weight of a volume of the vapor corresponding to the capacity of the globe; supplying thus the necessary data for calculating the density of the vapor.

It is hardly necessary to remark that the volume of the vapor must first be calculated at the usual height of the barometer, and 32° (0° C.) of the thermometer, and consequently that the height of the barometer and thermometer must be correctly noted both during the first weighing and at the time of sealing the glass globe.

This method is of course applicable only to substances which volatilise without suffering decomposition. To obtain accurate results, it is indispensable that the examined substance be perfectly pure.

I will now proceed to describe the analytical process; for the manner of correcting and calculating the results, I refer to the chapter on the "Calculation of Analyses."

a. Apparatus and other requisites.

1. THE SUBSTANCE.—From six to eight grammes are required. The boiling point of the substance must be pretty accurately known.

2. A LIGHT GLASS GLOBE WITH A LONG AND BENT NECK.

A light globe of pure glass is selected, free from flaws, and holding from 250 to 500 cubic centimeters; it is carefully rinsed with water, and then thoroughly dried. After this, it is completely exhausted, dry air readmitted into it, and the same operation repeated several times (the apparatus illustrated by Fig. 70, § 143, is used for this purpose). The neck

of the globe is then softened near the bulb, and drawn out in the shape represented in Fig. 88.

The extreme point is cut off, and the edges slightly rounded over the spirit-lamp; this point having to be sealed air-tight with the greatest despatch, at a subsequent stage of the process, it is advisable to ascertain, in the first place, whether the glass of the globe is readily fusible or not; this may be done by trying to seal the point of the original neck of the balloon, previously to drawing it out; should this present any difficulty, the globe is totally unfit for the intended purpose.

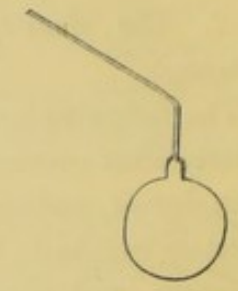


Fig. 88.

3. A SMALL IRON OR COPPER VESSEL for the reception of the fluid in which the globe is to be heated (see Fig. 89). The fluid which is to serve as *bath*, must admit of being heated to at least 36, but better 54 or 72 degrees beyond the boiling point of the substance under examination. Oil will answer the purpose in all cases when a higher temperature is required than that of boiling water; however, a chloride of calcium bath—if its temperature, which in a perfectly saturated bath may be raised to 356° suffices—is more convenient than an oil-bath, as the globe may be more easily cleaned.

4. AN APPARATUS TO KEEP THE BALLOON IN POSITION.—This may be readily made with a handle and some iron wire. During the operation, this is supported by the arm of a retort stand (see Fig. 89).

5. A quantity of MERCURY more than sufficient to fill the globe.

6. An accurately GRADUATED TUBE of about 100 cubic centimeters capacity.

7. SPIRIT-LAMP and BLOWPIPE.

8. A correct BAROMETER.

9. A correct THERMOMETER capable of indicating the highest degree of heat the case under examination may require.

b. Analytical process.

a. Weigh the globe on the balance, placing a thermometer inside the case. Leave the balloon for ten minutes on the scale, to ascertain whether its weight remains constant. If so, the weight is noted, together with the height of the barometer and the temperature indicated by the thermometer, inside the case.

β. Introduce about eight grammes of the fluid or—by the application of a gentle heat—liquefied substance into a glass; heat the globe gently, and dip the pointed end deep into the liquid. If the substance under examination has a high fusing point, the neck and point of the globe likewise require heating, to guard against the fluid solidifying in the neck. As soon as the globe cools—which is accelerated by dropping

ether upon it—the fluid enters and spreads in it. Do not introduce more than from five to seven grammes.

Heat the contents of the vessel (3) to from 104° to 122°, and immerse the balloon by means of the apparatus (4), and also a thermometer, in the bath as illustrated in Fig. 89.

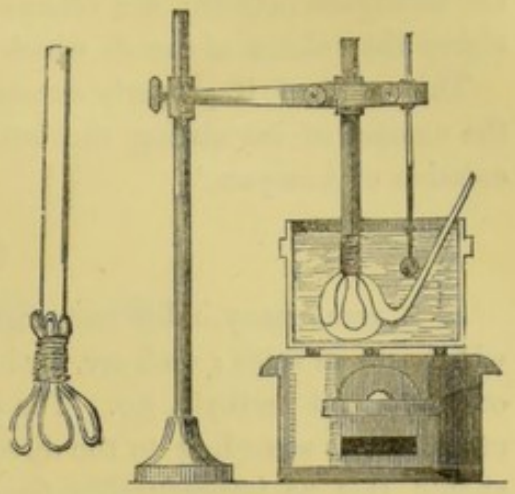


Fig. 89.

Raise the temperature of the bath to the height required.* As soon as the temperature in the globe is somewhat higher than the boiling point of the substance, the vapor of the latter rushes out at the neck; the force of the stream increases at first with the temperature of the bath, but diminishes afterwards by degrees, and ceases ultimately altogether (after about fifteen minutes). Should any of the vapor have condensed into drops in the projecting point of the globe, these may be at once reconverted into vapor, by moving a piece of red-hot charcoal to and fro round it. The moment that a perfect equilibrium is fully established at the desired temperature, seal the point of the globe quickly air-tight, by means of a spirit-lamp and blowpipe, and note immediately after the height of the thermometer. To ascertain whether or not the point is really sealed air-tight, you need simply direct a stream of air through the blowpipe upon the projecting point of the globe: if the tube is closed hermetically, a small portion of the vapor condenses, forming a column of fluid, which is retained in the end of the tube by capillary attraction; this is not observed if the tube is not hermetically sealed. The height of the barometer also is noted again, if it has changed since the first observation.

δ. Remove the sealed globe from the bath, allow it to cool, wash it most carefully, wipe it perfectly dry, and weigh it again in the same manner as before.

ε. Immerse the pointed end of the globe to its entire length in mercury, scratch a mark with a file near the end, and break off the point; whereupon the mercury will immediately rush into the globe, a vacuum having been created in it by the condensation of the vapor. In this operation place the glass globe in the hollow of your hand, and rest the latter upon the edge of the mercurial trough. If the globe, at the moment of sealing, was perfectly free from air, it will fill completely with

* If the globe is immersed in a chloride of calcium or oil bath, you must endeavor to maintain a uniform temperature towards the end of the process, which may be easily effected by properly regulating the fire.

mercury; otherwise an air bubble will remain in it. In either case transfer the mercury from the globe to the graduated tube (6), and measure accurately; if there was air in the globe at the moment of sealing it, fill it now with water, and measure also the volume of the latter liquid: the difference between the volume of the mercury and that of the water shows the volume of the air which had remained in the globe.

This method, if properly executed, yields nearly accurate results; for the manner of calculating the latter, I refer to the chapter on the "Calculation of Analyses."

§ 162.

3. A great many indifferent organic bodies absolutely refuse to combine with bases, or acids; such are, for instance, the fats, salicine, the compounds of ethyle and methyle, &c. The atomic weight of such bodies is determined either according to the directions of the preceding paragraph, or, should this be impracticable, from the products of the decomposition of the substance obtained by the action of acids, bases, &c., upon it, and of which the atomic weight may always be determined by some known means; or, lastly, the atomic weight is inferred from the manner in which the compound in question has been formed. In cases of this description, that atomic weight is taken as the correct one which permits the most simple explanation of the processes of formation and decomposition.

This latter mode of determining the atomic weight of substances is intimately connected with the higher branches of organic chemistry, and cannot be considered here more in detail, as it is impossible to give universally applicable methods for determining the atomic weight of substances in this manner.

SUBDIVISION II.

CALCULATION OF ANALYSES.

§ 163.

The calculation of the results obtained by analysis presupposes, as an indispensable preliminary, a knowledge of the general laws of the combining proportions of bodies, on the one hand, and of the more simple rules of arithmetic on the other. Chemical calculations do not necessarily require a complete knowledge of mathematics, as is often erroneously supposed: decimal fractions and simple equations, will enable the student to make all the more common calculations. These remarks are not intended to dissuade students of chemistry and pharmacy from pursuing the higher mathematics; I merely wish to encourage those who have had no opportunity of doing so, and who, as I have often experienced, are afraid to venture upon chemical calculations. For this reason I have made the whole of the calculations given in the following paragraphs, in the most intelligible manner possible, and without logarithms.

I. *Calculation of the constituent sought, from the compound obtained in the analytical process, and exhibition of the percentage results.*

§ 164.

The bodies, the weight of which it is intended to determine are separated, as we have seen in the division treating of the "analytical methods and processes," either in the free state, or, and this most frequently, in combinations of known composition. The results are usually calculated upon 100 parts of the examined substance, since this gives a clearer and more intelligible view of the composition. In cases where the several constitutents have been separated in the free state, the calculation may be

made at once; but if the constituents have been separated in combination with other subtances, they must first be calculated from the compounds obtained.

1. *Calculation of the percentage results, in cases where the substance sought has been separated in the free state.*

a. Solid substances, fluids, or gases, which have been determined by weight.

§ 165.

The calculation here is so exceedingly simple that I will give but one illustration.

Suppose you have analysed subchloride of mercury, and separated the mercury in the metallic state (§ 94, 1). 2·945 grammes of subchloride of mercury have given 2·499 grammes of metallic mercury.

$$2{\cdot}945 : 2{\cdot}499 :: 100 : x$$

$$x = 84{\cdot}85,$$

which means that your analysis shows 100 parts of subchloride of mercury to contain 84·85 of mercury, and consequently 15·15 of chlorine.

Now as the subchloride of mercury is known to consist of two equivalents of mercury and one equivalent of chlorine, and as the equivalent numbers of both these elements are also known, the true percentage composition of the body may be readily calculated from these data. When analysing substances of known composition, for practice, the results theoretically calculated and those obtained by the analysis are usually placed in juxtaposition, as this enables the student at once to perceive the degree of correctness and accuracy with which the analysis has been performed.

Thus for instance—

	Found.	Calculated (compare § 63, *b.*).
Mercury . .	84·85	84·95
Chlorine . .	15·15	15·05
	100·00	100·00

b. Gases which have been determined by measure.

§ 166.

If a gas has been determined by measure, it is, of course, necessary first to ascertain the weight corresponding to the volume found, before the proportional amount of the gas in 100 parts by weight of the analysed substance can be calculated.

But as the exact weight of a certain definite volume of the various gases has been severally determined by minute and accurate experiments,

this calculation is also a simple rule of three question, if the gas may be measured under the same circumstances under which the experiments were made by which the weight of a certain definite volume of it has been determined. The circumstances to be taken into consideration here, are:

Temperature and atmospheric pressure,

besides these, the

Tension of the aqueous vapor

may also claim consideration in cases where water is used as the confining fluid.

The respective weights assigned in Table V. to one litre of the gases enumerated, refer to a temperature of 0° C. (=32° F.) and an atmospheric pressure of 0·76 (760 millimeters) of mercury (=29·9 inches of the English scale). We have, therefore, in the first place, to consider the manner in which volumes of gas measured at another temperature and another height of the barometer, are to be reduced to 0° of the centigrade thermometer, and 0·76 of the barometer.

a. *Reduction of a volume of gas of any given temperature to* 0° C. *or any other temperature between* 0° *and* 100° C.

The following propositions regarding the expansion of gases were formerly universally adopted:

1. All gases expand equally for every degree of the thermometer.

2. The expansion of one and the same gas for each degree of the thermometer, is independent of its original density.

Although the correctness of these propositions has not been fully confirmed by the minute investigations of *Magnus* and *Regnault*, yet they may be safely followed in reductions of the temperature of those gases which are most frequently measured in the course of analytical processes, as the co-efficients of the expansion of these gases scarcely differ from each other, and as there is never any very considerable difference in the atmospheric pressure under which the gases are severally measured.

The investigations just alluded to have given

0·3665

as the co-efficient of the expansion of gases which comes nearest to the point, in other words, as the extent to which gases expand when heated from the freezing to the boiling point of water. They expand, therefore, for every degree of centigrade

$$\text{thermometer}\frac{0{\cdot}3665}{100}=0{\cdot}003665.$$

If we wish to ascertain how much space a cubic centimeter of gas of 0° C. will occupy at 10° C., we find

$$1\times(1+10\times 0{\cdot}003665)\ i.\ e.=1{\cdot}03665.$$

If we wish to ascertain how much space 100 cubic centimeters of 0° C. will occupy at 10° C., we find

$$100 \times (1 + 10 \times 0{\cdot}003665) \textit{ i. e.}$$
$$100 \times 1{\cdot}03665 = 103{\cdot}665.$$

If we wish to know how much space 1 cubic centimeter of 10° C. will occupy at 0° C., we find

$$\frac{1}{(1 + 10 \times 0{\cdot}003665} = 0{\cdot}965.$$

How much space do 103·665 cubic centimeters of 10° C. occupy at 0° C.?

$$\frac{103{\cdot}665}{1 + (10 \times 0{\cdot}003665} = 100.$$

The general rule of these calculations may be briefly expressed as follows:

To calculate a volume of gas from a lower to a higher temperature, we have in the first place to find the expansion for the volume unit, which is done, by adding to 1, the product of the multiplication of the thermometrical difference by 0·003665 and then to multiply the product of this calculation by the number of volume units found in the analytical process. On the other hand, to reduce a volume of gas from a higher to a lower temperature, we have to divide the number of volume units found in the analytical process, by the product of the multiplication of the thermometrical difference by 0·003665.

β. Reduction of a volume of gas of a certain given density unto 760 millimeters barometric pressure, or any other given pressure.

According to the law of *Mariotte*, the volume of a gas is inversely proportional to the pressure upon it; or in other words, that a gas occupies the greater space, the less the pressure upon it, and the less space the greater the pressure upon its surface.

Thus, supposing a gas to occupy a space of 10 cubic centimeters, at a pressure of one atmosphere, it will occupy 1 cubic centimeter at a pressure of 10 atmospheres, and 100 cubic centimeters at a pressure of $\frac{1}{10}$ atmosphere.

Nothing, therefore, can be more easy than the reduction of a gas of a certain given tension, to 760 millimeters barometric pressure, or any other given pressure.

Supposing a gas to occupy 100 cubic centimeters, at 780 millimeters barometric pressure, how much space will it occupy at 760 millimeters?

$$760 : 780 : : 100 : x$$
$$x = 102{\cdot}63.$$

How much space will 100 cubic centimeters at 750 millimeters barometric pressure, occupy at 760 millimeters?

$$760 : 750 : : 100 : x$$
$$x = 98{\cdot}68$$

γ. Reduction of a volume of gas mixed with aqueous vapour, to its actual volume in the dry state.

It is a well-known fact that water has a tendency at all temperatures, to assume the gaseous state. The degree of this tendency (the tension of the aqueous vapor)—which is dependent solely and exclusively upon the temperature, and not upon the circumstance of the water being *in vacuo* or in any gaseous atmosphere—is usually expressed by the height of a column of mercury counterbalancing it. The following table indicates the degrees of tension for the various temperatures at which analyses are likely to be made. (Compare *Magnus, Pogg.* Ann. 61, p. 247.)

TABLE.

Temperature in degrees (Centigrade).	Tension of the aqueous vapor expressed in millimeters.	Temperature in degrees (Centigrade).	Tension of the aqueous vapor expressed in millimeters.
0	4·525	21	18·505
1	4·867	22	19·675
2	5·231	23	20·909
3	5·619	24	22·211
4	6·032	25	23·582
5	6·471	26	25·026
6	6·939	27	26·546
7	7·436	28	28·148
8	7·964	29	29·832
9	8·525	30	31·602
10	9·126	31	33·464
11	9·751	32	35·419
12	10·421	33	37·473
13	11·130	34	39·630
14	11·882	35	41·893
15	12·677	36	44·268
16	13·519	37	46·758
17	14·409	38	49·368
18	15·351	39	52·103
19	16·345	40	54·969
20	17·396		

Therefore, if a gas is confined over water, its volume is, *cæteris paribus*, always greater than if it were confined over cold mercury; since a quantity of aqueous vapor, proportional to the temperature of the water, mixes with the gas, and since the tension of this partly counterbalances the column of air that presses upon the gas, and to that extent neutralises

the pressure. To ascertain the actual pressure upon the gas, we must therefore subtract from the apparent pressure so much as is neutralised by the tension of the aqueous vapor.

Suppose we had found a gas to measure 100 cubic centimeters at 770 millimeters barometric pressure, the temperature of the confining water being 10° C.: how much space would this volume of gas occupy in the dry state and at 760 millimeters of the barometer?

Our table gives the tension of aqueous vapour at 10° C., = 9·126, the gas is consequently not under the apparent pressure of 770 millimeters, but under the actual pressure of 770—9·126=760·874.

The calculation is now very simple; it proceeds upon the formula given sub. β., viz.,

$$760 : 760{\cdot}874 :: 100 : x$$
$$x = 100{\cdot}115.$$

When the volume of a gas has thus been adjusted by the calculations in α. and β., or in α. and γ., to the thermometrical and barometrical conditions on which the data of Table V. are based, the proportion of it contained in 100 parts by weight of the analysed substances may now be readily calculated by substituting the weight for the volume, and proceeding by simple rule of three.

How many parts of nitrogen are contained in 100 parts of analysed substance, of which 5 grammes have yielded 300 cubic centimeters of dry nitrogen gas at 0° C., and 760 millimeters bar.?

In Table V. we find that one litre (1000 cubic centimeters of nitrogen gas of 0° C., and at 760 millimeters bar., weighs 1·2515 grammes.

We say accordingly:

$$1000 : 1{\cdot}2515 :: 300 : x$$
$$x = 0{\cdot}375 \text{ grammes.}$$

And then:

$$5 : 0{\cdot}375 :: 100 : x$$
$$x = 7{\cdot}50.$$

The analysed substance contains consequently 7·50 per cent. by weight of nitrogen.

2. *Calculation of the percentage results by weight, in cases where the substance has been separated in combination with another, or where a compound has to be determined from one of its constituents.*

§ 167.

If the body to be determined has not been weighed or measured by itself, but in some other form or combination, *e. g.* carbonic acid as carbonate of lime, sulphur as sulphate of baryta, ammonia as nitrogen, &c., its quan-

tity must first be estimated from that of the compound found before the calculation described in 1, can be made.

This may be accomplished either by rule of three or by some abridged method.

Suppose we have weighed hydrogen in the form of water, and have found 1 gram. of water: how much hydrogen does this contain?

One equivalent of water consists of:

$$\begin{array}{r} 12{\cdot}5 \text{ of hydrogen} \\ 100{\cdot}0 \text{ of oxygen} \\ \hline 112{\cdot}5 \text{ water.} \end{array}$$

We say accordingly:

$$112{\cdot}5 : 12{\cdot}5 :: 1{\cdot}00 : x$$

$$\therefore$$

$$x = 0{\cdot}11111.$$

From this formula results the following equation:

$$\frac{12{\cdot}5}{112{\cdot}5} \times 1{\cdot}00 = x.$$

$$\therefore$$

i. e. $$0{\cdot}11111 \times 1{\cdot}00 = x.$$

Or expressed in general terms:

$$\therefore$$

$$Water \times 0{\cdot}11111 = Hydrogen.$$

EXAMPLE.—

517 of water; how much hydrogen?

$$517 \times 0{\cdot}11111 = 57{\cdot}444.$$

The following equation results also from the above given formula:

$$\frac{112{\cdot}5}{12{\cdot}5} = \frac{1{\cdot}00}{x}$$

$$\frac{112{\cdot}5}{12{\cdot}5} = 9$$

$$\text{consequently} \quad 9 = \frac{1{\cdot}00}{x}$$

$$\text{consequently} \quad x = \frac{1{\cdot}00}{9}$$

Or, expressed in general terms,

$$Water \text{ divided by } 9 = Hydrogen.$$

EXAMPLE.—

517 of water, how much hydrogen?

$$\frac{517}{9} = 57{\cdot}444.$$

In this manner we may find for every compound constant numbers by which to multiply or divide the compound, in order to find the percentage proportion by weight of the constituent sought (compare Table III.).

Thus, for instance, the nitrogen may be estimated from the double bichloride of platinum and chloride of ammonium, by dividing the weight of the latter by 15·96, or multiplying it by 0·06269 ; thus the carbon may be estimated from the carbonic acid by multiplying the weight of the latter by $0{\cdot}27\dot{2}\dot{7}$, or dividing it by $3{\cdot}6\dot{6}\dot{6}$.

These numbers are by no means so simple, convenient, and easy of retention as the number for hydrogen. It is therefore advisable, in the case of carbonic acid, for instance, to fix upon another general term, viz.,

$$\frac{\text{Carbonic acid} \times 3}{11} = \text{Carbon};$$

which is derived from the formula

$$275 : 75 :: \text{the carbonic acid found} : x$$

Since $275 : 75 :: 55 : 15$ or $11 : 3$

The object in view may also be attained in a very simple manner, by reference to Table IV., which gives the amount of the constituent sought for every number of the compound found, from 1—9 ; the operator need, therefore, simply add the several values together.

As regards hydrogen, for instance, we find :

TABLE.

Found. water	Sought. hydrogen	1	2	3	4	5	6	7	8	9
		0·11111	0·22222	0·33333	0·44444	0·55555	0·66667	0·77778	0·88889	1·00000

From this table it is seen that one part of water contains 0·11111 of hydrogen, that five parts of water contain 0·55555 of hydrogen ; nine parts 1·00000, &c.

Now if we wish to know, for instance, how much hydrogen is contained in 5·17 parts of water, we find this by adding the values for five parts, for $\frac{1}{10}$ part, and for $\frac{7}{100}$ parts, viz.,

0·55555
0·011111
0·0077778
0·5744388

Why the numbers are to be placed in this manner, and not as follows,

0·55555
0·11111
0·77778
1·44444

is self-evident, since arranging them in the latter way, would be adding the values for 5, for 1, and for 7 (5+1+7=13) and not for 5·17. This

reflection shows also that, to find the amount of hydrogen contained in 517 parts of water, the points must be transposed as follows:

55·555
1·1111
0·77778
57·44388

3. Calculation of the percentage results of indirect analyses in parts by weight.

§ 168.

The import of the term "*indirect analysis*," as defined at page 278, shows sufficiently that no universally applicable rules can be laid down for the calculations which have to be made in indirect analyses. The selection of the right way must be left in every individual case to the intelligence of the operator. I will give here the mode of calculating the results in two of the indirect analyses described in Section V. They may serve as examples for other similar calculations.

a. *Indirect separation of soda from potassa* (compare § 120, 3).

Suppose you have found 1976·11 grammes of sulphate of soda + sulphate of potassa, and in these 1976·11 grammes, 1000 grammes of sulphuric acid: how much potassa is present, and how much soda?

Expressing sulphate of potassa by K, and sulphate of soda by N, we have the following equation:

$$K+N=1976{\cdot}11$$
$$\text{or } K = 1976{\cdot}11-N.$$

One part of sulphate of soda contains 0·56338; one part of sulphate of potassa 0·45919 of sulphuric acid.

The amount of sulphuric acid present in the mixture of sulphate of soda and sulphate of potassa, viz., 1000 grammes must consequently be = 0·56338 × the number of units present of sulphate of soda (*i. e.* × the quantity of the sulphate of soda present) + 0·45919 × the number of units present of sulphate of potassa (*i. e.* × the quantity of the sulphate of potassa present).

This gives us the second equation:

$$(K\times 0{\cdot}45919)+(N\times 0{\cdot}56338)=1000$$
$$\text{Or, } K=\frac{1000-(N\times 0{\cdot}56338)}{0{\cdot}45919}$$

Substituting for K its value according to the first equation, we obtain

$$1976{\cdot}11-N=\frac{1000-(N\times 0{\cdot}56338)}{0{\cdot}45919}$$

and, taking off the denominators of the fraction,

$$(1976{\cdot}11 \times 0{\cdot}45919) - (N \times 0{\cdot}45919) = 1000 - (N \times 0{\cdot}56338),$$

that is,

$$907{\cdot}41 - (N \times 0{\cdot}45919) = 1000 - (N \times 0{\cdot}56338).$$

Placing now the two N on one side, we obtain

$$(N \times 0{\cdot}56338) - (N \times 0{\cdot}45919) = 1000 - 907{\cdot}41,$$

or,

$$N = \frac{1000 - 907{\cdot}41}{0{\cdot}56338 - 0{\cdot}45919} = \frac{92{\cdot}59}{0{\cdot}10419} = 888{\cdot}66$$

The analysed mixture therefore contains 888·66 of sulphate of soda, and consequently

$$1976{\cdot}11 - 888{\cdot}66 = 1087{\cdot}45$$

of sulphate of potassa.

From these data are now calculated the quantities of soda and potassa, as directed in 2., and the proportions of these two substances contained in 100 parts by weight of the analysed compound, as directed in 1.

The following general formula may be deduced from the above calculation :—Assuming A to stand for the mixture, and N for the Na O, $S O_3$, K for the K O, $S O_3$, and S for the $S O_3$, contained in it :

$$N = \frac{S - (A \times 0{\cdot}45919}{0{\cdot}10419}$$

$$\text{and } K = A - N.$$

Suppose we have found 20 grammes of sulphate of potassa + sulphate of soda, and in these 20 grammes 10·5 grammes of sulphuric acid, how much sulphate of potassa does the mixture contain, and how much sulphate of soda?

$$N = \frac{10{\cdot}5 - (20 \times 0{\cdot}45919)}{0{\cdot}10419}$$

$$= \frac{10{\cdot}5 - 9{\cdot}1838}{0{\cdot}10419} = \frac{1{\cdot}3162}{0{\cdot}10419} = 12{\cdot}63$$

$$K = 20 - 12{\cdot}63 = 7{\cdot}37.$$

The 20 grammes of the mixture consist accordingly of 12·63 Na O,$S O_3$, and 7·37 K O, $S O_3$.

b. Indirect separation of chlorine from bromine (§ 137, 1, *a.*).

Let us suppose the mixture of bromide of silver and chloride of silver to have weighed 20 grammes, and the decrease of weight consequent upon the transmission of the chlorine to have amounted to 1 gramme. How much chlorine does the mixture contain, and how much bromine?

The decrease of weight here is simply the difference between the weight of the bromide of silver originally present and that of the chloride of silver which has replaced it; if this is borne in mind, it is easy to understand the calculation which follows.

The difference between the respective equivalents of bromide of silver and chloride of silver is to the equivalent of bromide of silver as the ascertained decrease of weight is to x, *i.e.* to the bromide of silver originally present in the mixture; or, expressed in numbers:

$$556{\cdot}34 : 2349{\cdot}28 :: 1 : x$$
$$x = 4{\cdot}2227.$$

The twenty grammes of the analysed mixture therefore contained 4·2227 grammes of bromide of silver, and consequently 20—4·2227= 15·7773 grammes of chloride of silver.

It results from this calculation, that we need simply multiply the ascertained decrease of weight by

$$\frac{2349{\cdot}28}{556{\cdot}34} \text{ } i.\ e. \text{ with } 4{\cdot}2227$$

in order to find the amount of bromide of silver originally present in the analysed mixture. And if we know this, we also know of course the amount of the chloride of silver; and from these data we deduce the quantities of chlorine and bromine, as directed in 2, and the proportions of these two substances contained in 100 parts by weight of the analysed compound, as directed in 1.

Appendix to I.

Mean value, deficiency, and surplus in analyses.

§ 169.

If, in the analysis of a substance, one of the constituents is estimated from the loss or deficiency, or, in other words, by subtracting from the original weight of the analysed substance the ascertained united weight of the other constituents, it is evident that in the subsequent percentage calculation the sum total must invariably be 100. Every loss suffered or surplus obtained in the determination of the several constituents will, of course, fall exclusively upon the one constituent which is estimated from the loss. It is evident, therefore, that quantitative estimations of this kind can afford no guarantee of correctness, unless the other constituents have been determined by good methods, and with the greatest care. The accuracy of the results will, of course, be the greater, the less the number of constituents determined in the direct way.

If, on the other hand, every constituent of the analysed compound has been determined separately, it is obvious that, were the results absolutely accurate, the united weight of the several constituents must be exactly equal to the original weight of the analysed substance. Since, however, as we have seen in § 75, certain inaccuracies attach to every analysis, with-

out exception, the sum total of the results in the percentage calculation, will sometimes exceed, and at others fall short of one hundred.

In all cases of this description, the only proper way is to give the results as actually found.

So, for instance, *Pelouze* found, in his analysis of chromate of chloride of potassium,

Potassium	21·88
Chlorine	19·41
Chromic acid	58·21
	99·50

Berzelius, in his analysis of uraniate of potassa,

Potassa	12·8
Sesquioxide of uranium	86·8
	99·6

Plattner, in his analysis of magnetic iron pyrites.

	Of Fahlun.	*Of Brasil.*
Iron	59·72	59·64
Sulphur	40·22	40·43
	99·94	100·07

It is altogether inadmissible to distribute any chance deficiency or surplus, proportionally among the several constituents of the analysed compound, as such deficiency or surplus never arises from the several estimations in the same measure; moreover, such a way of arranging the calculation of the results deprives other chemists of the power of judging of the accuracy of the analysis. No one need be ashamed to confess having obtained somewhat too little or somewhat too much in an analysis, provided, of course, the deficiency or surplus be confined within certain limits, which are different in different analyses, and which the experienced chemist knows how to fix properly.

In cases where an analysis has been made twice, or several times, it is usual to take the arithmetical mean, as the correct result. It is obvious that an average of the kind deserves the greater confidence the less the results of the several analyses differ. The results of the several analyses must, however, also be given, or, at all events, the maximum and minimum.

Since the accuracy of an analysis is not dependent upon the quantity of substance subjected to the analytical process (provided always this quantity be not altogether too small), the average of the results of several analyses is to be taken quite independently of the quantities used, in other words, you must not add together the quantities used, on the one hand, and

the weights obtained in the several analyses on the other, and deduce from these data the percentage amount; but you must calculate the latter from the results of each analysis separately, and then take the arithmetical mean of the numbers so obtained.

Suppose a substance, which we will call AB. contains fifty per cent of A.; and suppose two analyses of this substance have given the following results:

1)2 grammes of AB. have given 0·99 grms. of A.
2)50 „ „ „ 24·00 grms. „

From analysis

No. 1, it results that AB. contains 49·50 per cent. of A.
„ 2, „ „ „ 48·00 „ „ „

Total . . .	97·50
Mean . . .	48·75

It would be quite erroneous to say

2+50=52 of AB. gave 0·99+24·00=24·99 of A.

therefore 100 of AB contain 48·06 of A.;

for it will be readily seen that this way of calculating destroys nearly altogether the influence of the more accurate analysis of the two (1) upon the average, on account of the proportionally small amount of substance used in that analysis.

II. Deduction of empirical formulæ.

§ 170.

If the percentage composition of a substance is known, a so-called *empirical* formula may be deduced from this; in other words, the relative proportion of the several constituents may be expressed in equivalents—in a formula which, upon recalculation in percents will give numbers corresponding perfectly, or nearly with those obtained by the analysis of the substance in question. We are compelled to confine ourselves to the expression of empirical formulæ, in the case of all substances of which we cannot determine the atomic weight, such as *e. g.* mannite, woody fibre, mixed substances, &c.

The method of deducing empirical formulæ is very simple, and will be readily understood from the following reflections:

How should we proceed to find the relative number of equivalents in carbonic acid?

We should say:

The equivalent of the oxygen is to the amount of oxygen in the atomic

weight of carbonic acid, as 1 is to x, *i. e.* to the number of atoms of oxygen contained in carbonic acid; accordingly

$$100 : 200 : : 1 : x$$

$$x = 2.$$

In the same manner we should find the number of atoms of carbon present in carbonic acid, by the following proportion:

75	:	75	: :	1	:	x
(equivalent of carbon)		(carbon in one equivalent of carbonic acid.)				

$$x = 1.$$

Now let us suppose we did not know the atomic weight of carbonic acid, but simply the percentage composition of this acid, viz.,

27·27 of carbon
72·73 of oxygen

100·00 of carbonic acid;

yet the relative proportion of the equivalents must appear, even though we select any other given number, *e. g.* 100, as the atomic weight of carbonic acid. Let us suppose we adopt 100 as the atomic weight of carbonic acid; thus,

100	:	72·73	: :	1	:	x
(Equ. of O)		(Amount of oxygen in the assumed atomic weight of 100)				

$$x = 0{\cdot}7273;$$

and

75	:	27·27	: :	1	:	x
(Equ. of C)		(Amount of carbon in the assumed atomic weight of 100)				

$$x = 0{\cdot}3636.$$

We see here that although the *numbers* which express the relative proportion of the atoms of oxygen and carbon, have changed, yet the *relative proportion* remains the same; since

$$0{\cdot}3636 : 0{\cdot}7272 : : 1 : 2.$$

The method may accordingly be expressed in general terms as follows:

Assume any number, say 100 (because this is the most convenient), as the atomic weight of the compound for which you wish to establish an empirical formula, and ascertain how often the equivalent number of every constituent severally is contained in the amount of the same constituent resulting from the analysis. When you have thus found the numbers expressing the relative proportion which the several constituents bear to one another, you have attained your purpose, viz., the deduction of an empirical formula. Still it is usual to reduce the numbers found to the most simple expression.

Now let us take a somewhat more complicated case, *e. g.* the deduction of the empirical formula for mannite.

The percentage composition of mannite is

39·56 of carbon
7·69 of hydrogen
52·75 of oxygen

100·00

This gives the following proportions:

1. $100 : 52{\cdot}75 :: 1 : x$
$x = 0{\cdot}5275.$
2. $12{\cdot}5 : 7{\cdot}69 :: 1 : x$
$x = 0{\cdot}6152.$
3. $75 : 39{\cdot}56 :: 1 : x$
$x = 0{\cdot}5275.$

We have now the empirical formula for mannite, viz.,

$$C_{5275}\ H_{6152}\ O_{5275}$$

A glance shows us that the number of the atoms of carbon is equal to those of the oxygen; and the question is now whether the relative proportion found may not be expressed by smaller numbers.

A simple calculation suffices to answer this question, viz.,

$$5275 : 6152 :: 60 : x$$

(Any other number might be substituted for 60, as the third term of the proportion, but 60 is the most convenient, since it is divisible without remainder by most of the numbers.)

$$x = 70.$$

We have now accordingly the more simple formula,

$$C_{60}\ H_{70}\ O_{60} = C_6\ H_7\ O_6.$$

The percentage composition of mannite given above having been deduced from the results of actual analyses, the correctness of the formula derived from it cannot be called in question. Now let us take the results of a direct analysis of mannite.

Oppermann obtained, upon the combustion of 1·593 grm. of mannite, with oxide of copper, 2·296 grammes of carbonic acid and 1·106 grm. of water. This gives by calculation in percents

39·31 of carbon
7·71 of hydrogen
52·98 of oxygen

100·00

which, calculated as above, gives

$$C_{5241}\ H_{6168}\ O_{5298}.$$

as the first expression of the empirical formula; and by the proportion;

$$5298 : 6168 : : 60 : x$$
$$x = 69{\cdot}8.$$

A glance at these numbers shows that 69·8 may be properly exchanged for 70, and also that the difference between 5241 and 5298 is so trifling that both may be expressed by the same number. These considerations lead therefore likewise to the formula

$$C_6 \quad H_7 \quad O_6$$

The proof whether the formula is correct or not is obtained by its re-calculation in percents. The less the calculated percentage differs from that found, the more reason there is to believe in the correctness of the empirical formula. If the difference is more considerable than can be accounted for by the defects inherent in the methods, there is every reason to believe the formula fallacious, in which case it is necessary to establish a more correct one; for it will be readily seen that, in the case of substances of which the atomic weight is not known, different formulæ may be deduced from one and the same analysis, or from several very nearly corresponding analyses; since the numbers found are never absolutely correct but only approximate.

Thus, for instance, in the case of mannite:

	Calculated for		for	found
C_6	39·56	C_8	39·67	39·31
H_7	7·69	H_9	7·44	7·71
O_6	52·75	O_8	52·89	52·98
	100·00		100·00	100·00

III. Deduction of rational formulæ.

§ 171.

If both the percentage composition and the atomic weight of a substance are known, it is easy to deduce its *rational* formula—that is, a formula expressing not only the relative proportion of the atoms, but also their absolute number.

The following examples may serve for illustration:

1. *Deduction of the rational formula of hyposulphuric acid.*

The analysis has shown, in the first place, the percentage composition of hyposulphuric acid, and, in the second place, the percentage composition of hyposulphate of potassa, viz.,

Sulphur	44·44	Potassa	39·551
Oxygen	55·56	Hyposulphuric acid . .	60·449
Hyposulphuric acid	100·00	Hyposulphate of potassa	100·000

(Equivalent of potassa=588·86.)

From the proportion :

$$39{\cdot}551 : 60{\cdot}449 : : 588{\cdot}86 : x$$
$$x = 900$$

results, as x, the sum of the equivalents of the constituents contained in hyposulphuric acid—in other terms, the atomic weight of hyposulphuric acid.

Having thus ascertained the correct atomic weight of hyposulphuric acid, it is unnecessary to assume a hypothetical one, as we were obliged to do in the case of mannite.

Thus we may state at once :

$$100 : 44{\cdot}44 : : 900 : x$$
$$x = 400 ;$$

i. e. like the sum of the equivalents of the sulphur ; and again :

$$100 : 55{\cdot}56 : : 900 : x$$
$$x = 500 ;$$

i. e. like the sum of the equivalents of the oxygen.

Now the equivalent of sulphur, *i. e.* 200, is contained twice in 400 ; and the equivalent of oxygen, *i. e.* 100, is contained five times in 500 ; the rational formula for hyposulphuric acid is accordingly,

$$S_2 O_5.$$

2. *Deduction of the rational formula of benzoic acid.*

Stenhouse obtained from 0·3807 grm. of hydrated benzoic acid dried at 212° 0·9575 of carbonic acid and 0·1698 of water.

0·4287 grm. of benzoate of silver, dried at 212° yielded 0·202 of silver. From these numbers results the following composition :

Carbon	68·67	Oxide of silver . . .	50·67
Hydrogen	4·95	Benzoic acid . . .	49·33
Oxygen	26·38		
		Benzoate of silver . .	100·00
Hydrated benzoic acid	100·00		

(Atomic weight of the oxide of silver = 1449·66.)

$$50{\cdot}67 : 49{\cdot}33 : : 1449{\cdot}66 : x$$
$$x = 1411{\cdot}3,$$

i. e. the atomic weight of anhydrous benzoic acid ; the atomic weight of the hydrated acid is accordingly = 1411·3 + 112·5 = 1523·8 ; we say therefore now :

$$100 : 68{\cdot}67 : : 1523{\cdot}8 : x$$
$$x = 1046{\cdot}39.$$
$$100 : 4{\cdot}95 : : 1523{\cdot}8 : x$$
$$x = 75{\cdot}43.$$
$$100 : 26{\cdot}38 : : 1523{\cdot}8 : x$$
$$x = 401{\cdot}97.$$

75	is contained in	1046·39	13·95 times
12·5	„	75·43	6·03 „
100	„	401·97	4·02 „

A glance at the numbers resulting from these divisions suffices to show that 13·95 may be exchanged for 14, and that 6 may be substituted for 6·03, and 4 for 4·02. The rational formula for the hydrate of benzoic acid is accordingly,

$$C_{14}\ H_6\ O_4.$$

This formula calculated gives,	The numbers found by *Stenhouse* were,
C 68·85	C 68·67
H 4·92	H 4·95
O 26·23	O 26·38
100·00	100·00

3. *Deduction of the rational formula of theine.*

Stenhouse's analysis of theine gave the following results:

1. 0·285 grm. of theine yielded 0·5125 of carbonic acid and 0·132 of water.

2. The combustion of theine with oxide of copper yielded a gaseous mixture of CO_2 and N, in the proportion of four of the former to one of the latter.

3. 0·5828 grm. of the double salt of hydrochlorate of theine and bichloride of platinum, yielded 0·143 platinum.

From these numbers results the following percentage composition:

Carbon .	. 49·05
Hydrogen .	5·14
Nitrogen .	28·61
Oxygen .	. 17·20
	100·00

and 2461·31 as the atomic weight of theine. There is every reason to suppose that the composition of the double salt of hydrochlorate of theine and bichloride of platinum is

$$\text{Theine} + H\,Cl + Pt\,Cl_2.$$

The atomic weight of this double salt is found by the following proportion:

$$0{\cdot}143 : 0{\cdot}5828 :: 1236{\cdot}75 \text{ (atomic weight of platinum)} : x$$

$$x = 5040{\cdot}4;$$

and consequently the atomic weight of theine, by subtracting from 5040·4 the sum of the atomic weight of one equivalent of bichloride of platinum (2123·31) and one equivalent of hydrochloric acid (455·78)

$$5040{\cdot}4-(2123{\cdot}31+455{\cdot}78)=2461{\cdot}31.$$

From the percentage composition of theine we may now deduce its empirical formula, by the following proportions :

$$75 : 49{\cdot}05 :: 1 : x$$
$$x=0{\cdot}654\,;$$
$$12{\cdot}5 : 5{\cdot}14 :: 1 : x$$
$$x=0{\cdot}411\,;$$
$$175{\cdot}0 : 28{\cdot}61 :: 1 : x$$
$$x=0{\cdot}163\,;$$
$$100 : 17{\cdot}20 :: 1 : x$$
$$x=0{\cdot}172\,;$$
$$C_{654}\,H_{411}\,N_{163}\,O_{172}\,;$$

By reducing these numbers in the manner stated page 415 (*i. e.* substituting 60 for the smallest of them and reducing the others in the same ratio), we get at the formula

$$C_{241}\,H_{151}\,N_{60}\,O_{63}\,;$$

and dividing these figures by 30, we obtain

$$C_{8{\cdot}03}\,H_{5{\cdot}03}\,N_2\,O_{2{\cdot}1}\,;$$

for which we may at once safely substitute

$$C_8\,H_5\,N_2\,O_2\,;$$

as the following percentage arrangement will show :

	Calculated.	Found.
8 C= 600·0	49·47	49·05
5 H= 62·5	5·15	5·14
2 N=350·0	28·89	28·61
2 O =200·0	16·49	17·20
1212·5	100·00	100·00

Now, looking at the atomic weight corresponding to the formula $C_8\,H_5\,N_2\,O_2$, viz., 1212·5, we find that this is contained 2·03 times in the atomic weight deduced from the analysis of the double salt of hydrochlorate of theine and bichloride of platinum, viz., 2461·31. Instead of 1 : 2·03, we may safely put 1 : 2 ; which gives us as the rational formula of theine,

$$2\times C_8\,H_5\,N_2\,O_2=C_{16}\,H_{10}\,N_4\,O_4.$$

The correctness of the assumed formula for the double salt of hydrochlorate of theine and bichloride of platinum, viz.,

$$\text{Theine}+HCl+Pt\,Cl_2$$

may now be readily tested and confirmed, by ascertaining whether the amount of platinum assumed in this formula agrees with the quantity actually found.

		In 100 parts. Calculated.	Found.
$C_{16}\ H_{10}\ N_4\ O_4$	= 2425·00		
HCl	= 455·78		
Platinum	= 1236·75	24·70 . .	24·53
Cl_2	= 886·56		
	5004·09		

4. *Special method of deducing rational formulæ for oxygen salts.*

a. In the case of compounds containing no isomorphous constituents.

The rational formulæ for oxygen salts may be deduced also by a method different from the foregoing, viz., by ascertaining the ratio which the respective quantities of oxygen bear to each other. This method is exceedingly simple.

In an analysis of crystallised sulphate of soda and ammonia, I found

Soda	17·93
Oxide of ammonium .	15·23
Sulphuric acid . .	46·00
Water . . .	20·84
	100·00

387·44 of Na O contain 100 of O, consequently 17·93 of Na O contain 4·63 of O.
325 ... $N H_4 O$ ... 100 ... O, ... 15·23 ... $N H_4 O$ ... 4·68 ... O.
500 ... $S O_3$ ... 300 ... O, ... 46·00 ... $S O_3$ ... 27·60 ... O.
112·5 ... H O ... 100 ... O, ... 20·84 ... H O ... 18·52 ... O.

The respective quantities of oxygen,

4·63 : 4·68 : 27·60 : 18·52,

stand to each other in the same ratio

as 1 : 1·01 : 5·97 : 4·00,

for which we may safely substitute

1 : 1 : 6 : 4,

which leads to the formula

$$Na O, N H_4 O, 2 S O_3 + 4 H O$$

or, $Na O, S O_3 + N H_4 O, S O_3 + 4$ aq.

b. In the case of compounds containing isomorphous constituents.

It is a well known fact that isomorphous constituents may replace each other in all proportions; therefore in establishing a formula for compounds containing isomorphous constituents, the latter are taken *collectively;* that is, they are expressed in the formula, as *one and the same* body. This very frequently occurs in the calculation of formulæ for minerals.

A. Erdmann found in *Monradite*

			Amount of oxygen.
Silicic acid	56·17	. . . . .	29·179
Magnesia	31·63	. 12·652 } . .	14·601
Protoxide of iron	8·56	. 1·949 }	
Water	4·04	. . . . .	3·590
	100·40		

Now the ratio between

$$3{\cdot}59 : 14{\cdot}601 : 29{\cdot}179$$

is as $1 : 4{\cdot}07 : 8{\cdot}1$,

for which we may safely substitute

$$1 : 4 : 8.$$

Designating one equivalent of metal by R, we find from those numbers the formula :

$$4\,(\mathrm{R\,O, Si\,O_2}) + \mathrm{HO} \text{ or } 4 \left\{ \begin{matrix} \mathrm{Mg} \\ \mathrm{Fe} \end{matrix} \right\} \mathrm{O, Si\,O_2}) + \mathrm{aq.}$$

Besides isomorphous substances, all bodies of analogous composition possess the faculty of replacing each other in compounds; thus we find that KO, Na O, Ca O, Mg O, &c., replace each other. These substances likewise must be expressed collectively in the formula.

Abich found in *Andesine*

			Amount of oxygen.	
Silicic acid	59·60	. . . . .		30·94
Alumina	24·28	. .	11·22	11·70
Sesquioxide of iron	1·58	. .	0·48	
Lime	5·77	. .	1·61	3·90
Magnesia	1·08	. .	0·43	
Soda	6·53	. .	1·68	
Potassa	1·08	. .	0·18	
	99·92			

The ratio between $3{\cdot}90 : 11{\cdot}70 : 30{\cdot}94$

is as $1 : 3 : 7{\cdot}93$;

for which we may safely substitute

$$1 : 3 : 8.$$

Designating one equivalent of metal by R, we find from these numbers the formula :

$$\mathrm{R\,O + R_2\,O_3 + 4\,Si\,O_2}$$
$$= \mathrm{R\,O, Si\,O_2 + R_2\,O_3, 3\,Si\,O_2},$$

which may likewise be written :

$$\left. \begin{matrix} \mathrm{Ca} \\ \mathrm{Mg} \\ \mathrm{Na} \\ \mathrm{K} \end{matrix} \right\} \mathrm{O, Si\,O_2} + \left\{ \begin{matrix} \mathrm{Al_2} \\ \mathrm{Fe_2} \end{matrix} \right\} \mathrm{O_3, 3\,Si\,O_2}.$$

Showing thus that this mineral is Leucite ($\mathrm{K\,O, Si\,O_2 + Al_2\,O_3, 3\,Si\,O_2}$), in which the greater part of the potassa is replaced by lime, soda, and magnesia, and a portion of the alumina by sesquioxide of iron.

These remarks respecting the deduction of formulæ for oxygen salts, apply of course equally to metallic sulphides.

IV. Calculation of the density of the vapors of volatile bodies and application of the results, as a means of controlling their analyses and determining their atomic weights.

§ 172.

The specific gravity of a compound gas is equal to the sum of the specific gravity of its respective constituents in one volume.

E. g. Two volumes of hydrogen gas, and one volume of oxygen gas, give two volumes of aqueous vapor. If they gave simply one volume of aqueous vapor, the specific gravity of the latter would be equal to the sum total of the specific gravity of the oxygen and double the specific gravity of the hydrogen, viz. :

$$\begin{aligned} 2 \times 0{\cdot}0691 &= 0{\cdot}13820 \\ &+ 1{\cdot}10563 \\ &= 1{\cdot}24383 \end{aligned}$$

But as they give *two* volumes of aqueous vapor, these 1.24383 are distributed between these two volumes ; accordingly

$$\frac{1{\cdot}24383}{2} = 0{\cdot}62192.$$

It will be readily seen that the knowledge of the density of the vapor of a compound substance supplies an excellent means of controlling the correctness of a formula with regard to the relative proportions of the equivalents.

For instance : from the results of the elementary analysis of camphor, we have deduced the empirical formula :

$$C_{10}H_8O.$$

Dumas found the density of the vapor of camphor=5·314. Now, by what means do we find whether the deduced formula is correct with respect to the relative proportions of the equivalents ?

Specific gravity of the vapor of carbon	0·8293
,, ,, ,, hydrogen gas	0·0691
,, ,, ,, oxygen gas	1·1056

$$\begin{aligned} 10 \text{ equ. C} &= 10 \text{ volumes} = 10 \times 0{\cdot}8293 = 8{\cdot}2930 \\ 8 \text{ equ. H} &= 16 \text{ volumes} = 16 \times 0{\cdot}0691 = 1{\cdot}1056 \\ 1 \text{ equ. O} &= 1 \text{ volume} = 1 \times 1{\cdot}1056 = 1{\cdot}1056 \\ & \qquad\qquad\qquad\qquad\qquad\qquad 10{\cdot}5042 \end{aligned}$$

This sum is almost exactly twice as large as the specific gravity found by direct experiment ($\frac{10{\cdot}5042}{2} = 5{\cdot}2521$) ; which shows that the relative proportions of the equivalents are correctly given in the empirical formula of camphor. But whether the formula is correct, also, with regard to the

absolute number of equivalents, cannot be determined from the density of the vapor, because we do not know to how many volumes of camphor vapor an atom of camphor corresponds. *Liebig* assumes the atom of camphor to correspond to two volumes, and gives accordingly the formula $C_{10} H_8 O$; whilst *Dumas* assumes it to correspond to four volumes, and gives the formula accordingly $C_{20} H_{16} O_2$.

The knowledge of the density of the vapor affords, therefore, simply a means of controlling the correctness of the analysis, but not of establishing a rational formula; and although it is made, nevertheless, to serve sometimes for the latter purpose, yet this can be done only in the case of substances for which we are able to infer from analogy a certain ratio of condensation: thus, for instance, experience proves that one equivalent of most of the hydrates of the volatile organic acids corresponds to 4 volumes.

In § 171, 2, we have deduced the rational formula of hydrated benzoic acid at $C_{14} H_6 O_4$. *Dumas* and *Mitscherlich* found the density of the vapor of this acid = 4·260.

Now nearly the same number is obtained by dividing by 4 the sum total of the specific gravities of the several constituents contained in one atom of hydrated benzoic acid.

14 volumes C =	11·6102
12 volumes H =	0·8292
4 volumes O =	4·4224
	16·8618

$$\frac{16{\cdot}8618}{4} = 4{\cdot}2154$$

Having thus shown how the knowledge of the density of the vapor of a body is turned to account as a means of controlling the results of an elementary analysis of the same, we will now proceed to show how the density of the vapor is calculated from the data obtained as described in § 161.

We will take as an illustration *Dumas's* estimation of the density of the vapor of camphor.

The immediate results of the process were as follows:

Temperature of the air	13·5° C.
Height of the barometer	742 millimeters
Temperature of the bath at the time of sealing the globe	244° C.
Increase of weight of the globe .	0·708 grm.
Volume of the mercury required to fill the globe . . .	295 cubic centimeters
Air remaining in the globe . .	0

Now, to find the density of the vapor, we have to answer three questions, viz.,

1. What is the weight of the air which the globe holds? (This we must necessarily know for the solution of the second question.)

2. What is the weight of the camphor vapor which the globe holds?

3. To what volume does the camphor vapor correspond at 0° C. and 0·760 millimeters bar.?

The solution of these questions is quite simple; and if the calculation, notwithstanding, appears somewhat circuitous and complicated, this is merely owing to the several reductions and corrections which are required.

1. The globe holds 295 cubic centimeters, as we see from the volume of mercury required to fill it.

Now, how much are 295 cubic centimeters of air of 13·5° C. and 0·742 millimeters bar., at 0° C. and 760 millimeters bar.?

This question is solved according to the directions of § 166, by the following proportions:

$$760 : 742 :: 295 : x$$

$x = 288$ cubic centimeters. (Of 13·5° C. and 760 millimeters bar.)

and again:

$$\frac{288}{1+(13{\cdot}5\times 0{\cdot}00366)} = \frac{288}{1{\cdot}04941} = 274 \text{ cubic centimeters (of 0° C. and 760 millimeters bar.)}$$

Now one cubic centimeter of air of 0° C. and 760 millimeters bar. weighs 0·0012932 grm.; 274 cubic centimeters weigh accordingly

$$0{\cdot}0012932 \times 274 = 0{\cdot}35434 \text{ grm.}$$

2. *What is the weight of the vapor?*

At the beginning of the experiment we tared the globe + the air within it; we afterwards weighed the globe + the vapor (but without the air);—to find, therefore, the actual weight of the vapor, it is not sufficient to subtract the tare from the weight of the globe filled with vapor, since (*glass* + *vapor*)—(*glass* + *air*) is not = *vapor*; but we have either to subtract, in the first place, the weight of the air from the tare, or to add the weight of the air to the increase of the weight of the globe. Let us do the latter:

Weight of the air in the globe	= 0·35434 grm.
Increase of the weight of the globe	= 0·70800 grm.
The weight of the vapor is accordingly	= 1·06234 grm.

3. *Now to what volume at* 0° C. *and* 760 *millimeters bar. does this* 1·06234 *grm. of vapor correspond?*

We know from the above given data that this weight corresponds to 295 cubic centimeters at 244° C., and 742 millimeters bar. Before we can proceed to reduce this volume according to the directions of § 166, the following corrections are necessary:

a. 244° C. of the mercurial thermometer correspond, according to *Magnus's* experiments, to 239° C. of the air thermometer—(see Table VI.)

b. According to *Dulong* and *Petit*, glass expands (commencing at 0° C.) $\frac{1}{35000}$ of its volume for every one degree C. The volume of the globe at the time of sealing, was accordingly :

$$295 + \frac{295 \times 239}{35000} = 297 \text{ cubic centimeters.}$$

If we now proceed to reduce this volume upon 0° C. and 760 millimeters bar., we find by the proportion,

$$760 : 742 :: 297 : x$$

x (*i. e.* cubic centimeters of vapor at 760 millimeters bar. and 239° C.) $= 290$; and by the equation,

$$\frac{290}{1 + (239 \times 0{\cdot}00366} = x$$

x (*i. e.* cubic centimeters of vapor at 760 millimeters bar. and 0° C.) $= 154{\cdot}6$

154·6 cubic centimeters of camphor vapor of 0° C, and 760 millimeters bar. weigh accordingly 1·06234 grm.

One litre (1000 cubic centimeters) weighs consequently 6·8715 grms. ; since

$$154{\cdot}6 : 1{\cdot}06234 :: 1000 : 6{\cdot}8715.$$

Now one litre of air of 0° C., and 760 millimeters bar. weighs 1·2932 grm.

The density of the camphor vapor consequently is = 5·314 ; since

$$1{\cdot}2932 : 6{\cdot}8715 :: 1 : 5{\cdot}314.$$

PART II.

SPECIAL PART.

I. ANALYSIS OF WATERS.

A. Analysis of fresh water in springs, wells, brooks, rivers, &c.*

§ 173.

The analysis of the several kinds of fresh water *usually* is restricted to the quantitative estimation of the following substances :

a. Bases : Soda, lime, magnesia.

b. Acids : Sulphuric acid, silicic acid, carbonic acid (combined), chlorine.

c. Suspended matters : Clay, &c.

We confine ourselves here therefore to these bodies. If the examination is to extend to other constituents besides these, the methods given in §§ 174 to 180 are resorted to.

I. *The water is clear.*

1. *Determination of the chlorine.* Take from 500 to 1000 grammes or c.c.† Acidulate with nitric acid, and precipitate with nitrate of silver. Filter when the precipitate has *completely* subsided (§ 112, I. *a.*). If the quantity of the chlorine is so inconsiderable that the solution of nitrate of silver produces only a slight turbidity, evaporate a larger portion of the water to one-half, a quarter, one-sixth, &c., filter, wash the precipitate, and treat the filtrate as directed.

2. *Determination of the sulphuric acid.* Take about 1000 grammes. Acidulate with hydrochloric acid and mix with chloride of barium. Filter when the precipitate has *completely* subsided (§ 105, I. 1). If the quantity of the sulphuric acid is very inconsiderable, evaporate the acidified water to one-half, one quarter, one-sixth, &c., before adding the chloride of barium.

3. *Determination of the total amount of the salts, and also of the soda, lime, magnesia, and silicic acid.*

* Compare the chapter on the same subject in Fresenius's Qualitative Analysis.

† As the specific gravity of the fresh water of springs, rivers, &c., differs but little from that of pure water, the several quantities of water may safely be measured instead of weighed. The calculation is facilitated by taking a round number of cubic centimeters.

a. Evaporate 1000 grammes of the water cautiously to dryness, in a platinum or porcelain dish, first over a lamp, finally on the water-bath. Expose the residue, in the air-bath, to a temperature of about 390° until no further diminution of weight takes place. This gives the *total amount of the salts.*

b. Treat the residue with water, and then cautiously add dilute sulphuric acid in moderate excess; cover the vessel during this operation with a dish, to avoid loss from spirting, and lastly place on the water-bath. After ten minutes rinse the cover by means of a washing bottle, evaporate the contents of the dish to dryness, expel the free sulphuric acid, ignite the residue intensely (§ 77, 1), and weigh. The residue consists of sulphate of soda, sulphate of lime, sulphate of magnesia, and some silicic acid which has separated.

c. Heat the contents of the dish with water nearly to boiling; * allow it to deposit, and pass the solution through a filter. Repeat this operation four or five times with small quantities of water, to ensure the solution of all the sulphate of soda and sulphate of magnesia.

Put the small dish with the undissolved sulphate of lime, which contains silicic acid, temporarily aside under a bell-glass; dry the filter through which the fluid has passed, and then burn it on a platinum wire so that the ashes may fall into the dish.

d. Mix the fluid with chloride of ammonium, and add some oxalate of ammonia. Filter when the small quantity of oxalate of lime (corresponding to the sulphate of lime which has got into the solution) has subsided. Wash and dry the filter, and then burn it in or over the dish which contains the principal portion of the lime as sulphate; treat the contents of the dish cautiously with some dilute sulphuric acid; evaporate, ignite, and weigh. Heat the weighed contents of the dish with concentrated hydrochloric acid, to dissolve the sulphate of lime. Treat the undissolved residuary *silicic acid* repeatedly with hydrochloric acid, and, lastly, wash it thoroughly on a small filter. Deduct the weight of the silicic acid from that of the last weighed contents of the dish; the difference expresses the weight of the sulphate of lime, from which the *lime* is then ultimately calculated.

e. In the fluid filtered from the oxalate of lime determine the *magnesia* with phosphate of soda (§ 82, 2). Calculate the precipitate obtained for sulphate of magnesia, and deduct the quantity of sulphate found, together with that of the sulphate of lime and the silicic acid, from the total amount of the salts as ascertained in *b.*: what remains is *sulphate of soda.*

4. Calculate the numbers found in 1 to 3, for 1000 parts of water, and

* If the quantity of the lime is inconsiderable you may also heat the contents of the dish with hydrochloric acid, until all is dissolved, except the silicic acid. Filter the fluid, well wash the silicic acid, dry and weigh it. Treat the filtrate as directed in *d.*

determine from the data obtained the amount of *carbonic acid* in combination, as follows :

Add together the quantities of sulphuric acid corresponding to the bases found, and subtract from the sum, first, the amount of sulphuric acid precipitated from the water by chloride of barium (2), and secondly, an amount corresponding to that of the chlorine found (for one equivalent of Cl, one equivalent of SO_3) ; the difference expresses the quantity of the carbonic acid combined with the bases in the form of *neutral* carbonates. 500 parts of sulphuric acid remaining after the subtraction of the quantities just stated, correspond to 275 parts of carbonic acid.

5. *Control.*

If the quantities of the soda, the lime, the magnesia, the sulphuric acid, the silicic acid, the carbonic acid, and the chlorine, are added together, and an amount of oxygen corresponding to the chlorine (since this is combined with metal and not with oxide) is subtracted from the sum, the balance remaining must closely correspond to the total amount of the salts found in 3, *a*. *Perfect* correspondence cannot be expected, since, 1, upon the evaporation of the water chloride of magnesium is partially decomposed, and converted into a basic salt ; 2, the silicic acid expels some carbonic acid ; 3, it is difficult to free carbonate of magnesia from water without incurring loss of oxygen ; and 4, the residue remaining upon the evaporation of the water, contains the carbonate of magnesia as a *basic* salt, whilst in our calculation we have assumed the quantity of carbonic acid corresponding to the *neutral* salt.

II. *The water is not clear.*

Fill a large flask of known capacity with the water, close with a glass stopper, and allow the flask to stand in the cold until the suspended matter is deposited ; draw off the clear water with a siphon as far as practicable, filter from the residuary sediment, dry or ignite the contents of the filter, and weigh. Treat the clear water as directed in I.

Respecting the calculation of the analysis, I refer to § 180, remarking simply that it is *usually** arranged upon the following principles :

Chlorine is calculated in combination with the sodium ; if there is an excess, this is calculated in combination with the magnesium ; if there is still an excess, this is calculated in combination with the calcium. If, on the other hand, there remains an excess of soda, this is calculated in combination with sulphuric acid. The *sulphuric acid* or, if part of this has been calculated already in combination with soda, the remainder of it is estimated in combination with lime. The *silicic acid* is put down in the free state, the remainder of the *lime* and the *magnesia* as carbonates, and this, according to the circumstances, as neutral carbonates, or as bicarbonates.

* There is a certain latitude allowed in the mode of arranging the calculation of the results.

It must always be borne in mind that the results of the *qualitative* analysis may render another arrangement of the calculation necessary. In the statement of the results the quantities are often calculated for 10000 parts of water instead of 1000 parts; and frequently also in grains per pound of water (1 pound=7680 grains).

B. ANALYSIS OF MINERAL WATERS.*

§ 174.

In the analysis of mineral waters we have a larger number of substances than claim our attention in that of fresh waters. In general the following substances have to be quantitatively determined in an analysis of a mineral water:

a. Bases: Potassa, soda, lithia, ammonia, lime, baryta, strontia, magnesia, alumina, protoxide of iron, protoxide of manganese (oxide of zinc, oxide of copper, oxide of lead, binoxide of tin, teroxide of antimony).

b. Acids: Sulphuric acid, phosphoric acid, silicic acid, carbonic acid, boracic acid, nitric acid, chlorine, iodine, bromine, fluorine, hydrosulphuric acid, crenic acid, apocrenic acid (arsenious and arsenic acids).

c. Non-combined elements and indifferent gases: Oxygen, nitrogen, carbide of hydrogen.

d. Indifferent organic substances.

Many of these substances occur in most springs, in predominant proportions; of the bases, more particularly soda, lime, magnesia, and sometimes also protoxide of iron; and of the acids,—sulphuric acid, carbonic acid, silicic acid, chlorine, and sometimes also hydrosulphuric acid. The others are almost invariably found in exceedingly minute proportions only. The substances between brackets occur usually only in the muddy, ochreous or solid sinter deposits of springs,† which form, in most mineral springs, in the parts where the air acts upon the water flowing off, or kept in a reservoir.

We shall discuss the subject of the analysis of mineral waters under two heads, viz., 1. *The performance of the analytical process;* and, 2. *The calculation and arrangement of the results.*

* Compare the chapter on the same subject in Fresenius's Qualitative Analysis.

† If they contain oxide of lead, oxide of copper, &c., which might proceed from metal tubes, stopcocks, &c., the real origin of the oxides must be most carefully ascertained (see qualitative analysis).

1. Performance of the analytical process.

The performance of the analytical process is divided into two parts, viz., 1, operations and experiments at the source; and, 2, operations and experiments in the laboratory.

A. Operations and experiments at the source.

§ 175.

I. Apparatus and other requisites.

1. A pipette (frequently called a siphon) of from three hundred to four hundred cubic centimeters capacity (see Fig. 90). The exact capacity of the pipette is ascertained by filling it with water, and measuring the contents.



Fig. 90.

2. Five bottles, provided with good corks; each of these bottles should hold about one and a half times the contents of the pipette.

3. A good thermometer. One with cut, or etched divisional lines on the stem answers best.

4. A mixture of two volumes of solution of ammonia and one volume of solution of chloride of barium. This mixture generally becomes turbid, which, however, is of no consequence. It is filtered.

5. About eight white glass bottles of from one and a half to two litres capacity, with well fitting stoppers; ground glass stoppers answer the purpose best; if corks are used it is advisable to cover them with a thin piece of vulcanised india-rubber.

6. Some larger bottles, holding together at least fifty pounds of water, with tight-closing corks or glass-stoppers; instead of these a small carboy may be used.

7. One middle sized and two large funnels.

8. Swedish filtering paper.

9. Flasks, beakers, lamp, glass rods, glass tubes, caoutchouc tubes, files, scissors, knife, corks, string, &c.

10. Reagents, more especially the following: ammonia, hydrochloric acid, acetic acid, tannic acid, and gallic acid (infusion of galls), tincture of litmus (newly prepared), test papers. Besides these articles, the following are also required under certain circumstances:

a. If the water contains sulphuretted hydrogen or an alkaline sulphide.

11. A solution of iodine in iodide of potassium of known strength. This must be very dilute; the best way is to prepare it by adding to one

volume of *Bunsen's* solution of iodine (§ 114, Appendix) four volumes of water; which gives a mixture containing in 100 c. c. about 0·100 grms. of iodine.

12. Acetic acid.

13. Starch.

14. A burette.

b. If the water contains a large proportion of protoxide of iron, and this is to be determined at the source in the direct way (volumetrically).

15. A solution of permanganate of potassa. For waters abounding in iron, this solution must be of that degree of dilution that 100 c. c. of it convert about 0·04 grm. of iron from the state of protoxide to that of sesquioxide. If the water contains only a moderate proportion of iron, the solution must be still more largely diluted. As it is necessary to fix its strength on the spot, a burette, a pipette, and a weighed piece of pianoforte wire are also required.

c. To determine the indifferent gases dissolved in the water (nitrogen, oxygen, &c.).

16. A glass globe of known capacity (this should hold about 770 c. c.).

17. A delivery tube, fitted air-tight into the perforated cork of the globe (16).

18. A graduated cylinder of about 150 c. c.'s capacity; and a number of tubes of the kind described in 23.

19. A small pneumatic trough.

20. Solution of potassa.

21. A tripod for supporting the globe.

22. Some wax.

d. To determine the gases evolved at the source.

23. A blowpipe, and a number of tubes of the shape illustrated in Fig. 91.



Fig. 91.

These tubes should be from two to three centimeters wide, and the part *a b* from ten to twelve centimeters long. They are intended to receive the gas at the source, that it may afterwards be examined in the laboratory. To examine the gas *thoroughly* on the spot would require a complete mercurial pneumatic apparatus; whilst simply to ascertain the amount of the carbonic acid absorbable by solution of potassa, as compared to that of the other gases, which are not absorbed by that agent, requires only a graduated tube, some solution of potassa, and a small funnel.

If the water evolves sulphuretted hydrogen, the analyst must provide himself, in addition to the above enumerated articles, with,

24. A flask with the neck somewhat drawn out; and with a caoutchouc tube and compression stop-cock; and,

25. An ammoniacal solution of chloride of copper (see § 176, 14).

II. Analytical processes.

§ 176.

1. Examine the water as regards its outward appearance (color, clearness, &c.). A water will often appear clear at a first glance, and yet upon closer inspection in a large white bottle show a few or even a great many colored or colorless flakes, &c. If this happens to be the case, the bottle is allowed to stand a day or two; the clear water is then decanted, and the matters which may have subsided are examined under the miscroscope. This examination often reveals the presence of infusoria, plants of the lowest order, &c.*

2. Observe whether gas is disengaged at the source; whether the water in a glass forms small pearly bubbles; and whether it evolves gas when shaken in a half-filled bottle.

3. Examine the taste and smell of the water. To detect very minute portions of odorous matters, half fill a tumbler, or better still, a water bottle, cover with the hand, shake vigorously, take off the hand, and smell the water.

4. Ascertain the reaction of the water by testing with the several test papers (or, better still, with blue and but very slightly reddened tincture of litmus); and observe whether the color which it has acquired changes upon drying in the air.

5. Examine the temperature of the water. The simplest and best way of effecting this is, if practicable, to plunge the thermometer into the spring, and to note accurately the height of the mercury whilst the thermometer still remains in the water; or a long bottle with a thermometer in it, is filled with water by immersion in the spring, and left some time in the latter; it is then taken out, and the height of the thermometer in the flask accurately noted. If the water flows from a pipe, it is received in a small wide-necked flask, which is then emptied and re-filled; it is emptied again and refilled once more; the bulb of the thermometer is exposed for a time to the action of the water flowing from the pipe, and then ultimately plunged into the water in the flask.

In addition to the temperature of the spring must be noted also:

a. The date;

* Compare "Chemische Untersuchung der wichtigsten Mineralwasser des Herzogthums Nassau, von Professor Dr. *Fresenius*, III. Die Quellen zu Schlangenbad. Wiesbaden bei *W. C. Kreidel*, 1852;" and, more particularly *Schulz* in "Jahrbücher des Vereins für Naturkunde im Herzogthume Nassau," Heft VIII.

b. The temperature of the air.

c. The circumstance whether the temperature of the water is constant, or varies in the different seasons of the year; which may generally be ascertained on the spot.

6. Fill the bottles named in § 175, 5, with water. This must be effected with great care, to prevent the turbid water entering into the bottles, which is very likely to happen, if you knock against the bottom or sides of the basin at the source. If you cannot succeed in procuring the water quite clear, filter it in four of the eight bottles, using for this purpose large funnels with folded filters of Swedish paper, which will greatly expedite the process of filtration. Close the bottles well, and mark them distinctly.

7. Pour about 80 c. c. of the newly filtered and perfectly clear ammoniacal solution of chloride of barium (§ 175, 4) into each of the five bottles named in § 175, 2.

8. Immerse the pipette slowly until the upper part is below the surface of the water; close the aperture tight with the thumb, and lift the pipette out of the spring; transfer the contents of the pipette to one of the five bottles, and immediately insert the cork tightly. Fill the other four bottles in the same way. For greater safety secure the corks with string. If the water flows from a pipe, this mode of filling the bottles will not answer. In such cases I weigh the bottle and cork with the ammoniacal solution of chloride of barium in it. I then allow the water to enter until the bottle is nearly full, when I quickly insert the cork, and weigh again.

9. If the water contains hydrosulphuric acid, determine the latter in a large measured portion of the water with the aid of the solution of iodine (§ 175, 11), as directed § 116, I. *a*. Take care to lose as little gas as possible in the measuring, which may be effected with the pipette. If the water contains an alkaline carbonate, you must add some acetic acid or chloride of barium before adding the solution of iodine (§ 116, II. 2, *b*. *a*.).

It is often desirable to know whether sulphuretted hydrogen escapes upon ebullition. To ascertain this, fill a flask about three-fourths with a measured portion of the water, close the mouth of the flask with a perforated cork into which a bent tube is fitted air-tight. Boil the water in the flask, and when the ebullition has lasted twenty minutes, place over the end of the bent tube a piece of a caoutchouc tubing which is closed at the other end with a piece of a glass rod. Acidify the cold fluid with acetic acid, and test with solution of iodine. The difference between the results of this operation, and those obtained by the process described in 9, shows the quantity of sulphuretted hydrogen which has escaped.

10. If the water contains a somewhat large proportion of carbonate of

protoxide of iron—which is indicated by the rather dark violet color exhibited upon addition of gallic and tannic acids—endeavour to determine the carbonate of protoxide of iron volumetrically with the aid of the dilute solution of permanganate of potassa (§ 175, 15. Compare § 89, 2, *a*.). Take for the experiment about 500 c. c. of the water. Perform the experiment in a white bottle standing on a sheet of white paper. Mix the water previously with *pure* hydrochloric acid.

Repeat the experiment several times until you obtain sufficiently constant results.*

If the water smells of sulphuretted hydrogen, or if it contains a notable proportion of organic substances, this method cannot be employed.†

11. If you wish to determine the indifferent gases (nitrogen, oxygen, carbide of hydrogen) which the water holds in solution, and which escape upon boiling, fill the glass globe (§ 175, 16), quite full with the mineral water, and fix the delivery tube, also quite full of the water and closed at the exit aperture with a little wax stopper, in the globe by means of a perforated cork. Place the globe on the tripod; let the delivery tube dip into the pneumatic trough, which is filled with weak solution of potassa, and in which the graduated glass cylinder, also filled with that fluid, is inverted. Take out the little wax plug, insert the exit end of the delivery tube into the mouth of the cylinder, and heat the globe; keep the water boiling with a lamp for about ten minutes, and then remove the delivery tube from the trough. Leave the cylinder with the expelled gases a very long time inverted in the trough with the solution of potassa, until the volume of the unabsorbed gas suffers no further diminution; then read off the volume with due regard to the temperature and atmospheric pressure. This operation gives the total volume of the indifferent gases. If you wish to ascertain the actual nature of the gases, repeat the experiment, but receive the

* By this expeditious process we may readily ascertain how much protoxide of iron the water of a chalybeate spring loses in its passage to the reservoir, and thence to the baths: or after being kept for a shorter or longer time in a stone jar. The quantitative estimation of the iron, which I made in a preliminary examination of the springs of Schwalbach, corresponded almost exactly with the results of a careful analysis made afterwards in the laboratory.

† The following modification which, however, I have not yet tried, might, perhaps, be adopted in the analysis of mineral water in which hydrosulphuric acid only is present with the protoxide of iron. Determine the amount of solution of iodine which corresponds to a certain definite quantity of solution of permanganate of potassa, in its action upon an equal quantity of very dilute pure sulphuretted hydrogen water. Test 500 c. c. of the mineral water with solution of iodine, and another 500 c. c. with solution of permanganate of potassa; the former process gives the amount of the sulphuretted hydrogen present in the analysed water; the latter, after deducting from the quantity of solution of permanganate of potassa used an amount exactly corresponding in its action upon sulphuretted hydrogen to the quantity of solution of iodine used, gives the proportion of the iron contained in the analysed water.

gases over solution of potassa in tubes of the form described § 175, 23, and illustrated in Fig. 91 ;* close the tubes by fusion with the aid of the blowpipe, whilst the aperture remains still in the solution of potassa ; carry the tubes home for the ulterior processes in the laboratory. In sealing the tubes, bear in mind that the water must stand higher inside the tube than outside, since, if this is not the case, the glass will inevitably bulge upon the application of the blowpipe.

12. If you wish to ascertain with precision the nature of the gases evolved, receive them in tubes of the same kind as in 11 (§ 175, 23), by inverting the latter filled with mineral water, inserting a small funnel, and receiving the ascending bubbles ; when the tube is nearly full, immerse it in a beaker filled with the water, and seal at the narrowed part with the blowpipe, as in 11. It is necessary to fill several tubes in this way.

13. As the evolved gases consist mostly only of carbonic acid, oxygen, and nitrogen, it often suffices to determine the first in the direct way, and to estimate the sum of the other two from the loss. For this purpose receive the gases in a somewhat narrow graduated cylinder ; when the latter is quite full, close the mouth with the finger, invert it in a glass with solution of potassa, and determine the quantity of the unabsorbed gas. Repeat the experiment several times. If you wish to determine approximately the oxygen in the residuary gaseous mixture, introduce a ball of phosphorus fused on a platinum wire, and leave it in the mixture, until the volume of the gas suffers no further diminution. The gas absorbed by the phosphorus is oxygen.

14. If sulphuretted hydrogen is given off, fill a rather large sized flask, with the neck somewhat drawn out, with the mineral water, push over the neck a piece of a wide caoutchouc tube provided with a strong compression stopcock ; insert into the other end of the caoutchouc tube a funnel, and fill the latter also with water. Invert the whole under the surface of the water, and receive the gases. When the flask is full close the compression stop-cock, and invert the flask in a beaker containing solution of chloride of copper mixed with ammonia in excess ; open the stopcock, and let a sufficient quantity of the solution enter the flask ; shut the cock, shake, allow the mixture to stand some time, filter the sulphide of copper formed, and determine the sulphur in it as directed § 116, II. 2, *a*. Calculate from the quantity of the sulphur found the amount of sulphuretted hydrogen. By subtracting this from the gases absorbable by solution of potassa and determined in 13, you obtain the volume of the carbonic acid.

* The narrow passage in the tubes impedes the entrance of the gases ; this may be remedied by introducing a strong pianoforte wire beneath the confining fluid, and moving it slowly up and down.

15. Fill the large bottles (§ 175, 6) with the mineral water. Generally it is unnecessary to filter it.

16. Pay attention to every particular connected with the spring, and to every circumstance which may have a bearing upon the investigation: as, for instance, the quantity of water which the spring yields,—whether the level remains the same or not,—whether a muddy deposit, or solid sinter forms in the outlet pipes or in the reservoir (in which case a tolerably large quantity of the deposit must be taken),—to what geological formation the mountain belongs from which the water springs,—the depth from which the spring rises,—the nature of the basin,—the predominant action and effects of the water, &c.

B. Operations in the laboratory.

I. Qualitative analysis.

This is effected in the manner described in my Qualitative Analysis.*

II. Quantitative analysis.

§ 177.

The course to be pursued in the quantitative analysis of mineral waters, varies according to the presence or absence of alkaline carbonates. As the analytical course is more simple in the case of alkaline than in that of non-alkaline waters, we will begin here with the latter, which, in fact, almost entirely includes the processes, &c., required in the analysis of alkaline waters, and we will afterwards point out the modifications required respectively, in the analysis of alkaline and of sulphuretted waters. We proceed upon the assumption that all the matters are present which are usually found associated in saline springs.

As the evaporation of large quantities of water, which is necessary to effect the determination of the substances present in very minute proportions, consumes much time, it is advisable to carry the evaporation on concurrently with the other analytical processes, and accordingly to begin with it first. From 10000 to 20000 grammes of the water are gradually evaporated in a platinum or porcelain dish,† with addition of a sufficient

* Mineral waters which have been kept a long time in stone jars, often smell of sulphuretted hydrogen, though in the fresh state they were entirely free from that odor. This is owing to the circumstance that the contact with the moist cork reduces a portion of the sulphates to sulphides, from which the free carbonic acid afterwards evolves sulphuretted hydrogen.

† If you use a porcelain dish you must renounce the detection and determination of alumina.

quantity of absolutely pure carbonate of soda,* to impart a feebly alkaline reaction† to the fluid. The best way is to conduct the evaporation in a separate room, to which no one but the analyst has access, over gas or spirit-lamps, or on the sand-bath; that the greatest cleanliness is necessary in the operation need hardly be mentioned; it is not advisable therefore to allow this operation to be performed by another person. When the fluid is somewhat concentrated the evaporation is continued on the water-bath or on a very moderately heated sand-bath, until the residue is perfectly dry.

The actual analysis of the water is preceded by the

DETERMINATION OF THE SPECIFIC GRAVITY.

Equalise the temperatures of a bottle of the mineral water and a bottle of distilled water, and note the height of the thermometer. Fill an accurately tared small bottle of at least 100 grammes capacity, provided with a close-fitting glass stopper,‡ with the distilled water, and weigh; empty the bottle, refill it with the mineral water, and weigh again. The quotient obtained by dividing the weight of the mineral water by that of the distilled water, gives the specific gravity of the former. Take care that there are no gas bubbles in the bottles filled with water.

The respective quantities required for the estimation of the several constituents may be determined either by weight or by measure. I prefer the former. If they are estimated by measure, the small bottle or flask may be used which has served in the determination of the specific gravity, or any other measuring vessel may be employed.

1. ESTIMATION OF THE TOTAL AMOUNT OF THE FIXED INGREDIENTS.

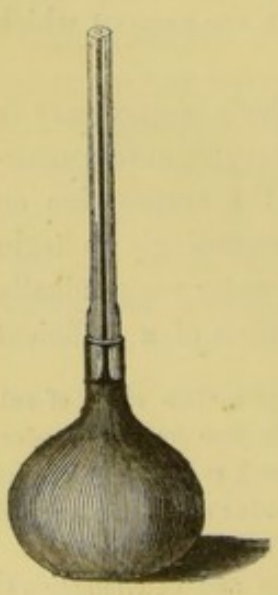


Fig. 92.

Weigh from 200 to 300 grammes of the mineral water in a small flask, and evaporate it cautiously and gradually in a weighed platinum dish at a temperature below the boiling point. If the water contains much gas cover the dish at first, and after each addition of a fresh portion of water, with a large

* Free more especially from phosphoric acid, alumina, and manganese.

† The addition of carbonate of soda is intended to prevent volatilisation of hydrobromic or hydriodic acid from bromide or iodide of magnesium. If a mineral water contains no sulphuric acid a very small quantity of sulphate of soda is also added.

‡ A flask with a long perforated ground stopper, as illustrated in Fig. 92, answers best for the determination of the specific gravity.

watch glass. The evaporation may be conducted over the lamp. Terminate it on the water-bath, and dry the residue in the air- or oil-bath, at a temperature of from 356° to 392°, until repeated weighings give the same constant result; note the weight.* Fill the dish again one-half with distilled water, and add from time to time a drop of dilute sulphuric acid, until you are quite sure that the quantity of the acid added is sufficient to convert all the salts into sulphates; keep the dish covered all the time with a glass dish; evaporate now to dryness, ignite the residue (§ 76, 1), and weigh. The weight found affords a very good control of the analysis (see below). The silicic acid in the residue may be determined by treating the mass first with water, then with concentrated hydrochloric acid (to dissolve the sulphate of lime), until all the soluble parts are removed.

2. Determination of the sulphuric acid.

If chloride of barium produces at once a marked turbidity in the water acidified with hydrochloric acid, take about 600 grammes of the water, mix with hydrochloric acid, add chloride of barium, allow the mixture to deposit twenty-four hours, and determine the sulphate of baryta as directed § 105. If the turbidity produced by the chloride of barium is only slight, evaporate from 1000 to 2000 grammes of the water, with addition of hydrochloric acid, to one-half, a quarter, &c., and treat the residuary fluid as just now directed.

3. Joint estimation of the chlorine, iodine, and bromine.

Acidify from 50 to 100 grammes of the water with nitric acid, precipitate with nitrate of silver, and determine the precipitate as directed § 112, I. *a*.

4. Estimation of the total amount of the lime, magnesia, iron, manganese (if present in a somewhat large proportion), silicic acid, and the alkalies.

Weigh one of the bottles filled at the source with perfectly clear, if necessary, filtered water (§ 176, 6), with its contents; pour some of the water cautiously, and without spilling a drop, into a beaker, and add to the water, both in the bottle and beaker, hydrochloric acid until the latter slightly predominates. Cover the bottle with a watch-glass, the beaker with a glass plate, and apply a very gentle heat, until the carbonic acid has escaped. Evaporate the contents of both vessels in a platinum or porcelain dish, to dryness, and separate the silicic acid as directed § 111,

* The quantity of the chloride of magnesium suffers in this operation a slight diminution of weight, as a small portion of it decomposes with the water into hydrochloric acid, which escapes, and magnesia, which remains behind. However, the error arising from this is but trifling, and may mostly be disregarded, since, for the reasons given in § 173, I. 5, the total amount of the fixed ingredients estimated jointly, can never be expected to correspond exactly to the sum total of the several constituents separately determined. Still this defect may be corrected, by evaporating the water with a weighed quantity of ignited carbonate of soda (*Mohr*).

II. *a.* Mix the hydrochloric acid solution with chloride of ammonium, add ammonia free from carbonic acid until it predominates, then some sulphide of ammonium, close the vessel, and let the mixture stand twelve hours at a gentle heat; filter quickly, and wash the precipitate with water to which some sulphide of ammonium has been added.

a. The *precipitate* may be assumed to contain iron, manganese, alumina, phosphoric acid. In most cases we determine in it simply the sesquioxide of iron, sometimes also the protoxide of manganese; whilst we determine the traces of the other substances in the residue left upon the evaporation of the large bulk of 10000 or 20000 grammes of the water.

Dissolve the precipitate by heating with hydrochloric acid; boil with some nitric acid, and filter; nearly saturate with carbonate of soda, then add carbonate of bartya (§ 128, A. 1), and filter. Dissolve the precipitate in hydrochloric acid, precipitate the baryta by sulphuric acid, and separate the iron and alumina as directed § 128, B. 1, 3, or 10. When you have weighed the sesquioxide of iron you must still ascertain whether it is free from silicic acid, that is, whether upon solution in hydrochloric acid it does not leave more silicic acid behind than corresponds to the filter ash.

From the fluid filtered from the precipitate produced by carbonate of baryta throw down the baryta by sulphuric acid, and then the manganese by ammonia and sulphide of ammonium (§ 86). Test the filtrate for lime and after this for magnesia. If you find traces of these substances collect them in small filters, and ignite the latter jointly with the filters containing the principal bulk of the same substances (see *b.*). Instead of precipitating the manganese with sulphide of ammonium, you may also add a little chloride of zinc to the fluid, precipitate with carbonate of soda, and determine the manganese in the ignited residue as directed § 128, B. 10, *d.* If you now precipitate the solution remaining in the flask with ammonia and sulphide of ammonium, you can still determine in the filtrate the traces of lime and magnesia which may be present.

Instead of employing this process, you may also at once determine the iron and manganese by the volumetrical method (§ 128, 10).

b. From the *filtrate* precipitate the lime with oxalate of ammonia, added only slightly in excess; filter, dry, and weigh the precipitate.* Evaporate the filtrate to dryness, with addition of some hydrochloric acid in the latter stage of the process; expel the ammonia salt by gentle ignition; and separate the magnesia from the alkalies as directed in § 121, A. 1. Evaporate the fluid which contains the chlorides of the alkali metals to dryness, adding in the last stage of the process, a fresh but very small quantity of oxide of mercury; ignite the covered dish gently, until

* The weighed precipitate must be carefully examined to make sure that it contains no magnesia, as admixtures of that substance are more frequently found in it than is generally believed.

you are sure that all the oxide of mercury is expelled; weigh. Treat the residuary mass with water, and if a trace of magnesia is still left undissolved, filter, and weigh it; deduct the weight found from that of the weighed contents of the dish, and add it to the principal bulk of the magnesia. Before entering the weight of the magnesia, ascertain whether it dissolves completely (except the filter ash) in hydrochloric acid; and whether ammonia produces a precipitate in the *sufficiently* acid solution (which precipitate would show the presence of alumina from the porcelain dish). Should an insoluble residue be left, or should ammonia produce a precipitate in the strongly acid solution, these impurities must be determined and deducted from the magnesia.

If the quantity of the sulphuric acid was small, the solution of the alkaline chlorides is free from that acid, since the trifling amount of sulphate has been decomposed by the ignition with chloride of ammonium. But as this can never be positively known, and as repeated evaporation with chloride of ammonium is somewhat tedious, the following proceeding may be adopted: transfer a few drops of the solution, by means of a glass rod, to a test tube, and add a few drops of alcoholic solution of strontium and a little spirits of wine. If no precipitate forms, this is a proof that the fluid contains no sulphuric acid, in which case add the contents of the test tube again to the solution, and determine the potassa in the latter as directed § 120, 1, *a*. But if a precipitate forms, treat the whole solution cautiously in the same way as the sample in the test tube, let the mixture stand some time, and then filter the fluid from the precipitated sulphate of strontia, which determine as directed § 80. Estimate the potassa in the filtrate as directed § 120, 1, *a*. It is necessary to weigh the sulphate of strontia, that the quantity of the soda may be accurately calculated. The quantity of the soda is ascertained, by subtracting from the weighed residue in the dish, 1, the trace of magnesia (if any remains); 2, the chloride of potassium; and, 3, the weight of sulphate of soda corresponding to the sulphuric acid found. The remainder is chloride of sodium. The soda is then calculated from the two latter salts.

The method described in 4, has not hitherto been usually employed; but I am convinced that, in skilful hands, it gives very good results. The common way, however, is to determine in the fluid filtered from the lime, only the magnesia, by precipitating the filtrate at once with phosphate of soda. The determination of the alkalies is then effected in a fresh portion of the water, this is concentrated by boiling; the sulphuric acid is thrown down from it, without previous filtration, by chloride of barium, and then the magnesia by baryta water. The fluid is now filtered, and the excess of baryta, together with the lime, thrown down

from the filtrate, by carbonate of ammonia; the precipitate is filtered, and the filtrate evaporated to dryness; the residue is ignited, redissolved in water, and the solution again, and even a third time, precipitated with ammonia and carbonate of ammonia; and even then the chlorides of the alkali metals often retain a trace of magnesia. Putting these several operations together, the process which I have recommended here will certainly appear the more expeditious of the two.

5. ESTIMATION OF THE LIME, MAGNESIA, IRON (AND MANGANESE), IN THE PRECIPITATE FORMED UPON THE EBULLITION OF THE WATER; AND OF THE LIME AND MAGNESIA IN THE BOILED WATER.

Boil from 600 to 800 grammes of the water in a glass flask for about an hour, replacing from time to time what has evaporated by distilled water. (If this precaution were neglected, sulphate of lime might separate in conjunction with the carbonates of the alkaline earths.)

Filter the precipitate and wash it.

Separate and determine the lime and magnesia in the filtrate as directed § 122.

Dissolve the precipitate in dilute hydrochloric acid, heat with some nitric acid, and determine the iron, lime, and magnesia in the solution as in 4.

6. ESTIMATION OF THE TOTAL AMOUNT OF CARBONIC ACID PRESENT.

The bottles prepared at the spring as stated § 176, 8, are employed for the purpose. The determination is effected in two or three bottles, exactly as directed § 110, I. *b*. The results must pretty nearly agree; the mean of them is taken. If the water which has given the baryta precipitates has been measured, the number of cubic centimeters must be multiplied by the specific gravity found, to ascertain the number of grammes of water to which the carbonic acid found corresponds.

7. ESTIMATION OF THE BARYTA, STRONTIA, PROTOXIDE OF MANGANESE, ALUMINA, AND PHOSPHORIC ACID; AND ALSO OF THE IODINE AND BROMINE.

The residue left upon evaporating from 10000 to 20000 grammes of the water (see the beginning of this paragraph) is used to effect the determination of these substances, which are present only in small proportions.

Triturate and digest the perfectly dry saline mass repeatedly with spirits of wine of 90 per cent, until you are quite sure that the iodides and bromides of the alkali metals which may be present are completely dissolved.

a. Evaporate the *alcoholic filtrate* cautiously, to dryness, and determine the iodine in the residue by means of chloride of palladium, the bromine

in the filtrate as directed § 137. As this fluid might contain traces of lithia, remove the metals by sulphuretted hydrogen, and keep the fluid for the determination of the lithia (see below, *b. bb. β.*).

b. Treat the residue with water, add hydrochloric acid cautiously until the solution is acid, and evaporate to dryness. Dissolve the saline mass in water, with addition of very little hydrochloric acid, and filter from the undissolved residue, which, besides silicic acid, contains all the baryta and strontia present, in the form of sulphates, and besides these also sulphate of lime.

aa. Dry this residue and add the filter ash to it; boil the mass with carbonate of soda and solution of soda, to dissolve the principal portion of the silicic acid. Fuse the undissolved part with some carbonate of soda and potassa, and treat the fused mass with boiling water, until no trace of sulphuric acid can be detected in the washings. Dissolve the residue (which must contain baryta and strontia in the form of carbonates) in a very small proportion of dilute hydrochloric acid, and separate the baryta, strontia, and lime, as directed § 122, B. I.

bb. Oxidise the *fluid* filtered from the silicious residue with nitric acid, *nearly* neutralise it with *absolutely* pure carbonate of soda or potassa (quite free from phosphoric acid), and then precipitate with perfectly pure carbonate of baryta (free from lime, strontia, and phosphoric acid). Let the mixture stand in a stoppered flask for twelve hours in the cold, then filter and well wash the precipitate.

a. Heat the precipitate,—which, besides the excess of carbonate of baryta and sulphate of baryta, contains all the sesquioxide of iron, and also alumina* and phosphoric acid, and may contain, besides, traces of fluoride of calcium—with hydrochloric acid, and throw down the baryta from the solution by sulphuric acid added very slightly in excess. Evaporate in the water-bath to remove the excess of hydrochloric acid as far as practicable; dissolve the residue in water, transfer the solution to a small flask, add tartaric acid, then ammonia, and allow the fluid to stand twelve hours. If a trifling precipitate subsides, filter and examine it; it may contain fluorine† and phosphoric acid in combination with lime. Mix the clear, or as the case may be, filtered fluid with sulphide of ammonium and let the mixture stand in a stoppered flask until the fluid exhibits a pure yellow color. Filter from the sulphide of iron (§ 90, 1, *b.*), and evaporate the filtrate in a platinum dish, adding some pure carbonate of

* If the evaporation of the 10000 or 20000 grammes of the water has been conducted in a porcelain dish, the residue left upon that evaporation (and accordingly also the fluid of *bb.* and the precipitate thrown down from it) contains, besides the alumina originally present in the water, also alumina proceeding from the porcelain of the evaporating dish.

† As the greater portion of the fluorine has, in the evaporation with hydrochloric acid, volatilised as fluoride of silicon, the fluorine found in *a.* gives, of course, no clue to the proportion of that element contained in the water.

soda—that there may be an excess of fixed base for the phosphoric acid—and some pure nitrate of potassa, the more readily to destroy the tartaric acid. Finally heat to redness until the residue looks perfectly white. Add water and hydrochloric acid until all is dissolved, and then ammonia to the clear fluid. If a precipitate forms filter and weigh it. Mix the filtrate with a little sulphate of magnesia. If this gives a precipitate of *phosphate* of magnesia and ammonia (which determine as directed § 106, I. *b.*), the alumina precipitate may be entered in the calculation as *phosphate of alumina* (PbO_5, Al_2O_3). But if no precipitate forms, the phosphoric acid in the alumina precipitate has to be determined as directed § 106, II. *f.*, *m.*, or *o.* I have to remark here, once more, that the alumina found can only be calculated as an ingredient of the analysed water, if the processes of evaporation, &c., have been conducted in platinum vessels.

β. Mix the fluid filtered from the precipitate produced by carbonate of baryta, in a stoppered bottle, with chloride of ammonium, ammonia, and sulphide of ammonium. Let the mixture stand twelve hours, and then filter the precipitated sulphide of manganese; dissolve it in hydrochloric acid, precipitate once more with ammonia and sulphide of ammonium, and ultimately determine the manganese as directed § 86, 1; or mix the hydrochloric acid solution of the first precipitate of sulphide of manganese with some chloride of barium, precipitate with carbonate of soda, and determine the manganese by the volumetrical method (§ 127, 4, *b.*).

In the fluid filtered from the sulphide of manganese there still remains the lithia to determine. To effect the determination of that substance mix the filtrate with ammonia and carbonate of ammonia, allow it to deposit, and filter the fluid from the carbonate of lime and baryta. Add the filtrate to the fluid filtered from the sulphide of palladium, &c. (§ 177, 7, *a.*), evaporate to dryness, and remove the chloride of ammonium by gentle ignition; then separate the magnesia by oxide of mercury (§ 82, 3, *b.*). Treat the ignited residue with a mixture of absolute alcohol and anhydrous ether. If chloride of lithium is present it will dissolve in this mixture. Evaporate the solution, dissolve the residue in water, and test the concentrated aqueous solution with ammonia and carbonate of ammonia. If the slightest turbidity is perceptible you must go through the same processes again, to remove the still remaining traces of baryta, lime, or magnesia. Evaporate again to dryness, ignite gently, treat the residue once more with absolute alcohol and ether, and filter, if an undissolved sediment remains; evaporate the solution, and weigh the residue. Redissolve it in a very little absolute alcohol, and ignite the solution: a carmine flame shows chloride of lithium. Upon evaporating the solution with phosphate of soda, phosphate of soda and lithia, difficultly soluble in water, must be formed.

8. Estimation of the ammonia.

To effect the estimation of the ammonia in mineral waters I can recommend the following method, which I have employed with good results in my analysis of the Wiesbaden *Kochbrunnen :*

Evaporate about 2000 grammes of the mineral water, with addition of a small measured amount of hydrochloric acid, in a tubulated retort, until only a small quantity of the fluid is left. Add to this, through a funnel tube, a measured quantity of newly prepared solution of soda, put the neck of the retort a little upwards, and keep the contents boiling until the fluid is almost entirely evaporated. Conduct the whole of the vapors escaping through a *Liebig's* cooling apparatus, and receive the distillate in a flask containing a little water acidified with a small measured quantity of hydrochloric acid. Convert the chloride of ammonium contained in this fluid into ammonio-bichloride of platinum (bichloride of platinum and chloride of ammonium), by evaporation with a measured quantity of bichloride of platinum (§ 78, 2). Make now a counter-experiment with the same quantities of hydrochloric acid, solution of soda, and bichloride of platinum, and deduct the small amount of ammonio-bichloride of platinum obtained in this from that obtained in the first experiment: the difference expresses the quantity proceeding from the analysed water.

Instead of this method you may also employ the more simple process which *Boussingault** has lately proposed, and which is conducted as follows:

Distil in a distilling apparatus about 10 litres of the water, until about two-fifths have passed over. In the analysis of saline springs, you must add some solution of soda or milk of lime to ensure the ammonia passing over. Transfer the distillate to a glass flask connected with a *Liebig's* cooling apparatus, and distil over one-fifth. Determine the ammonia in this distillate by adding five or ten c. c. of very dilute sulphuric acid, and saturating the excess of the latter with a solution of soda, of which five c. c. neutralise one c. c. of the dilute sulphuric acid used (comp. § 78, 3). Let another fifth distil over, and determine the ammonia in this (if any is still present) in the same way. But the first portion usually contains the whole of the ammonia.

9. Detection and estimation of the crenic and apocrenic acids.

Boil a rather large quantity of the precipitate formed upon the evaporation of the water, about one hour, with solution of potassa; filter, acidify the filtrate with acetic acid, add ammonia, and after twelve hours filter the precipitate of silicic acid and alumina, which usually forms. Add to the filtrate acetic acid to acid reaction, then neutral acetate of copper. If a brownish precipitate forms, this consists of apocrenate of copper (which,

* Compt. rend., 36, 814. Pharm. Centralblatt, 1853, 369.

according to *Mulder*, contains variable quantities of ammonia); an analysis of apocrenate of copper dried at 284°, gave 42·8 per cent of oxide of copper. Mix the fluid filtered from the precipitate with carbonate of ammonia, until the green color is changed to blue; then apply heat. If a bluish-green precipitate forms, this is crenate of copper, which, dried at 284°, contains 74·12 per cent of oxide of copper (*Mulder*).*

10. Detection and estimation of the organic extractive matter.

Almost all mineral waters, when boiled in large quantities, filtered and evaporated, leave a residue which, when heated, turns brown and black: this is owing to the presence of organic extractive matter. To determine the amount of this a weighed portion of the filtered mother liquor is evaporated to dryness with carbonate of soda; the residue is boiled with water, and the solution filtered; the filtrate is evaporated to dryness, and the residue dried at 284°, until it suffers no further diminution of weight. It is then gently ignited until the black color which it acquires at first has disappeared. The difference between the weight of the dried and that of the ignited residue indicates the amount of the extractive matter. The residue contains sometimes an admixture of resinous matter, in which case it is treated with alcohol, and water added to the solution; the alcohol is then evaporated, whereupon the resinous part, being insoluble in water, separates.

11. I omit giving special methods for the quantitative estimation of boracic acid, nitric acid, and fluorine, in mineral waters, as it is generally sufficient simply to detect the presence of these substances.

12. To examine the gases collected at the spring in tubes, and brought in them to the laboratory, take a graduated tube, bent at the open end, as shown in Fig. 93, and about twenty centimeters long, and having an inner diameter of two centimeters. Moisten this tube inside with a drop of water, and then fill it with mercury. Immerse the tube with the gas in the mercurial trough, break off the point, and, giving the tube the proper inclination, cause the gas to ascend into the graduated tube. Read off the volume of the gas, with due regard to the temperature and atmospheric pressure; then introduce into the gas, by means of a platinum wire on



Fig. 93.

* For more detailed information on the subject of crenic acid and apocrenic acid, I refer to *Mulder's* paper on these acids, in the Journal f. prakt. Chem. XXXII., S. 321—344.

which it is cast, a ball of hydrate of potassa* moistened with water. Take care not to allow the other end of the wire to project above the surface of the mercury, otherwise a diffusion of the confined gas with the outer atmospheric air will take place along the wire, which is not moistened by the mercury. When the volume of the gas shows no further diminution, remove the potassa-ball, and read off the volume of the gas. The gas absorbed is carbonic acid, and in cases where sulphuretted hydrogen is present, also the latter gas, which, however, has already been determined.

The gaseous residue consists usually only of oxygen and nitrogen, in which case it may be examined as directed in the chapter on the analysis of atmospheric air (§ 226, &c.). If there is reason to suspect the presence of marsh gas (light carbide of hydrogen), the oxygen is removed by means of a wetted ball of phosphorus introduced into the gaseous mixture, and left in contact with it as long as white fumes of phosphorous acid are visible round the ball. The phosphorous acid fumes, the tension of which cannot well be taken into account, are ultimately absorbed by a moistened potassa-ball, and the gas is measured in the dry state. The composition of the gaseous residue is now ascertained by transferring it, wholly or partially, to a eudiometer, burning the marsh gas, should any of this happen to be present, with oxygen, and absorbing the carbonic acid formed. Compare "Handwörterbuch der Chemie von *Liebig, Poggendorff,* und *Wöhler,*" Art. "Eudiometer" (von *Kolbe*), in which *Bunsen's* methods for the analysis of gases are accurately described, and from which the instructions given above are taken.

Modifications required by the presence of a fixed alkaline carbonate.

§ 178.

1. A mineral water containing an alkaline carbonate cannot contain salts of lime and of magnesia soluble *per se;* all the lime and all the magnesia found are to be regarded as carbonates dissolved by free carbonic acid, though the whole of the magnesia does not precipitate upon the ebullition of the water, as a small quantity of double carbonate of magnesia and soda is invariably formed under these circumstances. The separate determination of the lime and magnesia in the precipitate sub-

* Balls of this kind are made by pouring fused hydrate of potassa into a pistol bullet-mould of about six millimeters inner diameter, and into the middle of which a platinum wire is inserted. After cooling they are found attached to the wire. The neck which has formed on the wire is scraped off with a knife.

siding upon the ebullition of the water, and in the boiled water, is therefore dispensed with. However, if desirable, these substances may be determined according to the directions of § 177.

2. If you prefer determining the alkalies in a separate portion of water, you may best effect this in the following manner: boil the water cautiously down to half the original bulk, in a platinum, silver, or porcelain dish, and filter; well wash the precipitate with boiling water; acidify the filtrate slightly with hydrochloric acid, concentrate the fluid considerably, add a little finely divided oxide of mercury, and evaporate to dryness; ignite the residue gently to effect the separation of the small quantity of magnesia left in the boiled water in form of carbonate of magnesia and soda. Treat the residue with water, filter the solution from the small quantity of magnesia and silicic acid which has separated, and wash; add to the filtrate one or two drops of carbonate of ammonia, and see if this throws down an additional trace of lime. If a precipitate forms, filter, and evaporate the filtrate, or, (if no precipitate forms,) the unfiltered fluid in a platinum dish to dryness, ignite the residue cautiously and weigh. The residue contains soda and potassa, partly combined with the known quantity of sulphuric acid, partly in the form of chlorides. Treat with an alcoholic solution of chloride of strontium, and determine the potassa as directed § 120, 1, *a*. Deduct from the total weight found of the alkaline salts, the weight of the alkaline sulphates as calculated from the sulphuric acid, and the weight of the alkaline chlorides as calculated from the chlorine of which the amount is also known; the difference is chloride of sodium, formed from, and equivalent to, the carbonate of soda.

3. In the analysis of a water so highly dilute that a preliminary concentration is required, before the estimation of the chlorine and the sulphuric acid can be effected; I recommend the following method:

1. ESTIMATION OF THE CHLORINE, PROTOXIDE OF IRON, PROTOXIDE OF MANGANESE, LIME, AND MAGNESIA.

Transfer the water of several weighed bottles (about 2000 grammes), to a porcelain dish; rinse the bottles, and add the rinsings to the water to be evaporated; a sediment of sesquioxide of iron may have formed in the bottles; it is a matter of indifference whether the rinsing removes this completely or not. Evaporate the water to one-fifth; pass the concentrated fluid through a filter thoroughly washed with some nitric acid and water, and well wash the precipitate with boiling water.

a. Acidify the *filtrate* with nitric acid, precipitate with nitrate of silver, filter, and determine the chloride of silver in the usual way. Free the filtrate from the excess of silver by means of hydrochloric acid, evaporate the filtrate, and throw down, with oxalate of ammonia and phosphate of soda, the small quantity of magnesia which is never absent,

and traces of lime which may be present. (The precipitates are ignited and weighed with the principal quantities.)

b. Dissolve the *precipitate*, together with the residuary sediment which may still remain in the bottles, in hydrochloric acid, and treat the solution by one of the methods given in § 129.

2. ESTIMATION OF THE SILICIC ACID, THE SULPHURIC ACID, AND THE ALKALIES.

Evaporate the contents of several weighed bottles in a porcelain dish; pour a little hydrochloric acid into the bottles, to dissolve the deposit of sesquioxide of iron, &c., which may have formed in them, and add the solution to the contents of the dish. Continue to evaporate the now acid fluid for some time longer, then transfer it to a platinum dish, and evaporate to dryness on the water-bath. Moisten the residue with hydrochloric acid, and evaporate again to dryness; moisten once more with hydrochloric acid, add water, apply heat, and filter off the silicic acid.

Precipitate the filtrate with chloride of barium, added in the least possible excess, and filter the fluid from the sulphate of baryta. Evaporate the filtrate nearly to dryness, dissolve the residue in water, and cautiously add *pure* milk of lime until the fluid manifests a strongly alkaline reaction. Heat, and filter; precipitate with ammonia and carbonate of ammonia, and filter again; evaporate the filtrate to dryness in a platinum dish, and gently ignite the residue until all salts of ammonia are expelled. Dissolve the residue in a little water, precipitate again with ammonia and carbonate of ammonia, filter, evaporate, weigh the now pure chlorides of the alkali metals, and separate potassa and soda as directed § 120.

The quantity of the alkaline carbonate is determined most accurately in the indirect way, in the calculation of the results—provided always the various analytical processes have been carefully conducted.—Of the direct methods proposed, I will give the following:

Boil from 300 to 400 grammes of the water for some time, filter, and wash the precipitate with hot water. Mix the filtrate intimately with the washings, divide the mixture into two equal parts, and determine in one the chlorine in the usual way, after previous addition of nitric acid. Mix the other half with pure hydrochloric acid until the fluid distinctly manifests an acid reaction; evaporate to dryness, and gently ignite the residue, then dissolve in water, filter, and determine the chlorine also in this solution. It is evident that you will obtain in this second operation more chlorine than in the first: every equivalent of chlorine by which the results of the second operation exceeds that of the first, corresponds to one equivalent of carbonic acid which existed in combination with an alkali. This method gives a little too much, as the filtrate always contains some

carbonate of soda and magnesia. If you wish to correct this error, you must determine the small quantity of magnesia which existed as chloride of magnesium in the fluid precipitated with solution of nitrate of silver, and deduct from the difference between the two determinations of the chlorine, an amount of the latter substance corresponding to the magnesia. The carbonate of soda must not be converted into chloride of sodium by evaporating the solution with chloride of ammonium; since the excess of the chloride of ammonium would decompose the alkaline sulphate present, and more chlorine would accordingly be found than corresponds to the alkaline carbonate.

Note on the analysis of sulphuretted waters.

§ 179.

A mineral water smelling of sulphuretted hydrogen, without manifesting an alkaline reaction, can only contain this gas in a free state. But if the reaction is alkaline, the water may also, besides sulphuretted hyd rogen, contain an alkaline sulphide, or a hydrosulphate of a sulphide. The estimation of the total amount of sulphur combined with hydrogen or with metals has been effected already at the source (§ 176, 9), where we have been shown also how to ascertain the quantity of sulphuretted hydrogen which escapes upon boiling. Now, I have to remark here that in the analysis of water containing free carbonic acid or bicarbonates, it cannot be accurately inferred from these data how much of the sulphuretted hydrogen exists in a free state, and how much in combination; since, as is well known, free carbonic acid, and even alkaline bicarbonates, readily decompose sulphide of potassium or sulphide of sodium upon boiling, and evolve sulphuretted hydrogen. To say, as is often stated, that mineral waters containing alkaline carbonates contain no free sulphuretted hydrogen, but a soluble metallic sulphide is going too far; as waters of the kind often smell very strongly of sulphuretted hydrogen, and disengage a quantity of that gas when shaken in a half-filled bottle. (Compare my examination of the mineral springs of Krankenheil, near Tölz, Journal f. prakt. Chem. 58, 156).

2. Calculation, control, and arrangement of the results of analyses of mineral waters.

§ 180.

The results found in the several analytical processes described in 1, are obtained by direct experiments. They are altogether independent of any theoretical views which may be entertained as to the manner in which the several constituents are combined or associated with each other.

As our theoretical views on the subject may change with the progress of chemistry, it is absolutely indispensable, in reports of analyses of mineral

waters, to give the direct results obtained, and the methods by which they were obtained. An analysis so recorded is of service for all times. With respect to the principles that guide chemists in the hypothetical association of the acid and bases found in the water, it is assumed that the combination of these bases and acids to form salts is governed by their respective affinities, *i.e.* the strongest acid is assumed to be combined with the strongest base, &c.; due attention being paid, however, to the greater or less degree of solubility of the salts, since it is well known that this exercises a considerable influence upon the manifestations of the force of affinity. Thus, for instance, when lime, potassa, and sulphuric acid are found in the boiled water, the sulphuric acid is assumed in the first place to exist in combination with the lime, &c. It cannot be denied, however, that this way of proceeding leaves much to the individual views and discretion of the analyst, and consequently, that different modes of associating the several ingredients found may lead to different results for one and the same analysis.

A general understanding upon this point would be very advantageous, because without it the comparison of two mineral waters is beset with difficulties. As long as an agreement of this kind is wanting, a comparison between two mineral waters can only be made as regards the direct and immediate results of the respective analyses.

One point, I think, should be at once agreed upon, viz., to put all the salts down in the calculation as anhydrous salts.

To illustrate the principles which I conceive ought to guide chemists in this matter, and also the way of controlling the results obtained, I select the following example.

Analysis of the boniface well at Salzschlirf.*

a. The percentage results of the analysis.

Specific weight=1·011164.

1. Total amount of the fixed constituents: 1·3778 per cent.
2. Joint amount of chlorine, iodine, and bromine: 2·8071 per cent silver precipitate.
3. Total amount of lime, magnesia, iron, and silicic acid:
   - *a*. Lime 0·10442 per cent.
   - *b*. Silica 0·00114 per cent.

(The gross amount of magnesia and iron was not determined.)

* Compare "Chemical Investigations of the mineral spring at Salzschlirf in the bishopric of Fulda (Electorate of Hesse), by *Fresenius* and *Will:* Annalen der Chemie und Pharmacie, LII. 66. To facilitate references to the original paper, I have copied the results as they stand, and have refrained from altering them according to the corrected atomic weights.

4. *α.* LIME, MAGNESIA, AND IRON IN THE PRECIPITATE WHICH SEPARATES UPON BOILING:

a. Lime 0·03642 per cent.

b. Magnesia 0·00041 per cent.

c. Sesquioxide of iron 0·00066 per cent.

β. LIME AND MAGNESIA IN THE BOILED AND FILTERED WATER.

a. Lime 0·064724 per cent.

b. Magnesium 0·028855 per cent.

5. ALKALIES:

a. Potassa 0·00865 per cent.

b. Soda 0·54783 per cent.

6. SULPHURIC ACID: 0·10853 per cent.

7. TOTAL AMOUNT OF CARBONIC ACID: 0·194301 per cent.

8. BROMINE AND IODINE:

a. Bromine: 0·000402 per cent.

b. Iodine: 0·000447 per cent.

The remaining constituents, such as lithia, phosphoric acid, protoxide of manganese, crenic acid, apocrenic acid, and extractive matter, were not determined by weight.

b. Calculation of the results.

α. The salts precipitated upon boiling are assumed to be present as carbonates held in solution by free carbonic acid.

1. 0·00066 sesquioxide of iron correspond to 0·00096 of CARBONATE OF PROTOXIDE OF IRON, which contain 0·00038 of carbonic acid.

2. 0·03642 of lime correspond to 0·06533 of CARBONATE OF LIME, which contain 0·02891 of carbonic acid.

3. 0·00041 of magnesia correspond to 0·00085 of CARBONATE OF MAGNESIA (MgO, CO_2), which contain 0·00044 of carbonic acid.

β. The amount of carbonic acid present in the free state, and in combination with carbonates (in the form of bicarbonates) may now be readily calculated by subtracting the amount of the acid in the carbonates, from the total weight of the carbonic acid found in the analysed water, viz.,

Total amount of the carbonic acid . .		0·194301
Carbonic acid existing in combination		
With lime . . .	0·02891	
With magnesia . .	0·00044	
With protoxide of iron .	0·00038	
		0·029730
There remain carbonic acid in the free state and partially combined		0·164571

γ. The sulphuric acid is assumed to exist in the first place; in combi-

nation with lime; should an excess remain, this is assumed to exist in combination with potassa, and should there still remain an excess, this is supposed to exist as sulphate of soda.

1. The boiled water contains 0·064724 of lime, which combine with 0·09261 of sulphuric acid, giving 0·15733 of SULPHATE OF LIME.

2. 0·00865 of potassa combine with 0·00737 of sulphuric acid, giving 0·01602 of SULPHATE OF POTASSA.

3. Total amount of sulphuric acid present		0·10853
Of which there are combined		
With lime	0·09261	
With potassa	0·00737	
Total		0·09998
There remain		0·00855

of sulphuric acid, which combine with 0·00666 of soda, giving 0·01521 of SULPHATE OF SODA.

δ. The rest of the soda present exists as chloride of sodium.

Total amount of soda present	0·54583
Combined with sulphuric acid	0·00666
There remain	0·53917

of soda, which correspond to 0·40123 of sodium, which latter, combining with 0·61040 of chlorine, give 1·01163 of CHLORIDE OF SODIUM.

ϵ. The whole of the iodine and bromine are assumed to exist in combination with magnesium; and the rest of the magnesium as chloride of magnesium.

1. 0·000447 of iodine combine with 0·000044 of magnesium, giving 0·000491 of IODIDE OF MAGNESIUM.

2. 0·000402 of bromine combine with 0·000065 magnesium, giving 0·000467 of BROMIDE OF MAGNESIUM.

Total amount of magnesium contained in the boiled water		0·028855
Of which there are combined		
With iodine	0·000044	
With bromine	0·000065	
Total		0·000109
There remain		0·028746

of magnesium which are combined with 0·080220 of chlorine, giving 0·108966 of CHLORIDE OF MAGNESIUM.

c. Control.

I. The joint amount of the lime in the boiled water and in the precipi-

tate which forms upon ebullition must be equal, or, at least, nearly equal, to the total amount of the lime.

Total amount of lime		0·10442
Combined with carbonic acid	0·03642	
Combined with sulphuric acid	0·06472	
Total		0·10114

II. The amount of chlorine directly determined must correspond to the joint amount of the chlorine contained in the chlorides of sodium and magnesium.

The joint amount of the chloride, bromide, and iodide of silver is		2·807100
Subtract from this the amount of iodide of silver corresponding to 0·000491 of iodide of magnesium, viz.	0·000828	
And the amount of bromide of silver corresponding to 0·000467 of bromide of magnesium, viz.	0·000958	
Total		0·001786
There remains		2·805314
which correspond to chlorine		0·69202

According to δ. . . 0·61040 of chlorine are combined with sodium.

And according to ϵ. . . 0·08022 of chlorine are combined with magnesium.

Total	0·69062	0·69062

III. The total amount of the fixed constituents must correspond to the joint amount of the several ingredients (the iron is here calculated as sesquioxide, since it is contained in that form in the residue).

Total amount of the fixed constituents = 1·37780

The respective estimations of the several constituents gave:

Carbonate of lime	0·06533
,, magnesia	0·00085
Sulphate of lime	0·15733
,, potassa	0·01602
,, soda	0·01521
Chloride of sodium	1·01163
,, magnesium	0·10896
Iodide of magnesium	0·00049

Bromide of magnesium .	0·00047
Sesquioxide of iron . .	0·00066
Silica	0·00114
Total	1·37809*

d. Arrangement and classification of the results.

The analyst should state, in the first place, how many parts of the several constituents are contained in 100 (or 1000 or 10000) parts of the water; and, in the second place, how many grains (1 lb. = 7680 grs.) of the several constituents are contained in one pound of the water.

The most appropriate way of classifying the results, is to enumerate them under the following heads:

A. Fixed constituents.

a. Present in ponderable quantity.

b. Present in imponderable quantity.

B. Volatile constituents.

As regards the carbonates it is a question whether they should be put down as neutral salts, the excess of carbonic acid being considered partly as forming bicarbonates, and partly as free acid, or whether they should be calculated at once as bicarbonates, the excess of the carbonic acid being deemed as existing in the free state. Chemists sometimes adopt the one way, sometimes the other, but the former more frequently than the latter.

Besides stating the weight of the carbonic acid (and of the gases in general), it is customary to give also the volumes, calculated both in cubic centimeters and in cubic inches (1 lb. of water = 32 cubic inches, Rhen. measure). These calculations are adjusted to the temperature of the spring.

For similar examples to guide the young chemist in calculating and controlling the results of analyses of mineral waters, I refer to the following:

1. Analysis of the *Kochbrunnen* at Wiesbaden† (saline water).

2. Analysis of the hot spring at Asmannshausen, by *Fresenius* and *Will*, Ann. der Chem. und Pharm. 47, 198 (alkaline water).

* This control gives properly corresponding results only in the analysis of waters containing but small quantities of magnesium and silicic acid, for the reasons stated § 173, 5. In cases where these constituents are present in larger proportions, it is advisable to make, instead of, or besides this control, a comparison of the sulphates (the iron being estimated as pure sesquioxide) with the residue obtained by the evaporation of the water with sulphuric acid, and subsequent ignition (§ 177, 1).

† Chemische Untersuchungen der wichtigsten Mineralwasser des Herzogthums Nassau, von Professor Dr. R. Fresenius, Wiesbaden, bei C. W. Kreidel, 1850—1852.

3. Analysis of the mineral springs at Ems* (alkaline water).

4. Analysis of the mineral springs at Krankenheil, near Tölz, by *Fresenius*, Journ. f. prakt. Chemie, 58, 156 (alkaline sulphuretted water).

Papers 1 and 3 contain also a detailed description of the methods employed to determine the muddy ochreous, and the solid sinter deposits of these springs.

II. ANALYSIS OF SUCH TECHNICAL PRODUCTS AND MINERALS WHICH ARE OF FREQUENT OCCURRENCE, INCLUDING PROCESSES FOR TESTING THEIR QUALITY AND ESTIMATING THEIR COMMERCIAL VALUE.

1. Determination of the amount of anhydrous acid in solution (acidimetry).

A. Estimation by specific gravity.

§ 181.

The specific gravity of an acid of course varies with the degree of dilution of that acid. Tables, based upon the results of exact experiments, have been drawn up, expressing in numbers the relations between the specific gravity of the several aqueous solutions of an acid, and the amount of anhydrous acid contained in them. Therefore, to know the amount of anhydrous acid contained in an aqueous solution of an acid, it suffices, in many cases, simply to determine its specific gravity. Of course the acids must, in that case, be perfectly or at least nearly free from admixtures of other substances dissolved in them. Now, as most acids are volatile (sulphuric acid, hydrochloric acid, nitric acid, acetic acid), any non-volatile contamination may be readily detected by evaporating a sample of the acid in a small platinum or porcelain dish.

The determination of the specific gravity is effected either by comparing the weight of equal volumes of water and acid (§ 177), or by means of a good hydrometer. The results must, of course, be adjusted to the temperature to which the Tables refer.

The following Tables give the relations between the specific gravity and the amount of anhydrous acid, for sulphuric acid, hydrochloric acid, and nitric acid.

* Chemische Untersuchungen der wichtigsten Mineralwasser des Herzogthums Nassau, von Professor Dr. R. Fresenius, Wiesbaden, bei C. W. Kreidel, 1850—1852.

TABLE I.

Specific gravity of sulphuric acid at different degrees of dilution, by *Bineau;* calculated for 15° C. (59° F.), by *Otto.*

Hydrated acid.	Specific gravity.	Anhydrous acid.	Hydrated acid.	Specific gravity.	Anhydrous acid.
100	1·8426	81·63	50	1·398	40·81
99	1·842	80·81	49	1·3886	40·00
98	1·8406	80·00	48	1·379	39·18
97	1·840	79·18	47	1·370	38·36
96	1·8384	78·36	46	1·361	37·55
95	1·8376	77·55	45	1·351	36·73
94	1·8356	76·73	44	1·342	35·82
93	1·834	75·91	43	1.333	35·10
92	1·831	75·10	42	1·324	34·28
91	1·827	74·28	41	1·315	33·47
90	1·822	73·47	40	1·306	32·65
89	1·816	72·65	39	1·2976	31·83
88	1·809	71·83	38	1·289	31·02
87	1·802	71·02	37	1·281	30·20
86	1·794	70·10	36	1·272	29·38
85	1·786	69·38	35	1·264	28·57
84	1·777	68·57	34	1·256	27·75
83	1·767	67·75	33	1·2476	26·94
82	1·756	66·94	32	1·239	26·12
81	1·745	66·12	31	1·231	25·30
80	1·734	65·30	30	1·223	25·49
79	1·722	64·48	29	1·215	23·67
78	1·710	63·67	28	1·2066	22·85
77	1·698	62·85	27	1·198	22·03
76	1·686	62·04	26	1·190	21·22
75	1·675	61·22	25	1·182	20·40
74	1·663	60·40	24	1·174	19·58
73	1·651	59·59	23	1·167	18·77
72	1·639	58·77	22	1·159	17·95
71	1·637	57·95	21	1·1516	17·14
70	1·615	57·14	20	1·144	16·32
69	1·604	56·32	19	1·136	15·51
68	1·592	55·59	18	1·129	14·69
67	1.580	54·69	17	1·121	13·87
66	1·578	53·87	16	1·1136	13·06
65	1·557	53·05	15	1·106	12·24
64	1·545	52·24	14	1·098	11·42
63	1·534	51·42	13	1·091	10·61
62	1·523	50·61	12	1·083	9·79
61	1·512	49·79	11	1·0756	8·98
60	1·501	48·98	10	1·068	8·16
59	1·490	48·16	9	1·061	7·34
58	1·480	47·34	8	1·0536	6·53
57	1·469	46·53	7	1·0464	5·71
56	1·4586	45·71	6	1·039	4·89
55	1·448	44·89	5	1·032	4·08
54	1·438	44·07	4	1·0256	3·26
53	1·428	43·26	3	1·019	2·445
52	1·418	42·45	2	1·013	1·63
51	1·408	41·63	1	1·0064	0·816

TABLE II.

Specific gravity of dilute hydrochloric acid containing different proportions of hydrochloric acid gas, by *Ure*. Temperature 15° C. (59° F.)

Specific gravity.	Hydrochloric acid gas.	Specific gravity.	Hydrochloric acid gas.
1·2000	40·777	1·1000	20·388
1·1982	40·369	1·0980	19·980
1·1964	39·961	1·0960	19·572
1·1946	39·554	1·0939	19·165
1·1928	39·146	1·0919	18·757
1·1910	38·738	1·0899	18·349
1·1893	38·330	1·0879	17·941
1·1875	37·923	1·0859	17·534
1·1857	37·516	1·0838	17·126
1·1846	37·108	1·0818	16·718
1·1822	36·700	1·0798	16·310
1·1802	36·292	1·0778	15·902
1·1782	35·884	1·0758	15·494
1·1762	35·476	1·0738	15·087
1·1741	35·068	1·0718	14·679
1·1721	34·660	1·0697	14·271
1·1701	34·252	1·0677	13·863
1·1681	33·845	1·0657	13·456
1·1661	33·437	1·0637	13·049
1·1641	33·029	1·0617	12·641
1·1620	32·621	1·0597	12·233
1·1599	32·213	1·0577	11·825
1·1578	31·805	1·0557	11·418
1·1557	31·398	1·0537	11·010
1·1537	30·990	1·0517	10·602
1·1515	30·582	1·0497	10·194
1·1494	30·174	1·0477	9·786
1·1473	29·767	1·0457	9·379
1·1452	29·359	1·0437	8·971
1·1431	28·951	1·0417	8·563
1·1410	28·544	1·0397	8·155
1·1389	28·136	1·0377	7·747
1·1369	27·728	1·0357	7·340
1·1349	27·321	1·0337	6·932
1·1328	26·913	1·0318	6·524
1·1308	26·505	1·0298	6·116
1·1287	26·098	1·0279	5·709
1·1267	25·690	1·0259	5·301
1·1247	25·282	1·0239	4·893
1·1226	24·874	1·0220	4·486
1·1206	24·466	1·0200	4·078
1·1185	24·058	1·0180	3·670
1·1164	23·650	1·0160	3·262
1·1143	23·242	1·0140	2·854
1·1123	22·834	1·0120	2·447
1·1102	22·426	1·0100	2·039
1·1082	22·019	1·0080	1·631
1·1061	21·611	1·0060	1·124
1·1041	21·203	1·0040	0·816
1·1020	20·796	1·0020	0·408

TABLE III.

Specific gravity of dilute nitric acid containing different proportions of anhydrous acid, by *Ure*. Temperature 15° C. (59° F.).

Specific gravity.	Percents of acid.	Specific gravity.	Percents of acid.	Specific gravity.	Percents of acid.
1·500	79·7	1·378	52·6	1·183	25·5
1·498	78·9	1·373	51·8	1·177	24·7
1·496	78·1	1·368	51·1	1·171	23·9
1·494	77·3	1·363	50·2	1·165	23·1
1·491	76·5	1·358	49·4	1·159	22·3
1·488	75·7	1·353	48·6	1·153	21·5
1·485	74·9	1·348	47·9	1·146	20·7
1·482	74·1	1·343	47·0	1·140	19·9
1·479	73·3	1·338	46·2	1·134	19·1
1·476	72·5	1·332	45·4	1·129	18·3
1·473	71·7	1·327	44·6	1·123	17·5
1·470	70·9	1·322	43·8	1·117	16·7
1·467	70·1	1·316	43·0	1·111	15·9
1·464	69·3	1·311	42·2	1·105	15·1
1·460	68·5	1·306	41·4	1·099	14·3
1·457	67·7	1·300	40·4	1·093	13·5
1·453	66·9	1·295	39·8	1·088	12·7
1·450	66·1	1·289	39·0	1·082	11·9
1·446	65·3	1·283	38·3	1·076	11·2
1·442	64·5	1·276	37·5	1·071	10·4
1·439	63·8	1·270	36·7	1·065	9·6
1·435	63·0	1·264	35·9	1·059	8·8
1·431	62·2	1·258	35·1	1·054	8·0
1·427	61·4	1·252	34·3	1·048	7·2
1·423	60·6	1·246	33·5	1·043	6·4
1·419	59·8	1·240	32·7	1·037	5·6
1·415	59·0	1·234	31·9	1·032	4·8
1·411	58·2	1·228	31·1	1·027	4·0
1·406	57·4	1·221	30·3	1·021	3·2
1·402	56·6	1·215	29·5	1·016	2·4
1·398	55·8	1·208	28·7	1·011	1·6
1·394	55·0	1·202	27·9	1·005	0·8
1·388	54·2	1·196	27·1		
1·383	53·4	1·189	26·3		

In all cases in which the determination of the specific gravity fails to attain the end in view, or which demand particular accuracy, one of the two following methods is employed, but more commonly the first.

B. Determination of the anhydrous acid by saturation with an alkaline fluid of known strength.

§ 182.

This method requires :

a. A dilute acid of known strength.

β. An alkaline fluid also of known strength.

aa. Preparation of the solutions.

a. To prepare the *acid* mix in a large flask 1020 cubic centimeters of water intimately with 60 grammes of concentrated sulphuric acid; allow the mixture to cool, take two portions of it of 20 c. c. each, and determine the amount of sulphuric acid in them by precipitation with chloride of barium. If the two experiments agree pretty closely, take the mean of the results as the amount of sulphuric acid contained in your solution, and dilute the latter with the necessary quantity of water to give a fluid *containing in* 1000 *c. c. exactly* 40 *grammes* of anhydrous sulphuric acid. Suppose you have found that 1000 c. c. of your solution contain 42 grammes of sulphuric acid, then, according to the proportion,

$$40 : 1000 :: 42 : x\,;\ x = 1050$$

you will have to add to 1000 c. c. of your solution 50 c. c. of water. This you may effect most simply and accurately in the following manner:

Fill a measuring flask holding one litre, up to the litre mark with the dilute acid, and pour the latter from this flask cautiously into the larger flask, in which you intend to keep it; measure in a pipette 50 c. c. of water, transfer them to the measuring flask which contained the acid, shake the water well about in the flask, and then add it to the solution in the larger bottle. Shake the mixture well, pour back about half of it into the measuring flask, shake it about in the latter, and then transfer it again to the large bottle. Shake, and keep for use. As the fluid only half fills the larger bottle, water will after a time evaporate, which will condense again on the sides in the upper part of the flask; it is necessary therefore to shake the bottle each time before using its contents, otherwise the portion poured out first will contain more water, and accordingly less acid, than the fluid remaining in the bottle.

An acid fluid of the same power of saturation may be prepared also by dissolving 63 grammes of crystallised oxalic acid ($C_2O_3,HO+2$ aq.) in the necessary quantity of water to give exactly one litre of solution. Care must be taken to employ oxalic acid perfectly pure, absolutely free from moisture, and not in the least effloresced (*Mohr*).

β. To prepare the *alkaline solution*, take newly prepared solution of soda, perfectly free from carbonic acid, and which has been allowed to settle completely in a closed vessel, and dilute it with the requisite quantity of water to give a fluid of which 1 *volume exactly neutralises* 1 *volume of your test acid;* the neutralisation point being indicated by the blue coloration imparted by the last drop of solution of soda added to the acid solution reddened by litmus.

To effect this, dilute the solution of soda in the first place to a specific gravity of about 1·05 which corresponds to about 3·6 per cent of soda. Measure off 50 c. c. = 1001 of your test acid, transfer to a beaker, impart

a red colour to the fluid by means of tincture of litmus),* and let your dilute solution of soda flow into the reddened fluid, either from a burette, or—and this is the more convenient way—from a pipette with compression-cock (see Fig. 94), until the mixture just shows a blue tint, and consequently leaves both red and blue litmus paper unaltered. Dilute now the still somewhat too concentrated solution of soda with the requisite quantity of water to give a fluid of which exactly 100° are required to saturate 100° of your test acid. Close the flask in which the dilute solution of soda is kept, with a cork into which is fitted a common chloride of calcium tube, filled with a finely triturated mixture of sulphate of soda and caustic lime, and bearing a thin open tube in the exit aperture. Besides this solution of soda, prepare another 5 times more dilute, and a third, 10 times more dilute. This is effected best—for instance, as regards the latter fluid—by measuring in a pipette 50 c. c. of the more concentrated solution of soda (of which 100° neutralise 100° of the test acid), transferring the fluid to a measuring flask holding exactly 500 c. c., then filling the flask with water exactly up to the mark, and mixing intimately by shaking.

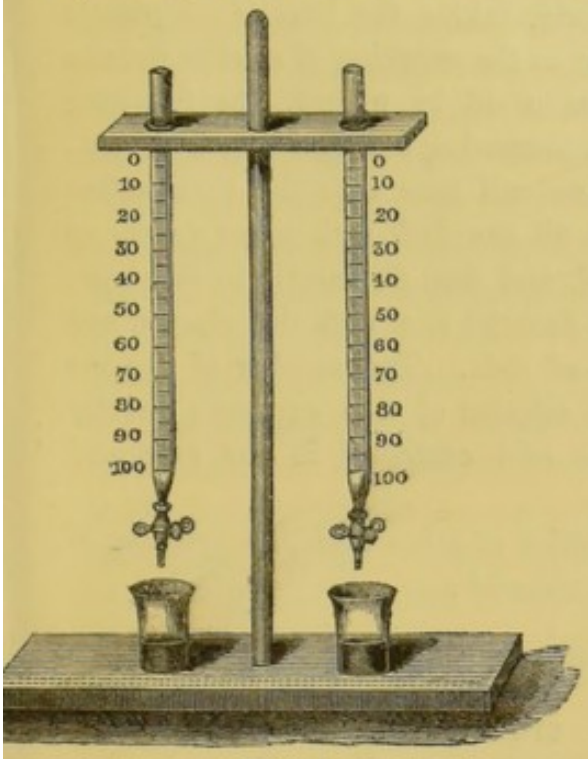


Fig. 94.

bb. Process of examination.

As 50 c. c = 100° of the more concentrated solution of soda correspond to 2 grammes, of the fifth dilution to 0·4 grm. of the tenth dilution, to 0·2 grm. of anhydrous sulphuric acid, and accordingly also to equivalent quantities of all other acids, there is hardly anything to add regarding the process of examination. According to the quantity of acid to be neutralised, the one or the other, or the third, of the alkaline fluids is selected; the neutralisation of the weighed or measured acid fluid should take about from 60 to 100° of the burette.

In scientific investigations, I recommend the analyist accurately to weigh off any quantities of the acid fluid, as this may be done with comparative ease on a chemical balance, and the trifling trouble of calcu-

* As the tincture of litmus is often so alkaline that a perceptible amount of acid is required to redden it, the excess of alkali must, if necessary, be neutralised with acid, by which means a violet fluid is obtained upon dilution with water to which a trace of acid imparts a red, and the least quantity of alkali a blue color.

lation is not worth notice. But in technical investigations it is usually desired to see the percentage strength of the acid indicated directly by the degrees of the burette. To effect this, the analyst has simply to weigh the quantity of the acid under examination corresponding to 2 grammes of anhydrous sulphuric acid, taking the burette or pipette to hold as usual 50 c. c.=100°. But as the weighing of smaller definite quantities is not quite so accurate as could be wished, the following method is preferred. Weigh off in a measuring flask holding 500 c. c., 20 grammes of the sulphuric acid (we will here take the examination of this acid by way of example), and fill the flask with water *nearly up* to the mark line; let the mixture cool, and then fill exactly to the line; shake the fluid, then take out of the flask 50 c. c. with the pipette, and treat with the concentrated solution of soda. The number of degrees of the burette used of the concentrated solution of soda, expresses directly the percentage amount of anhydrous acid contained in the examined fluid.

The following table gives the quantities of other acids, or hydrates of acids, equivalent to 20 grms. of sulphuric acid :—

20 grms. of	sulphuric acid	are equivalent to	24·5	of hydrate of sulphuric acid.
Ditto	ditto	ditto	27·°	of nitric acid.
Ditto	ditto	ditto	31·5	of hydrate of nitric acid.
Ditto	ditto	ditto	18·25	of hydrochloric acid.
Ditto	ditto	ditto	25·5	of acetic acid.
Ditto	ditto	ditto	30·0	of hydrate of acetic acid.

C. Estimation by weighing the carbonic acid expelled by the free acid from bicarbonate of soda (*Fresenius* and *Will*).

§ 183.

Weigh a portion of the acid under examination in the flask A (Fig. 95), and if the acid is concentrated, add water; the fluid should occupy about one-third of the flask. Fill a small glass tube compactly with bicarbonate of soda or potassa,* tie a thread round it, and suspend it by this in the flask A, by confining the thread between the cork and the neck of the flask; arrange the apparatus exactly in the manner described in § 110, and equipoise it on the balance. Release the thread,

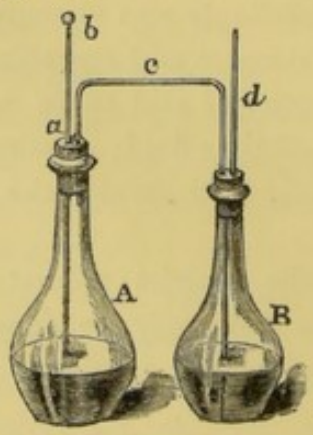


Fig. 95.

* The bicarbonate used may contain chloride of sodium, sulphate of soda, &c.; but it must be quite free from neutral carbonate; the quantity must be more than sufficient to saturate the acid in the flask.

by raising the cork, whereupon the small tube together with the thread, will drop into the flask A; insert the cork again air-tight the instant the thread is released. A lively evolution of carbonic acid commences at once, which continues for some time at a uniform rate, then diminishes, and ultimately ceases altogether. When this point is reached, put the flask A in a water-bath of about from 120—130°. When the renewed evolution of carbonic acid to which this proceeding has given rise, has again deceased, open the wax stopper *b*, on the tube *a* a little, remove the flask from the water-bath, and apply suction to *d*, by means of a perforated cork, until all the carbonic acid still lingering in the apparatus is replaced by atmospheric acid. Let the apparatus cool; replace it now on the balance and put additional weights on the other scale until the equilibrium is restored. The weight added gives the quantity of carbonic acid expelled. For every one equivalent of acid used, two equivalents of carbonic acid are obtained; *e. g.* (NaO, $2\ CO_2 + NO_5 = NaO,\ NO_5 + 2\ CO_2$). The results are very satisfactory.* In this method also all calculation may be avoided, by weighing off the exact quantity of acid which, if it were pure and anhydrous, would be required to give 1 gramme of carbonic acid; the number of centigrammes of carbonic acid obtained, indicates in that case directly the percentage amount of anhydrous acid contained in the examined fluid. The quantity required is found for sulphuric acid, for instance by the following proportion:

$$44 : 40 :: 1{\cdot}00 : x;\ x = 0{\cdot}909.$$

Instead of the quantities based upon the production of 1 gramme of carbonic acid, multiples of them may of course be employed, according as the degree of dilution of the acid under examination may require. But in that case the number of centigrammes of carbonic acid obtained must be divided by the number corresponding to the multiple; the quotient gives the percentage amount of anhydrous acid contained in the examined fluid. The best way is always to take a sufficient quantity of the acid to give from 1 to 2 grammes of carbonic acid.

2. Estimation of the amount of free alkali and alkaline carbonate contained in a substance (Alkalimetry).

A. Estimation of potassa, soda, or ammonia, from the specific gravity of their solutions.

* Compare New Methods of Alkalimetry, and of determining the commercial value of Acids and Manganese, by Dr. *R. Fresenius* and *H. Will*. Taylor and Walton. 1843.

§ 184.

In the case of pure or almost pure solutions of hydrate of soda, or hydrate of potassa, or of ammonia, the amount of alkali present may be estimated from the specific gravity of the solution.

TABLE I.

Amount of potassa in solutions of different specific gravities (*Dalton*).

Specific gravity.	Potassa per cent.	Specific gravity.	Potassa per cent.
1·68	51·2	1·32	26·3
1·60	46·7	1·28	23·4
1·52	42·9	1·23	19·5
1·47	39·9	1·19	16·2
1·44	36·8	1·15	13·0
1·42	34·4	1·11	9·0
1·39	32·4	1·06	4·7
1·36	29·4		

TABLE II.

Amount of soda in solutions of different specific gravities (*Dalton*).

Specific gravity.	Soda per cent.	Specific gravity.	Soda per cent.
2·00	77·8	1·40	29·0
1·85	63·6	1·36	26·0
1·72	53·8	1·32	23·0
1·63	46·6	1·29	19·0
1·56	41·2	1·23	16·0
1·50	36·8	1·18	13·0
1·47	34·0	1·12	9·0
1·44	31·0	1·06	4·7

TABLE III.

Amount of ammonia ($N H_3$) in solutions of ammonia of different specific gravities. Temperature 16° C.= 60·8° F.

Specific gravity.	Ammonia per cent.	Specific gravity.	Ammonia per cent.	Specific gravity.	Ammonia per cent.
0·9517	12·000	0·9607	9·625	0·9697	7·250
0·9521	11·875	0·9612	9·500	0·9702	7·125
0·9526	11·750	0·9616	9·375	0·9707	7·000
0·9531	11·625	0·9621	9·250	0·9711	6·875
0·9536	11·500	0·9626	9·125	0·9716	6·750
0·9540	11·375	0·9631	9·000	0·9721	6·625
0·9545	11·250	0·9636	8·875	0·9726	6·500
0·9550	11·125	0·9641	8·750	0·9730	6·375
0·9555	11·000	0·9645	8·625	0·9735	6·250
0·9556	10·950	0·9650	8·500	0·9740	6·125
0·9559	10·875	0·9654	8·375	0·9745	6·000
0·9564	10·750	0·9659	8·250	0·9749	5·875
0·9569	10·625	0·9664	8·125	0·9754	5·750
0·9574	10·500	0·9669	8·000	0·9759	5·625
0·9578	10·375	0·9673	7·875	0·9764	5·500
0·9583	10·250	0·9678	7·750	0·9768	5·375
0·9588	10·125	0·9683	7·625	0·9773	5·250
0·9593	10·000	0·9688	7·500	0·9778	5·125
0·9597	9·875	0·9692	7·375	0·9783	5·000
0·9602	9·750				

B. Estimation of the total amount of caustic alkali and alkaline carbonate in soda and potash of commerce.

It is well known that the potash and soda of commerce consist of a mixture of alkaline carbonate with a number of other salts. The commercial value of potash and soda depends entirely upon the proportional amount of alkaline carbonate (or caustic alkali) in them, the admixed salts being of no value to the purchaser. Now, as the quantity of the latter is very variable, it is evident that the commercial value of a sample of soda or potash submitted to the analyst can be determined only by ascertaining the proportion of alkaline carbonate (or caustic alkali) contained in it.

I will give here two methods of alkalimetry, based upon essentially different principles. The one of these methods is more expeditious, the other yields more accurate results; they are, as will be seen in § 188, sometimes employed jointly, in cases where it is wished to determine separately both the quantities of alkaline carbonate and caustic alkali.

I. *Alkalimetrical method of Descroizilles and Gay-Lussac.*

§ 185.

The principle of this method is the same as that on which the acidime-

trical method, described § 182, is based, *i. e.* if we know the quantity of an acid of known strength, required to saturate an unknown quantity of caustic potassa or soda, or of carbonate of potassa or soda, we may readily calculate from this the amount of alkali present.

The process requires only *one* fluid of known strength, viz., a test acid (sulphuric acid).

This is now almost universally made of that exact strength that 50 c. c. = 100° of it saturate 5 grammes of pure anhydrous carbonate of soda.

The following is the most simple way of preparing it:

a. Mix about 60 grammes of concentrated sulphuric acid with 500 c. c., or 120 grammes with 1000 c. c. of water, and let the mixture cool.

b. Weigh off accurately 5 grammes of pure anhydrous carbonate of soda, transfer to a flask, dissolve in 200 c. c. of water, and color the solution blue with violet tincture of litmus (see page 463, note).

N.B. This instruction is addressed only to those who do not weigh on delicate balances. Where chemical balances are used, in general therefore in laboratories, it answers the purpose much better to ignite gently in a platinum crucible between 4·5 and 5 grammes of carbonate of soda, let the crucible cool under a bell-glass over sulphuric acid, and then weigh it accurately with its contents. Transfer the latter to the flask, and weigh the crucible; in this manner the exact quantity of carbonate of soda in the flask is most accurately ascertained. An expert chemist, accustomed to the use of a delicate balance, performs this process with greater facility and expedition than the other; the results are also far more reliable, as the substance is weighed in a covered crucible. The potassa or soda to be examined is afterwards weighed in the same manner as the carbonate of soda.

c. Fill the burette or the pipette provided with a compression-cock, up to the 0 line with the cold dilute acid, and allow it to flow into the solution of soda, until complete saturation is effected (see below, determining the point of saturation). This experiment should be made twice. If you have not weighed off exactly five grammes of carbonate of soda, calculate from the results obtained how much acid the saturation of five grammes would have required.

d. Dilute the acid remaining with a sufficient quantity of water to give a test fluid of which exactly 100° are required to saturate 5 grammes of carbonate of soda. Suppose it has taken in the experiments (*c.*) 80° of the acid to saturate 5 grammes of carbonate of soda, you will have to add 20 volumes of water to every 80 volumes of the acid. This dilution of the acid is effected best in the manner described § 182, *aa.* Test the dilute acid now once more as above described. Keep the test acid in well stop-

pered bottles, and shake before every new series of experiments (see page 462). This test acid serves for the examination of all alkaline fluids; it indicates directly the percentage amount of alkaline carbonate or caustic alkali present, provided that the experiment is made with a weighed quantity of the alkaline fluid equivalent to 5 grammes of carbonate of soda.

The following table shows the equivalent quantities:

100°	of the test acid	saturate	5·000	grammes of carbonate of soda.
,,	,,		2·925	,, soda.
,,	,,		6·519	,, carbonate of potassa.
,,	,,		4·443	,, potassa.

Accordingly, if we take 6·519 grammes of a sample of potassa, the number of volumes used of the test acid gives directly the percentage amount of alkali, expressed as carbonate of potassa; if 4·443 grammes are taken, the number of volumes used of the test acid gives the percentage amount of alkali, expressed as anhydrous caustic potassa, &c.

In the examination of substances poor in alkaline carbonates or in caustic alkalies, a multiple (the double, triple, &c.) of the quantities given above, is used, the number of volumes required of the test acid being afterwards divided by the corresponding number (2, 3, &c.).

With respect to the process we have still to speak of the following:

1. *Determination of the point of saturation.*

With caustic alkalies it is easy to neutralise exactly, but in the case of alkaline carbonates, the liberated carbonic acid, which imparts a wine-red color to the fluid, causes some difficulty. This may be overcome in two different ways.

a. When you have added to the cold or, as the case may be, previously heated solution of soda or potassa, sufficient of the test acid to impart a wine-red color to the fluid, heat to ebullition, with frequent shaking: in proportion as the carbonic acid escapes, the fluid will change from red to blue. If you now add some more test acid to the nearly boiling fluid, occasionally replacing the vessel on the lamp, you will readily hit the exact point of saturation, or, more correctly speaking, of beginning supersaturation, which is indicated by the red color of the fluid, slightly tinged with a yellowish hue.

b. The point of saturation may be attained also, though not with the same degree of accuracy, without applying heat. A rather capacious flask is indispensable in this experiment. After every fresh addition of test acid, the fluid is carefully and vigorously shaken. The addition of the test acid may be continued as long as the red color of the fluid continues to show a tint of violet. When the point of saturation is at last approaching, the acid is added more cautiously, two drops at a time; after every fresh addition a glass rod is dipped into the fluid, and one or, which

answers still better, two spots made with it on a slip of fine blue litmus paper, the volume being read off each time, and the number marked between the spots. The operation is continued in this way until the spots on the litmus paper appear positively red. The litmus paper is then allowed to dry, and *that* lowest number is taken for the correct one where the red spots between which it is marked remain just visible.

Let it be borne in mind, as a rule, that the test acid must be tried by the same method which it is intended to use subsequently in the process.

2. *With regard to the examination of potash by this method*, the following points deserve attention :

The various sorts of potash of commerce contain, besides carbonate of potassa,

a. *Neutral salts* (*e. g.* sulphate of potassa, chloride of potassium).

b. *Salts with alkaline reaction* (*e.g.* silicate of potassa, phosphate of potassa).

c. *Admixtures insoluble in water*, more especially carbonate, phosphate, and silicate of lime.

The salts named in *a*. exercise no influence upon the results, but not so those named in *b*. and *c*. Those in *c*. may be removed by filtration ; but the admixture of the salts named in *b*. constitutes an irremediable, though slight source of error.

If it is required to ascertain whether a sample of potash contains, besides the other salts mixed with the carbonate of potassa, also water, the determination of the latter ingredient must precede the alkalimetrical examination. The same remark applies also to soda.

3. With regard to *the examination of soda by this method* the following points deserve attention :

The soda of commerce, prepared by *Leblanc's* method, contains, besides carbonate of soda, always, or at least generally, hydrate of soda, sulphate of soda, chloride of sodium, silicate and aluminate of soda, and not seldom also sulphide of sodium, hyposulphite and sulphite of soda.

The presence of the three last named substances and of the silicate and aluminate of soda, impedes the process, and interferes more or less with the accuracy of the results. The presence of the silicate and aluminate of soda is usually indicated by the precipitate which the solution of soda deposits when saturated with acid ; that of the other three substances is ascertained in the following way :

a. Mix with sulphuric acid ; a smell of sulphuretted hydrogen reveals the presence of *sulphide of sodium*.

b. Color dilute sulphuric acid with a drop of solution of chromate of potassa, and add some of the soda under examination, but not sufficient to neutralise the acid. If the solution retain its reddish-yellow color, this

proves the absence of both sulphite and hyposulphite of soda; but if the fluid turns green one of those salts is present.

c. Whether the green coloration of the solution in *b*. proceeds from sulphite or hyposulphite of soda, is ascertained by supersaturating a clear solution of the sample under examination with hydrochloric acid. If the solution, after the lapse of some time, becomes turbid, owing to the separation of sulphur (emitting at the same time the odor of sulphurous acid), this may be regarded as a safe sign of the presence of hyposulphite of soda; however, the solution may, besides the hyposulphite, also contain sulphite of soda.

The defects arising from the presence of the three last named compounds may be remedied in a measure by igniting the weighed sample of the soda with chlorate of potassa, before proceeding to saturate it. This operation converts the sulphide of sodium, hyposulphite of soda, and sulphite of soda, into sulphate of soda. But if hyposulphite of soda is present the process serves to introduce another source of error, as that salt upon its conversion into sulphate of soda, decomposes an equivalent of carbonate of soda, and expels the carbonic acid of the latter [$Na\,O, S_2O_2 + 4\,O$ (proceeding from the chlorate of potassa) $+ Na\,O, CO_2 = 2\,(NaO, SO_3) + CO_2$].

§ 186.

*Mohr** has lately proposed a modification of the preceding method of *Descroizilles* and *Gay-Lussac*, which gives very good results. The essential points of the modified process are the following:

1. Instead of the burette, which was formerly universally employed in the process, the pipette provided with a compression-cock is used.

2. Instead of the sulphuric acid, a solution of 63 grammes (one equivalent H=1) of crystallised oxalic acid in one litre of water, serves as test-acid.†

3. Besides this test acid the process requires also the aqueous solution of caustic soda described in § 182, *aa*. *β*.

4. The quantity of the soda or potash taken for the experiment is= one-tenth part of the respective equivalents of carbonate of soda or potassa accordingly 5·3 grammes for soda, 6·91 grammes for potash. As the test acid contains in 1000 c. c. one equivalent of oxalic acid, 100 c. c. of it are just sufficient to neutralise the quantity taken of the soda or potash—assuming the alkaline carbonates to be perfectly pure.

5. The alkali is dissolved in water, and the solution colored blue with

* Annal. der Chem. und Pharm., 86, 129.

† This is the same solution which has been mentioned already in the chapter on Acidimetry; instead of it the sulphuric acid prepared as directed § 182, *aa*. α., and which is equivalent to it, may be substituted.

some tincture of litmus. As much of the test acid is allowed to pass out of the pipette as will suffice to impart a violet color to the fluid, which is then boiled, and receives a further addition of acid, until the color looks decidedly yellowish red; more acid is now added to make up in full the next five or ten c. c. of the pipette, and the alkali is thus decidedly oversaturated; the last traces of carbonic acid are removed by boiling, shaking, blowing into the flask, and finally drawing the air out of the latter.

6. A pipette or burette, divided into one-tenth c. c. is now filled with the test solution of soda, and the latter is then added drop by drop to the mixture of 5., until the color changes from light red to violet, and then suddenly to bright blue.

7. The number of c. c. used of the solution of soda is marked, and deducted from that of the c. c. used of the test acid: the difference expresses directly in percents, the amount of pure alkaline carbonate contained in the examined sample.

II. *Fresenius and Will's Method.**

§ 187.

In this method the quantity of alkaline carbonate contained in a sample of potash or soda is calculated from the amount of carbonic acid disengaged from it. Its application demands therefore that all the alkali, which constitutes its commercial value, be present in the form of a neutral carbonate, and that the substance contain no other carbonate besides this. If the sample under examination fails to satisfy these conditions, it must be treated in the proper manner to bring them about.

The determination of the carbonic acid is effected in the way described § 110, II. *b*. *β*. *aa*. The flasks of the apparatus, illustrated in Fig. 45 (page 243), should not be too small: A should hold from two to two and a half, B from one and a half to two ounces of water. Though not absolutely necessary, it is always advisable to precede the determination of the carbonic acid by a quantitative estimation of the water contained in the sample under examination.

1. *Examination of potash.*

a. Determination of the water.

Place a small dish of sheet iron, about two inches in diameter, and provided with a somewhat loose-fitting cover, on one scale of a balance together with a ten gramme weight; equipoise the balance accurately by putting on the other scale small shot, and ultimately slips of tin-foil. Take several samples of the potash from different parts of the mass, triturate them with the greatest expedition in a dry mortar, remove the ten gramme

* Compare the little work named, page 465, note, which treats of the subject more in detail.

weight, and put portions of the pulverised potash into the dish until the equilibrium is perfectly restored.

You have now exactly ten grammes of the potash in the dish. Apply a gentle heat to the dish, and maintain it, until the whole of the water present in the potash is expelled, which may be ascertained by holding a glass plate over the open dish and observing whether any aqueous vapor continues to condense upon it or not. Cover the dish, let it get cold, then replace it on the balance, and restore the equilibrium by adding weights. The number of decigrammes required to restore the equilibrium indicates directly the amount of water contained in every 100 parts of the examined potash.

A porcelain crucible provided with a lid may be used instead of the iron dish.

b. Determination of the carbonic acid.

Weigh off 6·283 grammes of the anhydrous residue of *a.*, and determine the carbonic acid contained in that quantity, as directed § 110, II. *b. β. aa.* Divide by 2 the number of centigrammes of carbonic acid disengaged: the result expresses the quantity of carbonate of potassa contained in the examined sample. Suppose your 6·283 grammes of potash have given 1·80 grammes of carbonic acid (indicated by the loss of weight of the apparatus), the examined sample contains $\frac{180}{2} = 90$ per cent of carbonate of potassa.

If the potash contains carbonate of lime, which, however, is only very rarely the case, dissolve it in water, filter, concentrate the filtrate by evaporation, and then proceed in the manner just now directed (*b.*). In presence of sulphide of potassium and caustic potassa, proceed as with soda under the same circumstances (see 2).

2. *Examination of soda.*

The general method is the same as in 1; 4·817 grammes of the anhydrous residue are weighed off instead of 6·283 grammes.

If a soda contains sulphide of sodium, sulphite, or hyposulphite of soda, the liberation of the carbonic acid by the common process would be attended with the disengagement of sulphuretted hydrogen or sulphurous acid, which would of course go to swell the apparent amount of the carbonic acid. This defect may be readily remedied by adding to the solution of the soda in A a small quantity of solution of neutral chromate of potassa, which will effect the decomposition of the sulphuretted hydrogen or sulphurous acid; and the products of this decomposition being non-volatile, the carbonic acid only will be evolved. As most sorts of soda of commerce contain admixtures of either the one or the other of the substances named, and as it is far more simple to add at once some chromate of potassa to the soda solution than to test the latter first for the presence of either of the three salts—it is always

advisable to make it a rule in the examination of soda, to add some chromate of potassa.

If the soda under examination contains caustic soda, which may be detected by the alkaline reaction which the solution of the sample manifests, after the addition of chloride of barium in excess, the following modification of the common method is adopted.

a. Determination of the water.

This is effected in the usual way. (See 1, *a.* Examination of potash.)

b. Determination of the carbonic acid.

Weigh off 4·818 grammes of the anhydrous residue of *a.*, and triturate in a mortar with from three to four parts of pure quartz sand, and about one-third of carbonate of ammonia in powder; transfer the mixture to a small iron dish, and rinse the mortar with sand, transferring the sand used also to the dish. Moisten the mass in the dish with as much water as it can absorb; let it stand a short time, and then heat gently until the water is completely expelled. The residue contains now no longer the least trace of carbonate of ammonia. If the soda under examination contains sulphide of sodium besides caustic soda, the mass in the dish is moistened with solution of caustic ammonia instead of water, to effect the reduction of the sesqui-carbonate of ammonia to neutral carbonate; otherwise sulphide of ammonium would be formed, and part of the sulphide of sodium converted into carbonate of soda.

When the mass is cold transfer it from the dish to the flask A (which may be readily effected with the aid of a spatula); rinse the dish with a little water, and pour this also into A. Conduct the rest of the process in the usual way. The addition of sand is intended to prevent the caking of the mass, and the spirting which would otherwise attend the expulsion of the water, unless the greatest caution were used in the process of heating; moreover, the perfect removal of the dried mass from the dish would be rather difficult but for the sand.

The latter operation (viz., the transfer of the mass from the dish to the flask) may be still more facilitated by coating the inside of the dish with sand, previously to the introduction of the mixture; this is effected most simply by moistening the inner sides and bottom of the dish with water, throwing a handful of sand into it, and shaking out the superfluous quantity.

C. Determination of the caustic alkali which commercial potash and soda may contain beside the carbonate.

§ 188.

Many kinds of potash and soda, more especially the latter, contain, besides alkaline carbonate, also caustic alkali; and the chemist is often called upon

to determine the amount of the latter, as it is, for instance, by no means a matter of indifference to the soap-boiler how much of the soda is supplied to him in the caustic state. This may be effected most simply by combining the method described in § 185 or in § 186 with the one given in § 187, *i. e.* determining by one of the former the total amount of alkali present, both in the caustic state and as carbonate, and estimating by the latter the quantity of carbonic acid and therefore also of alkaline carbonate. The difference between the result of the two processes indicates accordingly the quantity of alkaline carbonate to which the caustic alkali contained in the examined article corresponds. To calculate the carbonate of soda as anhydrous caustic soda it is multiplied by 0·5849, to calculate it as hydrate of soda it is multiplied by 0·7547 ; to calculate the carbonate of potassa as anhydrous caustic potassa it is multiplied by 0·6817 ; to calculate it as hydrate of potassa it is multiplied by 0·8119.

It will be readily seen that this object may also be attained simply by the method given in § 187, by determining in *one* weighed sample the carbonic acid at once, in *another* after previous treatment with carbonate of ammonia.

3. Chlorimetry.

§ 189.

The chloride of lime, or bleaching powder of commerce, is a mixture of hydrate of lime with hypochlorite of lime and chloride of calcium ; in pure chloride of lime the two latter ingredients are always present in the proportion of one equivalent of the one to one equivalent of the other. The action of an acid upon chloride of lime effects the liberation of the whole of the chlorine present, since

$$Ca\,O,\,Cl\,O + Ca\,Cl + 2\,S\,O_3 = 2\,Ca\,O,\,S\,O_3 + 2\,Cl.$$

The bleaching powder of commerce varies exceedingly in the amount of chlorine which it yields when treated with acids. Now, as the commercial value of this article, which is extensively manufactured and sold, depends entirely upon the proportional amount of chlorine which it contains, it was very natural that chemists should endeavor to devise some simple method of determining the available amount of chlorine in any given sample of bleaching powder. The various methods proposed with the view of effecting this object have collectively received the name of "*Chlorimetry*."

The number of chlorimetrical methods that have been proposed is so great that I cannot give all of them, but must confine myself to a description of those, which are distinguished either for the facility of the process or for the accuracy of the results, or which deserve mention from the circumstance that they are commonly employed. In the description of the several methods I shall have occasion to speak of their respective advantages and defects.

Before I proceed to the description of the chlorimetrical methods, I have to remark that the results of the examination of chloride of lime are usually expressed in two different ways. Whilst the scientific chemist gives the percentage amount of available chlorine contained in a sample of chloride of lime by weight, the substance is valued and sold by chlorimetrical degrees. This latter method devised by *Gay-Lussac* how many litres of chlorine gas of 0° C. (32° F.), at 0·76 expresses met. atmospheric pressure (29·9° bar.), are contained in 1000 grammes of chloride of lime.

However, as we know that one litre of chlorine gas of 0° C. and 0·76 met. bar. weighs 3·17007 grammes, it is easy to calculate the results by measure in results by weight, and *vice versâ*.

Thus, for instance, a sample of chloride of lime of 90° contains 3·17007 $\times 90 = 285{\cdot}306$ grammes of chlorine in 1000 grammes, consequently 28·53 in 100; and a sample containing 34·2 per cent by weight of chlorine, contains 107·9°, since, as 100 grammes contain 34·2 grammes of chlorine, 1000 grammes contain 342,

$$\text{and } \frac{342}{3{\cdot}17007} = 107{\cdot}9 \text{ litres.}$$

Preparation of the solution of chloride of lime.

§ 190.

The solution is prepared alike for all methods, and this is done best in the following manner:

Weigh off 10 grammes, triturate finely with a little water, add gradually more water, stir the mixture up, let the grosser particles subside, and pour the supernatant liquid into the measuring flask, which must hold one litre; triturate the residue again with water, and rinse the contents of the mortar carefully into the flask; fill the latter to the litre mark, shake the milky fluid, and examine it at once in that state, *i. e.* without allowing it to deposit; and every time, before you measure off a fresh portion of it, shake it again. The results obtained with this turbid solution are much more constant and accurate than those arrived at in cases where, as is usually recommended, the fluid has been allowed to deposit, and the experiment made with the supernatant clear portion alone. Of the truth of this you may readily convince yourself, by making two separate experiments, one with the decanted clear fluid, the other with the residuary turbid mixture. Thus, for instance, in an experiment made in my own laboratory, the decanted clear fluid gave 22·6 of chlorine, the residuary mixture 25·0, the equally mixed turbid solution 24·5.

1 c. c. of the solution of chloride of lime so prepared corresponds to 0·01 grm. of chloride of lime.

A. *Method of Gay-Lussac* (somewhat modified).

§ 191.

Gay-Lussac's method, which till lately was employed in most manufactories, is based upon the circumstance that the contact of chlorine with arsenious acid, in presence of water, gives rise to the formation of arsenic acid and hydrochloric acid:

$$As O_3 + 2 Cl + 2 HO = As O_5 + 2 HCl.$$

One equivalent of arsenious acid = 1237·5 (or 99) requires accordingly two equivalents of chlorine = 886·6 (or 70·92) for its conversion into arsenic acid; or, in other terms, 100 parts by weight of chlorine oxidise 139·6 parts of arsenious acid. Consequently the amount of a solution of chlorine required to convert a definite quantity of arsenious acid into arsenic acid, indicates at once the proportional amount of chlorine present in that solution. The arsenious acid is best used in solution; it is prepared of definite strength as follows:

a. Preparation of the solution of arsenious acid.

Dissolve 13·96 grammes of pure arsenious acid in solution of potassa or soda, and add as much water as will give exactly one litre, in which case 10 c. c. of it will contain 0·1396 of arsenious acid corresponding to 0·1 grm. of chlorine.

b. The process.

Measure off with the pipette 10 c. c. of the solution of arsenious acid (*a*), transfer to a beaker-glass, and dilute with water; add hydrochloric acid until it predominates strongly; color the fluid blue with a drop or two of solution of indigo, and add the solution of chloride of lime made according to the directions of § 190, drop by drop, with continued stirring, until the blue color has nearly disappeared. Add now another drop of solution of indigo, and then again solution of chloride of lime until the fluid suddenly loses all color, which the addition of a very small drop of solution of indigo fails to restore.

The amount of solution of chloride of lime used contained 0·1 grm. of chlorine. Suppose 40 c. c. = 80° of the burette have been used: now, as every cubic centimeter corresponds to 0·01 of chloride of lime, the percentage amount of chlorine by weight in the chloride of lime is found by the following equation:

$$0{\cdot}40 : 0{\cdot}10 :: 100 : x ; x = 25 ;$$

or, by dividing 1000 by the number of c. c. used of the solution of chloride of lime or 2000 by the number of degrees of the burette (= one-half c. c.)

This method indeed gives satisfactory results; but it requires some practice to hit the exact point when the arsenious acid is fully converted into arsenic acid; moreover the process is liable to be vitiated by the

evolution of a little chlorine. The latter defect becomes more serious if, as is commonly done, a more concentrated solution of chloride of lime is used (see Analytical Notes and Experiments, No. 72).

B. *Penot's Method.**

§ 192.

This method also is based upon the conversion of arsenious acid into arsenic acid; but it effects that conversion in an alkaline solution. Iodised paper is employed to ascertain the exact point when the reaction is completed.

a. Preparation of the iodised paper.

Heat a mixture of 1 gramme of iodine, 7 grammes of crystallised carbonate of soda, 3 grammes of potato starch, and 250 c. c. of water, until all is dissolved and the solution appears colorless. Take the mixture from the fire, and dilute it with the quantity of water necessary to give the 500 c. c. of fluid. Moisten fine white (unsized) paper with this fluid, and dry it.

b. Preparation of the solution of arsenious acid.

Dissolve 4·425 grammes of pure arsenious acid and 13 grammes of crystallised carbonate of soda, in from 600 to 700 c. c. of water, with the aid of heat, let the solution cool, and then dilute it with the quantity of water required to give exactly one litre of fluid. Every 1 c. c. of this solution contains 0·004425 grm. of arsenious acid, corresponding to 1 c. c. of chlorine gas of 0° C. (32° F.) and 0·76 met. of atmospheric pressure; consequently every degree of the burette of the acid solution corresponds exactly to one degree of the burette of chlorine gas.†

c. The process.

Measure off with a pipette 50 c. c.=100° of the solution of chloride of lime prepared according to the directions given § 190; transfer to a beaker, and add the solution of arsenious acid (*b*) from a burette holding 50 c. c. =100°, or from a pipette of the same capacity, provided with a compression stopcock, with constant stirring, until a drop of the mixture produces no longer a blue-colored spot on the iodised paper; it is very easy to hit the point exactly, as the gradually increasing faintness of the blue spots

* Bulletin de la Société Industrielle de Mulhouse, 1852, No. 118. *Dingler's* Polytech. Journal, 127, 134.

† *Penot* gives the quantity of arsenious acid as 4·44; but I have corrected this number to 4·425, in accordance with the numbers which are at present assumed to represent the proper equivalent of the substances, and the correct weight of a litre of chlorine gas—after the following equation:—

70·92 (2 equ. of chlorine) : 99 (1 equ. of AsO_3, :: 3·17007 (weight of a litre of chlorine gas : x; x=4·425, *i. e.* the quantity of arsenious acid which 1 litre of chlorine gas converts into arsenic acid.

made on the paper by the fluid dropped on it, indicates the termination of the reaction, and warns the operator to confine the further addition of the solution of arsenious acid to a single drop at a time. The number of degrees ($\frac{1}{2}$ c. c.) used of the acid indicates directly the number of chlorimetrical degrees (*i. e.* the number of litres of chlorine gas contained in one kilogramme of the examined sample), as the following calculation shows: suppose you have used 80° ($\frac{1}{2}$ c. c) of solution of arsenious acid, the 100°=50 c. c. of the solution of chloride of lime, with which the experiment has been made, contains 80°=40 c. c. of chlorine gas. Now, these 100°=50 c. c. corresponds to 0·5 grm. of chloride of lime; and, accordingly, as they contain 40 c. c. of chlorine gas, 1000 grammes contain 8000 c. c.=80 litres. This method give very constant and accurate results, and appears to be the best adapted for manufacturers.

C. *Otto's Method.*

§ 193.

The principle of this method is as follows:

Two equivalents of sulphate of protoxide of iron, when brought into contact with chlorine, in the presence of water and of free sulphuric acid, give one equivalent of sulphate of sesquioxide of iron, and one equivalent of HCl., the process consuming one equivalent of chlorine.

$$2\,FeO,\,SO_3+SO_3+HO+Cl=Fe_2O_3,\,3\,SO_3+HCl.$$

Two equivalents of FeO, SO_3=1900, or, calculated as crystallised sulphate of protoxide of iron,

$$2\,(FeO,\,SO_3,\,HO+6\,aq)=3475{\cdot}0$$

correspond to 443·28 of chlorine, or, in other terms, 0·7839 grm. of crystallised sulphate of protoxide of iron correspond to 0·1 grm. of chlorine.

The sulphate of protoxide of iron required for these experiments is best prepared as follows:

Take iron nails, free from rust, and dissolve them in dilute sulphuric acid, applying heat in the last stage of the operation; filter the solution, still hot, into about twice its own volume of spirits of wine. The precipitate which is produced consists of

$$FeO,\,SO_3+HO+6\,aq.$$

Collect it upon a filter, wash with spirits of wine, spread upon a sheet of blotting paper, and dry in the air. When the mass smells no longer of spirits of wine, transfer it to a bottle and keep this well corked.

The process.

Dissolve 3·1356 grammes (that is, 4 × 0·7839 grm.) of the precipitated sulphate of protoxide of iron in the quantity of water required to give 200 c. c. of fluid; take 50 c. c. of the solution, by means of a pipette, dilute with from 150 to 200 c. c. of water, acidify strongly with pure

hydrochloric acid, and add from a burette holding 50 c. c.=100° the well shaken solution of chloride of lime, prepared according to the directions given in § 190, until the sulphate of protoxide of iron is completely converted into sulphate of sesquioxide. To know the exact point when the peroxidation is completed, sprinkle a number of drops of a solution of ferricyanide of potassium on a clean plate, and, when the operation is drawing to an end, apply some of the mixture with a stirring rod to one of the drops on the plate, and observe whether it produces a blue precipitate, repeat the experiment after every fresh addition of two drops of the solution of chloride of lime. When the mixture no longer produces a blue precipitate in the solution of ferricyanide of potassium on the plate, read off the number of volumes used of the solution of chloride of lime. As the amount of solution of chloride of lime used contained 0·1 grm. of chlorine, the calculation is made exactly as in § 191.

This method also gives very satisfactory results, provided always that the sulphate of protoxide of iron is perfectly dry and free from sesquioxide.

Modification of Otto's Method.

a. Instead of the solution of sulphate of protoxide of iron, a solution of protochloride of iron, prepared by dissolving pianoforte wire in hydrochloric acid (according to the directions given § 89, 2, *a. bb.*), may be used with the best results. If 0·6316 of pure metallic iron, that is 0·6335 of fine pianoforte wire, which may be assumed to contain 99·7 per cent of iron, are dissolved in the necessary quantity of water to give 200 c. c. of fluid, the solution so prepared contains exactly the same amount of iron as the solution of sulphate of protoxide usually employed in *Otto's* process—that is, 50 c. c. of it correspond to 0·1 grm. of chlorine. But as it is rather a difficult task to weigh off a definite quantity of iron wire, I prefer weighing accurately about 0·15 of iron, which I dissolve, then dilute the solution to about 200 c. c., oxidise the iron in it with the solution of chloride of lime prepared according to the directions given in § 190, and calculate the chlorine by the proportion

56 : 35·46 : : the quantity of iron used : x ;

the x found corresponds to the chlorine contained in the amount used of the solution of chloride of lime. This calculation may be dispensed with by the application of the following formula, which is calculated with due regard to the carbon in the pianoforte wire.

1. Multiply the weight of the pianoforte wire by 12626, and divide the product by the number of volumes of the burette ($\frac{1}{2}$ c. c.) used of the solution of chloride of lime: the result expresses the percentage amount of chlorine by weight; or,

2. Multiply the weight of the wire by 39829, and divide the product by

the number of volumes of the burette ($\frac{1}{2}$ c. c.) used of the solution of chloride of lime: the result expresses the chlorimetrical degrees of the chloride of lime (the number of litres of chlorine gas contained in one kilogramme of the specimen examined).

This method gives very good results. I have described it here principally because it dispenses altogether with the use of test-fluids of known strength. It is therefore especially well adapted for occasional examinations of samples of chloride of lime, and also by way of control.

b. Instead of exactly oxidising the protoxide or protochloride of iron by the chloride of lime, you may also proceed as follows: weigh accurately about 0·3 grm. of pianoforte wire, dissolve in hydrochloric acid, according to the direction given in § 89, 2, *a. bb.*; and dilute the still strongly acid solution to from 200 to 300 c. c.; add from a burette 100°=50 c. c. of the solution of chloride of lime, prepared according to the directions of § 190, stir the mixture, and lastly determine by means of permanganate of potassa the quantity of iron which still remains in the state of protoxide or protochloride (§ 89). By this means the quantity of iron which has been peroxidised by the chloride of lime is ascertained, and from this you may calculate, by the formulæ given in *a.*, the percentage, or in chlorimetrical degrees, the amount of chlorine contained in the specimen examined. The results are very accurate.

D. *Bunsen's Method.*

§ 194.

Pour 10 c. c. of the solution of chloride of lime, prepared according to the directions of § 190 (containing 0·1 of chloride of lime) into a beaker, and add about 6 c. c. of the solution of iodide of potassium, prepared according to the directions of § 114 (containing 0·6 of KI); dilute the mixture with about 100 c. c. of water, acidify with hydrochloric acid, and determine the liberated iodine as directed § 114. As one equivalent of iodine corresponds to one equivalent of chlorine, the calculation is easy. This method gives excellent results. (Compare Analytical Notes and Experiments, No. 72.)

4. Determination of the amount of binoxide in manganese ores.

§ 195.

The native ores of manganese are mixtures of binoxide of manganese with lower oxides of that metal, and besides these, with sesquioxide of iron, clay, sulphate of baryta, &c., and they invariably contain some moisture. Now, as the commercial value of manganese ores depends entirely upon the amount of binoxide which they contain, it is a matter of the greatest in-

terest for the manufacturer and the merchant to ascertain this. Of the many methods that have been proposed for the examination of manganese ores, I select three as the most expeditious and accurate. The first is more particularly adapted for technical examinations.*

A. *Fresenius and Will's Method.*

The principle upon which this method is based has been applied already by *Berthier* and *Thomson*.

The following remarks will serve to explain it.

a. When oxalic acid or an oxalate is brought into contact with binoxide of manganese, in presence of sulphuric acid in excess, sulphate of protoxide of manganese is formed, and carbonic acid evolved, as the oxygen, which we may assume to exist in the binoxide of manganese in combination with the protoxide of the metal, combines with the oxalic acid, and thus converts the latter into carbonic acid.

$$MnO_2 + SO_3 + C_2O_3 = MnO, SO_3 + 2(CO_2).$$

Every equivalent of available oxygen or, what amounts to the same, every equivalent of binoxide of manganese present, gives two equivalents of carbonic acid.

b. If this process is performed in a weighed apparatus from which nothing except the evolved carbonic acid can escape, and which, at the same time, permits the complete expulsion of that acid, the diminution of weight will at once show the amount of carbonic acid which has escaped, and consequently, by a very simple calculation, the quantity of binoxide contained in the analysed manganese ore.

c. But even this calculation may be avoided by simply using in the operation the exact weight of ore which, if the latter consisted of pure binoxide, would give 100 parts of carbonic acid; which weight is found by the following equation:—

$$\begin{array}{cccc} 2 \text{ eq. of } CO_2 & & 1 \text{ eq. of } MnO_2 & \\ 550{\cdot}00 & : & 544{\cdot}68 & :: 100 : x; \end{array}$$

$$x = 99{\cdot}033.$$

The number of parts or volumes evolved of carbonic acid expresses directly the number of parts of binoxide contained in 100 parts of the analysed ore. Suppose the experiment is made with 0·99033 grm. of

* The discrepancies which are but too often observed in the results of several analyses of the same manganese ore by different chemists, are attributable (as *De Vry* has remarked) principally to the varying amount of moisture in the several samples. It is, therefore, always advisable, to dry the finely pulverised sample of the ore, intended for analysis, at from 212° to 248°, and, on the other hand, to determine the moisture in another, but only coarsely pounded sample, by drying it at the same temperature, and noting the loss of weight.

the ore, the number of centigrammes of carbonic acid evolved in the process, expresses directly the percentage amount of binoxide contained in the analysed manganese ore. Now, as the amount of carbonic acid evolved from 0·99033 grm. of manganese would be rather small for accurate weighing, it is advisable to take a multiple of this weight, and to divide afterwards the number of centigrammes of carbonic acid evolved from this multiple weight by the same numbers by which the unit has been multiplied. The multiple which answers the purpose best is the triple, = 2·97099, or, 2·97 grammes.

The analytical process is performed in the apparatus illustrated in Fig. 96, and which has been described also in § 110.

The flask A should hold, up to the neck, about 100 or 120 c. c.; B about 90 or 100 c. c. The latter is half filled with sulphuric acid; the tube *a* is closed at *b* with a small wax stopper.

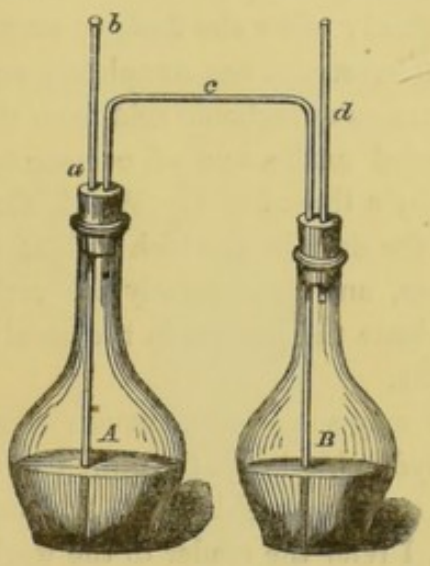


Fig. 96.

Reduce the manganese ore to a very fine powder, which is effected best by trituration in an agate mortar; introduce 2·97 grammes of the powder into A; add about 7·5 grammes of neutral oxalate of potassa* in powder, or about 6 grammes of neutral oxalate of soda, and as much water as will fill the flask to about one-third. Insert the cork into A, and place the apparatus in equilibrium upon the balance. Make some sulphuric acid flow from B into A, by applying suction to *d*, by means of a caoutchouc tube. The evolution of carbonic acid commences immediately in a steady and uniform manner. When the evolution begins to slacken, draw over a fresh portion of sulphuric acid into A, and repeat this until the manganese ore is completely decomposed, which, if the sample has been very finely pulverised, requires at the most about ten minutes. The complete decomposition of the analysed ore is indicated, on the one hand, by the cessation of the disengagement of carbonic acid, and its non-renewal, upon the influx of a fresh portion of sulphuric acid into A; and, on the other hand, by the total disappearance of every trace of black powder from the bottom of A.†

* This may be readily produced by saturating the common oxalate of potassa with carbonate of potassa, and evaporating to crystallisation.

† If the manganese ore has been pulverised in an iron mortar, a few black spots (particles of iron from the mortar) will often remain perceptible.

Now draw over some more sulphuric acid from B into A, that the fluid in the latter may become hot, which will expel the last lingering traces of carbonic acid dissolved in A; lift the small wax stopper *b*, and apply a gentle suction to *d* until the air drawn out tastes no longer of carbonic acid. Allow the apparatus to cool, replace it upon the balance, and restore the original equilibrium. The number of centigramme weights added, divided by three, expresses the percentage amount of binoxide contained in the analysed ore.

Some ores of manganese contain carbonates of the alkaline earths in admixture. To analyse ores of this description, the foregoing process is modified as follows: Introduce 2·97 grammes of the ore into A, and add a sufficient quantity of rather dilute sulphuric acid, to fill the flask to about one-third; allow the flask to stand at rest, with occasional agitation, until all effervescence has completely ceased; apply a gentle heat to expel the last traces of carbonic acid from the fluid. Introduce about 3 grammes of pounded oxalic acid of commerce into a small glass tube, and suspend this by a thread in A. Weigh the apparatus, and let the little tube drop into the fluid in A, which will at once induce decomposition of the manganese, and consequently the evolution of carbonic acid. Continue and terminate the process in the usual way. This method gives most accurate results.

It may sometimes, though rarely, be interesting to know the quantity of hydrochloric acid required to make a manganese ore give off its available oxygen as chlorine. For information on the way of accomplishing this, I refer the reader to the work mentioned page 465.

B. *Bunsen's Method.*

§ 196.

Reduce the ore to the very finest powder, weigh about 0·4 grm., introduce this into the small flask *a*, illustrated in Fig. 44, page 220, and pour pure fuming hydrochloric acid over it; conduct the process exactly as in the analysis of chromates by *Bunsen's* method (page 220). Boil until the ore is completely dissolved and all the chlorine expelled, which is effected in a few minutes. Every equivalent of iodine separated corresponds to an equivalent of chlorine evolved, and accordingly to an equivalent of binoxide of manganese.

In my own laboratory I have made some alterations in *Bunsen's* method, both in the form of the evolution and absorption apparatus, and in the mode of adding the sulphurous acid.

The small glass bulb which serves as a vent in *Bunsen's* apparatus (Fig. 44), cannot always be relied upon to prevent the receding of the fluid.

But this inconvenience may be avoided or at least rendered harmless, by modifying the form of the vessels, as shown in Fig. 97.

a is a pipette, bent at the top, and drawn out at the lower end into a point bent upwards. When the operation of boiling is terminated, take the caoutchouc tube *c*, with the left hand, and holding the spirit-lamp with the right hand under the small flask *d*, lift *a* so far out of the retort that the bent point is in the bulb *b*. When this is accomplished remove the lamp, after this the small flask, and proceed in the usual way.

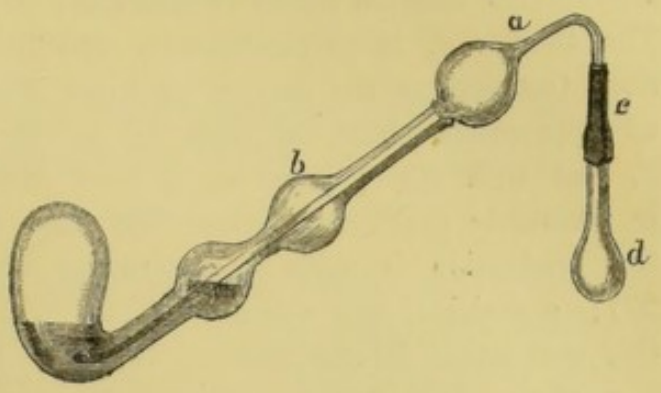


Fig. 97.

The addition of the sulphurous acid by means of a common pipette is attended with unnecessary trouble and loss of time, which the substitution of a small measuring flask tends still to increase, on account of the indispensable rinsing. I have therefore constructed a special apparatus for the purpose, which does excellent service in my own laboratory. Fig. 98 illustrates this apparatus.

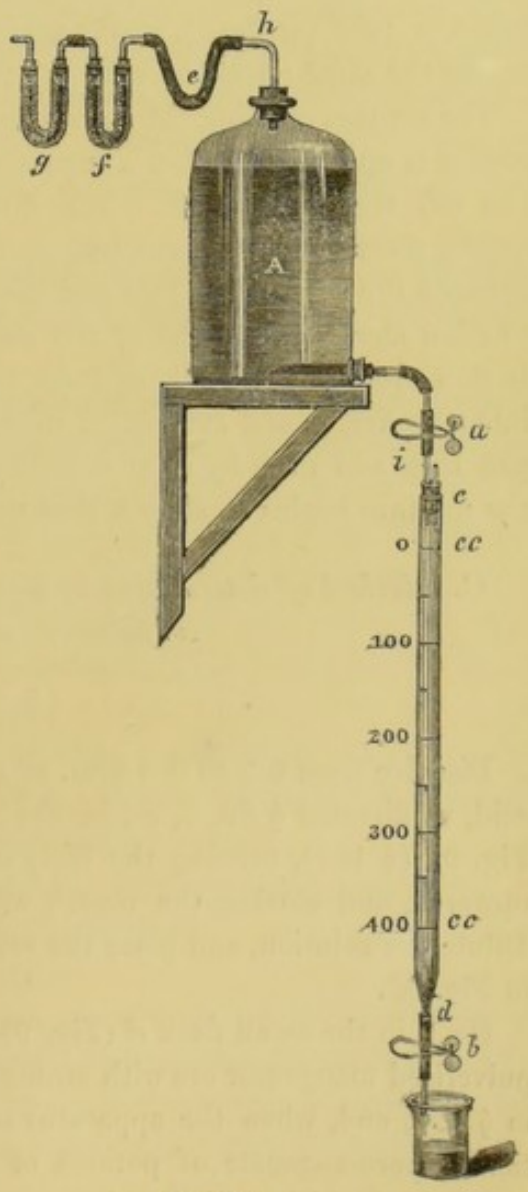


Fig. 98.

A is a large bottle (holding about 10 litres). Nearly fill it with water, add from 70 to 80 c. c. of a saturated solution of sulphurous acid, shake the mixture vigorously, and place the bottle on a raised firmly fixed stand. Join *h* to *f* and *g*, by means of the vulcanised india-rubber tube *e*, and push the end of the caoutchouc tube which projects below the compression cock *a*, over the tube which opens into *c d*, and the end of which is bent sideways,

by which arrangement the fluid running from *a* is made to flow quietly down the side of *c d*. *g* contains small lumps of phosphorus interspersed between pieces of asbestos; *f* contains hydrate of potassa. The tube *c d*, is perpendicularly attached, by means of two iron rings (omitted in the cut), or in some other way, to the wall, or to an appropriate stand, at from 10 to 12 centimeters distance from it, and with the 0 point on a level with the eye. The tube *c d*, is accurately graduated, proceeding from the top to the lower end; the graduation is made in accordance with the system *a* (see page 27); a division into volumes of 50 c. c. each suffices. To make this graduation, fill the tube up to the 0 line with water, and let 50 c. c. of the fluid flow out through the compression cock *b* into a tube graduated in accordance with the system *e* (see page 27), or 50 grammes at 4° C. (39·2° F.) into a tared flask. Mark the height of the fluid in *c d*, with the diamond, let another 50 c. c. (or 50 grammes at 39·2 F.) flow into the tube (or flask), mark again the height of the fluid in *c d*, and repeat the same operation until the tube is graduated in its entire length.

The manner of using the apparatus is self-evident. To fill *c d*, the stopcock *a* is opened; to allow a measured quantity of the sulphurous acid to run off, the stopcock *b*. The fluid running from *b* is made to glide quietly down the side of the beaker. To determine the relative proportion between the sulphurous acid and the solution of iodine, the best manner is to allow about nine-tenths of the necessary quantity of solution of iodine to flow from the burette, or from the pipette with a compression cock, into a beaker, to add 100 c. c. of the sulphurous acid, mix with starch paste, and then add drop by drop a further quantity of solution of iodine until the mixture begins to show a blue tint.

C. *Method of determining by means of iron the amount of binoxide contained in manganese ores.*

§ 197.

Dissolve from 0·5 to 0·6 grm. of pianoforte wire in dilute hydrochloric acid, as directed § 89, 2, *a.*, in the retort of the apparatus illustrated in Fig. 97 (§ 196), turning the body of the retort downwards and the neck upwards, and closing the mouth with a cork with an open glass tube. Dilute the solution, and place the retort in the position in which it appears in Fig. 97.

Heat in the small flask *d* (Fig. 97) from 0·35 to 0·4 grm. of the finely pulverised manganese ore with strong hydrochloric acid, exactly as directed in § 196, and, when the apparatus is cold, determine by means of a solution of permanganate of potassa of known strength (§ 89), the quantity of the iron which still remains unoxidised. By deducting this from the

weight of the wire employed you learn the quantity of iron which has been oxidised by the chlorine evolved with the aid of the manganese. That quantity multiplied by 0·77804 gives the amount of binoxide contained in the analysed ore.

5. Examination of the yellow and red prussiate of potassa of commerce.

§ 198.

The yellow prussiate of potassa of commerce consists, as is well known, of ferrocyanide of potassium (2 K Cfy, + 3 aq) mixed with smaller or larger quantities of other salts (carbonate of potassa, sulphate of potassa, chloride of potassium); the red salt consists of ferricyanide of potassium (3 K, 2 Cfy), which may contain similar impurities, and usually contains also some ferrocyanide of potassium.

To find a simple method of accurately determining in an easy and expeditious manner the amount of ferro- and ferricyanide of potassium contained in the yellow and red salts of commerce, was a great desideratum both for the estimation of the commercial value of these salts and the examination of the mother liquor, &c., obtained in the process of their manufacture.

I am glad to have it in my power to give a method lately devised by one of the students in my laboratory (Mr. *F. de Haen*), which answers the purpose admirably.

This method is based upon the simple fact that a solution of ferrocyanide of potassium acidified with hydrochloric acid (and in which the presence of free hydroferrocyanic acid may be assumed), is upon addition of permanganate of potassa converted into the corresponding ferricyanide. If this conversion is effected in a very dilute fluid, containing in from 200 to 300 c. c., about 0·2 grm. of ferrocyanide of potassium, the termination of the reaction is clearly and unmistakably indicated by the change of color of the fluid from a pure yellow to a reddish-yellow tint. The amount of the ferricyanogen is determined by converting the ferricyanide with the aid of a reducing agent into the corresponding ferrocyanide, and then treating the latter with permanganate of potassa.

The method demands two test fluids of known strength, viz.,

1. A solution of pure ferrocyanide of potassium.
2. A solution of permanganate of potassa.

The *former* is prepared by dissolving 20 grammes of perfectly pure and dry crystallised ferrocyanide of potassium in the necessary quantity of water to give 1 litre of solution; every c. c. of this solution therefore contains 20 milligrammes of ferrocyanide of potassium. The *latter* is diluted to

the extent that a somewhat less than a burette full is required for 10 c. c. of the solution of ferrocyanide of potassium. Accordingly, with a burette holding 50 c. c., and divided into $\frac{1}{5}$ c. c., the solution is more largely diluted than when a burette is used holding only 25 c. c. and divided into $\frac{1}{10}$ c. c.

To determine the strength of the permanganate of potassa in its action upon ferrocyanide of potassium, measure off, by means of a small pipette, 10 c. c. of the solution of ferrocyanide of potassium (containing 0·200 grm.) dilute with about 250 c. c. of water, acidify with hydrochloric acid, place the glass on a sheet of white paper, and allow the solution of permanganate of potassa to drop into the fluid, stirring it at the same time, until the change from the yellow to a *reddish*-yellow color indicates that the conversion is completed.* Repetitions of the experiment give always very accurately corresponding results. As the solution of permanganate of potassa is liable to alteration, its strength must always be determined before every new series of experiments. To determine the amount of ferrocyanide of potassium contained in any given sample of the yellow salt of commerce, dissolve 5 grammes of the latter in the necessary quantity of water to give 250 c. c. of solution; take 10 c. c. of this solution, and examine as just now directed. Suppose in determining the strength of the solution of permanganate of potassa in its action upon ferrocyanide of potassium, you have used 80 volumes of the burette, and you find now that 70 volumes suffice, the equation,

$$80 : 0{\cdot}200 : : 70 : x$$

will inform you how much pure ferrocyanide of potassium the analysed salt contains. This calculation may be dispensed with, by diluting the solution of permanganate of potassa so that exactly 100° of it correspond to 0·200 of ferrocyanide of potassium, as, in that case, the number of volumes used expresses directly the percentage amount of the ferrocyanide of potassium present in the analysed salt.

To determine the amount of ferricyanide of potassium in a compound containing no ferrocyanide of potassium, dissolve 5 grammes of the compound in the necessary quantity of water to give 250 c. c. of solution; measure off 10 c. c., add from 5 to 8 c. c. of concentrated solution of potassa, heat in a small dish nearly to boiling, and then add from 0·4 to 0·5 grm. of finely triturated oxide of lead, which, being partly converted into binoxide, will immediately turn brown. After a short digestion at a temperature near the boiling point, the reduction is completed, as

* If you wish for some additional evidence besides the change of color, add to a drop of the mixture on a plate a drop of solution of sesquichloride of iron: if this fails to produce a blue tint, the conversion is accomplished.

is clearly seen from the changed color of the solution.)* Dilute now the contents of the dish with water, filter, wash, dilute to about 250 c. c., and acidify with hydrochloric acid. This produces a strong white turbidity caused by the separation of ferrocyanide of lead. Disregarding this, add the solution of permanganate of potassa.

The precipitate dissolves in proportion as the conversion of the ferrocyanide into ferricyanide ensues, and the termination of the reaction is thus distinctly indicated, not only by the change of color, but also by the perfect clearness of the fluid.† Of various methods employed to reduce the ferricyanide of potassium, none were so accurate as this. Repeated experiments gave perfectly satisfactory results. The only thing to be observed is that the fluids must be concentrated.

Lastly, to analyse a substance, containing both ferro- and ferricyanide of potassium, prepare the solution as directed, and then examine one portion of 10 c. c. at once, and another portion of 10 c. c. after previous reduction. The first process gives simply the amount of ferrocyanide of potassium contained in the analysed salt, the second gives this together with the quantity of ferrocyanide formed from the ferricyanide originally present in the analysed salt.

Now, as two equivalents of crystallised ferrocyanide of potassium = 5281 correspond to one equivalent of ferricyanide of potassium = 4117, the quantity of the latter is found by multiplying by 0·7795, the difference between the results of the two processes, expressed as crystallised ferrocyanide of potassium. The reaction on which this method is based ensues in the manner shown in the following equation: 10 (Cfy, 2 H) + $Mn_2 O_7$ + 2 HCl = 5 (2 Cfy, 3 H) + 2 Mn Cl + 7 HO. This has been proved by direct experiments. The results are very accurate.

6. Analysis of common salt.

§ 199.

I select this example to show how to analyse with accuracy and tolerable expedition, salts which, with a predominant principal ingredient, contain small quantities of other substances.

a. Reduce the salt by trituration to a uniform powder, and put this into a stoppered bottle.

* Actual ebullition, more especially continued for any length of time, should be avoided, as it tends to cause the solution of a large proportion of oxide of lead, which would in some measure interfere with the ulterior process.

† As ferrocyanide of lead in not altogether insoluble, but simply difficultly soluble in a hydrochloric acid fluid, the fluid first becomes clear, and then only after addition of a few more drops, reddish-yellow. It is the latter point which must be attained before the reaction can be considered complete.

b. Weigh 10 grammes of the powder, and dissolve in a beaker by digestion with water; filter the solution into a measuring flask holding 500 c. c., and thoroughly wash the small residue which generally remains. Finally fill the flask with water up to the mark, and shake the fluid.

(If small, solid, white grains of sulphate of lime are left behind upon dissolving the salt, reduce them to powder in a mortar, add water, let the mixture digest for some time, pass the clear supernatant fluid through a filter, triturate the undissolved residue again, add water, &c., and repeat the operation until all is dissolved.)

c. Determine the dried insoluble residue as directed § 35.

d. Of the solution *b.* measure off one after another the following quantities :—

For *e.* 50 c. c. corresponding to 1 gramme of common salt.
„ *f.* 150 c. c. „ „ 3 grammes „ „
„ *g.* 150 c. c. „ „ 3 „ „ „
„ *h.* 50 c. c. „ „ 1 „ „ „

e. Determine in the 50 c. c. measured off, the *chlorine* as directed § 112, I. *a.* or *c.* (*α.* or *β.*).

f. Determine in the 150 c. c. measured off, the *sulphuric acid* as directed § 105, I. 1.

g. Determine in the 150 c. c. measured off, the lime and magnesia as directed § 122, 3, *a.*

h. Mix in a platinum dish with about ½ c. c. of pure concentrated sulphuric acid, and proceed as directed § 77, 1. The neutral residue contains the sulphates of soda, lime, and magnesia. By deducting from this the quantity of the two latter substances as resulting from *g*, you find that of the sulphate of soda.

i. Determine in another weighed portion of the salt the water, as directed § 18, *a.* (last paragraph).

k. Bromine and other bodies, of which only very minute traces are found in common salt, are determined by the methods described in the analysis of mineral waters.

7. Analysis of gunpowder.

§ 200.

a. Estimation of the moisture.—Weigh between watch-glasses about 2 grammes of the finely pulverised gunpowder, and dry it, either at a gentle heat, or, better still, under a bell-glass, over sulphuric acid, until no further diminution of weight is observed.

b. Determination of the nitrate of potassa. Put an accurately weighed quantity (about from 5 to 6 grammes) on a filter dried at 212°, but

moistened again with water before the powder is placed on it; add to the powder on the filter as much water as it will absorb, and after some time repeatedly pour small quantities of hot water upon it until the nitrate of potassa is completely dissolved.* When this is effected, dry the contents of the filter completely at 212°, and weigh (§ 33). On the other hand, evaporate the solution of the nitrate of potassa in a weighed platinum dish and determine the residue as directed § 76, 2. The diminution of weight of the gunpowder and the increase of weight of the dish must exactly correspond, as both express the quantity of the nitrate of potassa.

c. Determination of the sulphur.

α. In the dry way (Gay-Lussac).

Mix one part (from 1 to 1·5 grm.) of the powder finely triturated with the same quantity of pure anhydrous carbonate of soda (free from sulphuric acid), add one part of pure nitrate of potassa, and four parts of pure dry chloride of sodium, and heat the mixture in a platinum crucible, until the combustion is completed, which is indicated by the white color of the mass. Dissolve in water, acidify the solution with hydrochloric acid, and precipitate with chloride of barium the sulphuric acid formed by the oxidation of the sulphur (§ 105, I.).

β. In the humid way.

From 2 to 3 grammes of the powder are oxidised with concentrated pure nitric acid and chlorate of potassa, which latter is added in small portions at a time (§ 116, II. 2, *a. α.*). By this process both the sulphur and the charcoal are completely oxidised, and a clear solution is ultimately obtained, in which the sulphuric acid formed is then determined, as directed § 105, I. 1.

γ. In the indirect way.

Deduct the weight of the charcoal, determined as directed *d. α.*, from the joint weight of the charcoal and sulphur; the difference expresses the weight of the latter.

d. Determination of the charcoal.

α. By separation in the pure state.

aa. Digest a weighed portion of the powder repeatedly with sulphide of ammonium, until all the sulphur is dissolved, and collect the charcoal on a filter dried at 212°; wash, first with water containing sulphide of ammonium, then with pure water, dry at 212°, and weigh.

* The nitrate of potassa may also be estimated in an expeditious manner, and with sufficient accuracy for technical purposes by means of an hydrometer indicating the percentage weight of the nitrate of potassa, if a weighed quantity of the gunpowder is dissolved in a definite amount of water. A method based upon the same principle by *Uchatius* is given in the Wiener acad. Ber. X. 748, and also Ann. d. Chem. und Pharm. 88, 395.

bb. Replace the weighed filter containing the charcoal and sulphur (see *b.*) in the funnel, moisten it with absolute alcohol, and dissolve the sulphur with a mixture of sulphide of carbon and absolute alcohol. To accelerate the action, heat the funnel, by putting it into a wider one and filling the space between with hot water. Wash ultimately with pure alcohol, dry the charcoal at 212°, and weigh (*Marchand*).

β. By elementary analysis of the gunpowder (*Weltzien*).

Weltzien burns a weighed portion of the well-dried powder with oxide of copper in a long combustion tube, and thus ascertains the respective quantities of carbon and hydrogen contained in it. The knowledge of the quantity present of the latter element is of importance in this much, that it enables the analyst to draw a correct inference respecting the nature and inflammability of the charcoal. In the process of combustion the modifications given in §§ 151, 156, and 159, must be attended to.

If the carbon and hydrogen are determined by this method, the nitrate of potassa by *b.*, and the sulphur from the difference, the number found for the latter element is a little too high, as the oxygen and the ashes of the charcoal increase its weight.

8. Analysis of mixed silicates.

§ 201.

The analysis of those silicates which are completely decomposed by acids, has been described in § 111, II. *a.*; and that of those which are not decomposed by acids, in § 111, II. *b.* I have therefore here only to add a few remarks respecting the examination of mixed silicates, *i. e.* of such as are composed of silicates of the two classes (phonolites, clay slate, basalts, meteoric stones, &c.).

The silicate is very finely pulverised and dried; the dry powder is usually treated for some time at a gentle heat with moderately concentrated hydrochloric acid, and the mixture evaporated to dryness on the water-bath; the residue is moistened with hydrochloric acid, water added, and the solution filtered; it is often preferable, however, to digest the powder with dilute hydrochloric acid (of about 15 per cent) for some days at a gentle heat, and then at once filter the solution. Which of the two ways it is advisable to adopt, and indeed whether the method here described, and which was first employed by *Chr. Gmelin* in the analysis of phonolites, may be resorted to at all, depends upon the nature of the mixed minerals. The more readily decomposable the one of the constituent parts of the mixture is, and the less readily decomposable the other; the more constant the relative proportion between the undissolved and the

dissolved part is found to remain in different experiments ; and accordingly the less the undissolved part is affected by further treatment with hydrochloric acid, the more safely may this method of decomposition be resorted to.

The process gives :

a. An hydrochloric acid solution, in which the bases of the decomposed silicate are contained in the form of metallic chlorides, which are separated and determined by the proper methods.

b. An insoluble residue, which contains, besides the undecomposed silicate, also the silicic acid of the decomposed silicate.

Wash the residue *b*. well with water, to which it is advisable to add a few drops of hydrochloric acid, and while still moist, transfer it in small portions at a time to a platinum dish containing a boiling solution of carbonate of soda (free from silicic acid) ; boil for some time, and filter off each portion whilst still very hot through a weighed filter. Finally rinse the last particles of the residue which still adhere to the filter completely into the dish, and proceed as before. Should this operation not fully succeed, dry the filter, incinerate it, transfer the ash to the platinum dish, and boil once more with the solution of carbonate of soda. Wash the residue, first with hot water, then—to ensure the removal of every trace of carbonate of soda which may still adhere to it—with water slightly acidified with hydrochloric acid, and ultimately again with pure water. Collect the washings in separate vessels.

Acidify the alkaline filtrate with hydrochloric acid, and determine in it the silicic acid proceeding from the silicate decomposed by the hydrochloric acid in the first process, as directed § 111, II. *a*. Dry the undissolved silicate and weigh. The difference gives the quantity of the dissolved silicate. Treat the undissolved silicate exactly as directed § 111, II. *b*.

The following method of analysing the several varieties of clay, differ in some respects from the preceding method.

9. Analysis of clays.

§ 202.

The several varieties of clay, derived from the disintegration of felspar, or similar silicates, consist commonly of a mixture of true clay with quartz or felspar sand, and contain often also free silicic acid, which may be dissolved out by boiling with a solution of carbonate of soda.

Respecting the mechanical analysis of the several varieties of clay, I refer the reader to my "Untersuchung der wichtigsten nassauischen

Thone;" * and proceed here at once to give the method which it is advisable to adopt in the chemical analysis of these bodies.

a. Triturate the clay as finely as possible, and dry it for some days at 212°.

b. Fuse from 1 to 2 grammes with carbonate of soda and potassa, and proceed exactly as directed § 111, II. *b*. Treat the hydrochloric acid solution obtained, and filtered from the silicic acid, as directed § 129, 1. In the precipitate produced by carbonate of baryta, and which contains alumina and some sesquioxide of iron, separate and determine these two latter substances, after previous removal of the baryta, according to the directions given § 128, 10, *a*.

c. Decompose from 1 to 2 grammes with hydrofluoric acid (§ 111, II. *b*. β. or γ.), to ascertain the amount of alkali contained in the clay.

d. Heat a third portion (from 1 to 2 grammes) with an excess of sulphuric acid mixed with some water, until the acid begins to evaporate. Let the mass cool, add water, and separate in the undissolved residue the liberated silicic acid from the sand, by treating with boiling concentrated solution of carbonate of soda (§ 201).

e. To ascertain the amount of silicic acid which a boiling solution of carbonate of soda will remove from the clay, boil a somewhat larger weighed portion of the clay repeatedly with a solution of carbonate of soda, and determine the silicic acid in the filtrate, by evaporation with hydrochloric acid.

f. Determine the quantity of the water by long-continued ignition in a platinum crucible. The loss of weight indicates the quantity of the water; but the results in this respect are usually a little too high, as many varieties of clay contain traces of organic matter, which are decomposed upon ignition, and many of them evolve also small quantities of chloride of ammonium, when heated to redness (compare "Untersuchung der wichtigsten nassauischen Thone." Journal f. prakt. Chemie, 57, 65).

10. Analysis of limestones, dolomites, marls, etc.

As the minerals containing carbonate of lime and carbonate of magnesia play a very important part in manufactures and agriculture, the chemist is frequently called upon to analyse them. The analysis of these bodies presents no very great difficulties. I will here give, in the first place, a method to effect the complete analysis of limestones, dolomites, &c.; and, in the second place, a method of analysis by measure, by which the carbonate of lime (and the carbonate of magnesia) may be expeditiously determined.

* Journ. f. prakt. Chemie, 57, 65.

A. Method of effecting the complete analysis of limestones, dolomite, etc.*

§ 203.

a. Reduce a large piece of the mineral to powder, mix this uniformly, and dry at 212°.

b. Treat about 2 grammes of the powder, in a covered beaker, with dilute hydrochloric acid in excess, evaporate the mixture to dryness, moisten the residue with hydrochloric acid, heat with water, filter, wash the insoluble residue, dry, and weigh. The residue may consist of clay, sand, and separated silicic acid. If sufficiently considerable, examine it as directed § 202.

c. Mix the hydrochloric acid solution with chlorine water, then with ammonia, and let the mixture stand at rest for some time, in a covered vessel, at a gentle heat. Filter the precipitate, which contains—besides sesquioxide of iron, sesquioxide of manganese, and hydrate of alumina—the phosphoric acid which the analysed compound may happen to contain, and, moreover, invariably traces of lime and magnesia, wash slightly, and redissolve in hydrochloric acid; heat the solution, add chlorine water, and then precipitate again with ammonia; filter the fluid from the precipitate, wash, dry, ignite, and weigh. According to circumstances, you may now also determine the respective quantities of the several ingredients of the precipitate, which may be accomplished, as regards the sesquioxide of iron and the protosesquioxide of manganese, by analysis by measure (§ 128, 10).

d. Unite the fluids filtered from the first and second precipitates produced by ammonia, nearly neutralise with hydrochloric acid, leaving the ammonia predominating only very slightly, and determine the lime and magnesia as directed § 122, 3, *a*. After weighing the lime, test it invariably for an admixture of magnesia.

e. Determine the carbonic acid according to the directions of § 110, II. *b*. *a*. or *β*. *bb*.

B. Determination of the carbonate of lime (and carbonate of magnesia) by analysis by measure.

§ 204.

a. Requisites for the process.

1. *Hydrochloric acid,* of which 50 c. c. = 100° of the burette neutralise 5 grammes of carbonate of lime. This test acid is prepared exactly in the manner described § 185, with the aid of pure carbonate of soda, of which latter salt 50 c. c. of the acid must accordingly neutralise 5·3 grammes, *i. e.* the quantity equivalent to 5 grammes of carbonate of lime.

* Compare *Fresenius'* "Chemische Untersuchung der wichtigsten Kalksteine des Herzogthums Nassau." Journal f. prakt. Chemie, 54, 85, and 374.

2. *Solution of soda,* of which two volumes neutralise one volume of the hydrochloric acid (1). For the manner of preparing the solution of soda, I refer to § 182.

b. Analytical process.

α. In total, or almost total, absence of carbonate of magnesia.

Weigh 5 grammes of the finely pulverised mineral, introduce into a capacious flask, add about 50 c. c. of water, and then gradually, from a *Mohr's* pipette, 50 c. c. of the hydrochloric acid (*a.* 1.). In the analysis of very pure limestones it is better to add 105 c. c. in order to accelerate the solution. When the action of the acid has ceased, close the flask with a cork with a bent tube, and apply a gentle heat to expel the dissolved carbonic acid; conduct the gas bubbles through a little water. When the object has been attained, remove the lamp, allow the water to recede, mix the fluid with some tincture of litmus, and add the solution of soda (*a.* 2), from another *Mohr's* pipette or from a burette, until the fluid just begins to show a blue tint. If you subtract half of the number of volumes of the burette used of the solution of soda from the number of volumes of the burette used of the hydrochloric acid, the difference (*i. e.* the number of volumes of the burette of the hydrochloric acid which have served to neutralise the carbonate of lime) expresses directly the percentage of carbonate of lime in the analysed mineral. The results are very satisfactory. This method, in a somewhat modified form, was first employed and recommended by *Bineau.*

β. In presence of carbonate of magnesia.

As one equivalent of carbonate of magnesia neutralises exactly as much hydrochloric acid as one equivalent of carbonate of lime, the method described in α., gives, in analyses of minerals containing both carbonate of lime and carbonate of magnesia, the joint quantity of both salts; the latter represented by its equivalent of carbonate of lime, *i. e.* for every 42 of carbonate of magnesia we find 50 of carbonate of lime. If, therefore, you wish to know separately the respective quantities of the two salts, you must determine, besides the joint amount of the two, the separate amount of one of them. This may be effected by one of the following methods:

1. Mix the solution of 5 grammes of the mineral with 3 grammes of chloride of ammonium, then with ammonia and carbonate of ammonia in excess; let the mixture stand several hours, and then filter, leaving the carbonate of lime adhering to the sides of the vessel undisturbed. Wash the precipitate on the filter, and rinse the contents of the latter into the beaker in which the precipitation has been effected; incinerate the filter, introduce the ashes also into the beaker, and treat the contents of the latter as directed in α. This gives you separate quantity of the lime; the difference, properly calculated, as carbonate of magnesia (50 of carbonate of lime = 42 of carbonate of magnesia, represents the quantity of the latter).

2. Dissolve 5 grammes of the mineral in the least possible excess of hydrochloric acid, and mix with solution of lime in sugar water as long as a precipitate forms. By this operation the magnesia only is precipitated. Filter the fluid from the precipitate, wash the latter, and treat as directed in *a*. By this means you ascertain the quantity of the magnesia, represented by its equivalent quantity of carbonate of lime; the amount of the latter is found from the difference.

The method 2 is adapted only for the analysis of limestones, &c., containing only a small proportion of magnesia.

11. Analysis of iron ores.

The iron ores most commonly employed, and which the chemist is therefore most frequently called upon to examine, are, red hematite, brown hematite, bog iron, magnetic iron, and spathic iron ores. In some cases, a complete analysis of these ores is required; in others, simply a quantitative estimation of certain of its constituent parts (the iron, phosphoric acid, sulphuric acid, &c.); in others, merely the determination of the iron.

A. Methods of effecting the complete analysis of the ores.

§ 205.

I. Red hematite.

This ore contains the iron as sesquioxide; besides this, some moisture is always present, and commonly also an admixture (insoluble in acids) of the matrix in which the ore occurs; sometimes carbonates of the alkaline earths are also found associated with it.

Reduce the ore to a very fine powder, and dry at 212°.

a. Treat the powder with dilute nitric acid or dilute boiling acetic acid, to remove the admixture of carbonates of the alkaline earths which the ore may contain. Determine these (if any are present) in the solution obtained.

b. Ignite a sample of the powder, free from admixture of carbonates of the alkaline earths, first in the air, then in hydrogen gas (which is effected best in a small porcelain boat inserted in a porcelain tube; § 128, 3). The loss of weight expresses the quantity of oxygen in the sesquioxide, from which the amount of the latter may be calculated.

c. Treat the residue with dilute hydrochloric acid. The iron dissolves, the admixture from the matrix is left. Determine the iron in the solution at once and without filtering the fluid, by analysis by measure; then filter, wash the residuary mineral, dry, and weigh. The quantity of iron found in *c*. must correspond to that calculated from the oxygen expelled by the process *b*.

d. The water may be determined by igniting a separate portion of the powder. If the ore contains carbonates of the alkaline earths, the carbonic acid of the latter escapes with the water.

II. Brown hematite.

This ore contains the iron as hydrated sesquioxide, and besides, alumina and sesquioxide of manganese; often also small quantities of lime and magnesia, and of silicic acid (in combination with bases), phosphoric acid, and sulphuric acid, and always a larger or smaller admixture of quartz sand or of the matrix in which the ore occurs; and which admixture is insoluble in hydrochloric acid.

A complete and accurate analysis of this ore presents some difficulties. One of the following methods may be selected. The preliminary operations indispensable in all of them are the reduction of the ore to a fine powder, which is dried at 212°, and the ignition of a sample, to ascertain the amount of water.

a. Decomposition in the dry way. (This method is more particularly recommended for the analysis of ores containing only small quantities of silicic acid, alumina, lime, and magnesia.)

Fuse a weighed portion of the powder with three times its weight of carbonate of soda and potassa, and digest the fused mass with water until the soluble parts are dissolved; filter the solution from the residue, and well wash the latter.

aa. Acidify the filtrate with hydrochloric acid and separate the silicic acid in the usual way. Add to the filtrate a few drops of chloride of barium, let it stand for twenty-four hours, and then filter off the precipitate of sulphate of baryta which may have formed. Remove the baryta from the filtrate by means of a few drops of dilute sulphuric acid, and then precipitate the phosphoric acid as directed § 106, I. *b.*

bb. Dissolve the residue in hydrochloric acid, and treat the solution as directed § 129.

b. Decomposition in the humid way.

*First method.**

Heat about ten grammes of the finely pulverised mineral, in an obliquely placed flask, with concentrated hydrochloric acid until complete decomposition is effected; dilute with water, filter into a measuring flask holding 300 c. c., and wash; dry, ignite, and weigh the undissolved residue; it consists of quartzsand or some other substance, from the matrix in which the ore occurs, and of liberated silicic acid. The latter may be separated and determined, by boiling the residue with a solution of carbonate of soda (§ 201, *b.*).

* No attention is paid in this method to the possible presence of copper or arsenic.

The filtrate is treated as follows:

1. Mix 50 c. c. of the filtrate with chloride of barium, to determine the *sulphuric acid.*

2. Evaporate 50 c. c. on the water-bath, to expel the greater part of the free acid; dilute the fluid, add some carbonate of soda, and precipitate with carbonate of baryta; let the precipitated fluid stand for half an hour, and then filter.

a a. Dissolve the washed *precipitate* in hydrochloric acid; throw down the baryta from the solution, by sulphuric acid; filter, and mix the filtrate with ammonia until it manifests alkaline reaction, and then filter the fluid from the precipitate; wash, dry, ignite, and weigh the latter. It consists of sesquioxide of iron, alumina, some silicic acid and phosphoric acid. Digest with concentrated hydrochloric acid, and separate and determine the small quantity of silicic acid dissolved by that fluid; reduce the filtrate with sulphite of soda, and determine the iron, alumina, and phosphoric acid, as directed § 128, B. 1. Acidify the alkaline filtrate, boil with some chlorate of potassa, and then separate the alumina and phosphoric acid by one of the methods given in § 106, II. *f.* The joint weight of the component parts, as calculated from the results of these several processes, must be equal to the total weight of the precipitate produced by ammonia.

b b. In the *filtrate* determine the manganese and the alkaline earths as directed § 129.

3. In 100 c. c. determine, by way of control, the phosphoric acid as directed § 106, II. *o.* (This gives very accurate results.)

4. In 50 c. c. determine by way of control, the iron by analysis by measure, in the manner directed § 206.

Second method.

1. Decompose from 3 to 4 grammes of the powder with hydrochloric acid, and treat the insoluble residue by the first method.

2. Evaporate the hydrochloric acid solution to dryness, and separate the silicic acid in the usual way (§ 111, II. *a.*).

3. Reduce the filtrate with sulphite of soda (§ 106, II. *n.*), expel the excess of sulphurous acid by gentle ebullition, and saturate the fluid with sulphuretted hydrogen. If this produces a precipitate, test the latter for copper and arsenic.

4. Boil the filtrate until the sulphuretted hydrogen is expelled; precipitate now with carbonate of soda, add solution of potassa in excess, boil, and filter, exactly as directed § 128, B. 1, *a.* By this process you obtain a black precipitate and an alkaline filtrate.

5. Dissolve the precipitate, which consists principally of protosesquioxide of iron, and may contain carbonate of manganese and carbonate

and phosphate of lime and magnesia, in hydrochloric acid, and separate the phosphoric acid, according to the directions of § 106 II. *n.*, in combination with a small quantity of sesquioxide of iron; filter, and separate the phosphoric acid and sesquioxide of iron, as directed § 106, II. *h.* γ. Dissolve the protosesquioxide of iron so obtained in hydrochloric acid, and add the solution to the fluid filtered from the phosphate of sesquioxide of iron. Acidify the solution of the alkaline phosphate with hydrochloric acid, and put aside to add afterwards to the fluid containing the greater portion of the phosphoric acid.

6. Treat the fluid filtered from the phosphate of sesquioxide of iron, after adding to it the solution of protosesquioxide of iron obtained in 5, as directed § 129, 3, to effect the separation of the iron, manganese, lime, and magnesia.

7. Acidify the alkaline filtrate obtained in 4, which contains the alumina and the greater part of the phosphoric acid; boil with some chlorate of potassa, precipitate with ammonia, add chloride of barium, and proceed in all other respects exactly as directed § 106, II. *f.* δ.

8. Determine the sulphuric acid in a separate portion of the hydrochloric acid solution of the mineral as directed in the first method (1).

III. Bog iron ore.

Bog iron ore consists of a mixture of hydrated sesquioxide of iron with the basic salts of sesquioxide of iron with sulphuric acid, phosphoric acid, crenic acid, apocrenic acid, and humic acid, and contains besides these, substances from the formation or deposit in which it occurs, alumina, lime, and magnesia.

Reduce the ore to powder, and dry. Expose a portion of it in an open platinum crucible, at first to a dull red heat, to burn the organic acids, then gradually for some time to an intense red heat, with the crucible placed in an oblique position. Treat the residue by one of the methods given in II.

To detect and determine the organic acids, boil a larger portion of the finely pulverised ore with pure solution of potassa, until it is converted into a flocculent mass. Filter and treat the filtrate as directed § 177, 9.

IV. Magnetic iron ore.

Magnetic iron ore contains the metal as protosesquioxide. Analyse the ore in the same way as the red hematite, and determine afterwards in a separate weighed portion dissolved in hydrochloric acid, with exclusion of air, the protosesquioxide of iron by analysis by measure as directed § 89, 2, *a*.

V. Spathic iron ore.

Spathic iron ore contains carbonate of protoxide of iron, associated usually with carbonate of manganese and carbonates of the alkaline earths, and often mixed also with clay and substances from the matrix in which the ore occurs.

Reduce the mineral to powder, and dry.

a. Determine the water as directed § 19.

b. Determine the carbonic acid as directed § 110, II. *b*. *β*.

c. Dissolve a third portion of the powder in hydrochloric acid, with addition of nitric acid. When complete decomposition has been effected, filter the fluid from the residue which may have remained undissolved, and separate the bases in the filtrate by one of the methods given in § 129.

d. In a fourth portion of the powder, dissolved in hydrochloric acid, with the exclusion of air, determine the quantity of the protoxide of iron by analysis by measure as directed § 89, 2, *a*.

B. Determination of the iron in iron ores, by analysis by measure.

§ 206.

Heat one gramme (or a smaller quantity*) of the pulverised ore in a long-necked flask, placed obliquely, with concentrated hydrochloric acid until complete decomposition is effected; dilute with from 25 to 50 c. c. of water, and add a few small grains of granular zinc, or some pieces of pure sheet zinc. Close the flask with a perforated cork furnished with a bent tube with the outer arm slightly inclined; let this outer arm dip into a beaker containing some water, whose surface, however, the tube must not, or at least barely, touch. Heat the contents of the flask to boiling. If the fluid is not yet perfectly colorless when all the zinc is dissolved, add an additional small quantity of zinc (but not too much), and heat until complete solution is effected. When the flask has cooled a little, allow the water in the receiving beaker to recede; cool the flask, tranfer its contents to a beaker, and proceed as directed § 89, 2, *a*. I must here emphatically remark that I deem it more convenient and better calculated to secure accurate results, not to weigh off exactly 1 gramme of the pulverised ore, but some indefinite quantity (about 0·4 or 0·5 grm.); and that I prefer leaving the solution of permanganate of potassa (of course

* I usually take about 0·4 or 0·5 grm., and determine the iron by means of a solution of permanganate of potassa, of which 30 c. c. correspond to from 0·2 to 0·3 grm. of iron. I add this solution from a burette divided into $\frac{1}{10}$ c. c.

assuming it to have about the proper degree of concentration) undiluted, simply determining its strength; with a fluid so changeable as solution of permanganate of potassa, every unnecessary manipulation should be avoided. The calculation required is very simple.

12. Copper pyrites.

§ 207.

This mineral contains copper, iron, sulphur, and generally also substances from the matrix in which it is found. Whether it contains other metals, besides copper and iron, must be ascertained by a qualitative analysis.

The finely pulverised mineral is dried at 212°.

a. The estimation of the sulphur is effected according to the directions given § 116, II. 1, or, more commonly, according to the directions of § 116, II. 2, *a. a.* or *β.*

b. If the former method is employed, the oxides are dissolved in hydrochloric acid, and the copper and iron separated by sulphuretted hydrogen; —if the latter, either the excess of baryta is removed by sulphuric acid, and sulphuretted hydrogen then conducted into the fluid, or the bases are determined in a fresh portion of the powder.

The quantity of the copper may be determined also directly by *Schwarz's* method (§ 95, 3, *b.*); but, in effecting the reduction, care must be taken not to raise the heat above 176°, at which temperature iron will not precipitate from a fluid containing a large proportion of alkaline tartrate. However, even supposing some iron to precipitate with the copper, this could exercise no adverse influence on the quantitative estimation of the latter metal.

The following method of determining copper by analysis by measure, has recently been devised by one of the students at my own laboratory, *Mr. de Haen*, which, when properly applied, gives very satisfactory results.

The method is based upon the fact that, when a salt of oxide of copper in solution is mixed with iodide of potassium in excess, subiodide of copper and free iodine separate, which latter (the free iodine) remains dissolved in the solution of iodide of potassium: $2\,(CuO,\,SO_3)+2\,KI=Cu_2I+2\,KO,\,SO_3+I$. By determining the quantity of the iodine by *Bunsen's* method, the quantity of the copper is ascertained. The process is conducted as follows: Dilute the sulphuric acid solution of the copper—(which had better be neutral, though a moderate excess of sulphuric acid will not interfere with the accuracy of the results)—in a measuring flask with the requisite quantity of water to obtain a definite volume of fluid of which 100 c. c. contain from about 1 to 2 grammes of oxide of copper. Transfer about 10 c. c. of *Bunsen's* solution of iodide of potassium to a capacious

beaker, add 10 c. c. of the solution of copper, mix, and then add without delay sulphurous acid, and proceed in all other respects as directed § 114, Appendix. The solution of copper must contain no free nitric, nor free hydrochloric acid; delay in the addition of the sulphurous acid to the mixed solution of copper and iodide of potassium, would affect the accuracy of the results. With due attention to these points, the results are exceedingly accurate. Thus *Mr. de Haen* obtained 0·3567 grm. of sulphate of copper instead of 0·3566,—99·89 and 100·1 of metallic copper instead of 100.*

13. Galena.

§ 208.

Galena, the most widely spread of the lead ores, contains frequently larger or smaller quantities of iron, copper, silver, and commonly also substances (insoluble in acids) from the matrix in which it occurs.

The best way of analysing it, is as follows:

Reduce the ore to a fine powder, and dry at 212°.

Oxidise a weighed quantity of the powder (from 1 to 2 grammes) with highly concentrated red fuming nitric acid, free from sulphuric acid (see § 116, II. *a*. *α*.—however, the ore is not exposed in a tube to the action of the acid). If the acid is sufficiently strong, no sulphur will separate. After heating gently for some time, dilute with water, filter, and wash the residue.

a. Dry the *residue*, ignite, and weigh (§ 92, 2). It consists of sulphate of oxide of lead, mineral admixture from the vein, undecomposed by the acid, silicic acid, &c. Heat the whole, or a fractional part of it, with hydrochloric acid to boiling; let the residuary sediment subside, and then decant the supernatant clear liquid on a filter; pour a fresh portion of hydrochloric acid over the residue, boil again, let the residuary sediment subside, and decant, and repeat this operation until the sulphate of lead is completely dissolved; finally place the residue on the filter, and wash with boiling water until every trace of chloride of lead is removed; dry, ignite, and weigh. Subtract the weight found from that of the original residue: the difference expresses the quantity of sulphate of lead which the latter contained.

b. Evaporate the *filtrate* nearly to dryness, to expel the excess of free nitric acid; dilute again with water, and test for *silver*, with very dilute hydrochloric acid. If a precipitate forms, increase, if necessary, the quantity of the hydrochloric acid, filter the fluid from the precipitate,

* I think the strength of *Bunsen's* solution of iodine may be determined by this method, with the aid of weighed quantities of pure copper, as accurately as by means of bichromate of potassa (§ 114, Appendix, *c*. *β*.).

wash the latter with boiling water, and determine the chloride of silver in the usual way. Remove the sulphuric acid, which the filtrate may still contain, by means of acetate of baryta, and then precipitate with sulphuretted hydrogen. The precipitate contains, besides sulphide of lead, often sulphide of copper, and possibly also sulphides of other metals. These and the metals in the filtrate, which are precipitable by sulphide of ammonium, are separated by the methods given in Section VI.

Calculate the proportion of sulphur both in the sulphate of lead (*a.*) and in the sulphate of baryta (*b.*), and add the results together: this sum gives the total quantity of the sulphur contained in the analysed ore.

To determine very small quantities of silver and the trifling traces of gold which, according to *Percy* and *Smith*, are often found in galena, the best way is to fuse a large portion of the ore with carbonate of soda and nitrate of potassa (10 parts of the ore, 30 of carbonate of soda, 3 of nitrate of potassa), and determine the silver by cupellation in the metallic mass obtained (§ 131, 7), and then separate it from the gold by means of nitric acid.

14. Zinc ores.

§ 209.

A. Calamine and silicate of zinc ore.

The former of these ores consists of carbonate of zinc, which commonly contains larger or smaller admixtures of protoxide of iron, protoxide of manganese, oxide of lead, oxide of cadmium, lime, magnesia, and silicic acid; the latter consists of silicate of zinc, which may contain admixtures of silicates of lead, binoxide of tin, sesquioxide of manganese, sesquioxide of iron, &c.

The ore is reduced to a fine powder, dried at 212°.

a. A portion of the powder is treated as directed § 111, II. *a.*—that is, the silicic acid is separated in the usual way. As the silicic acid generally contains sand or undecomposed mineral from the matrix from which the ore is derived, it must be separated from this admixture by boiling with a solution of soda (§ 201).

b. In treating the residue with hydrochloric acid and water, 30 parts of acid are used to 100 parts of water (see page 316, note).

c. The solution obtained by this process, is precipitated with sulphuretted hydrogen, and the metals which may be thrown down by that reagent are separated by the proper methods described in Section V.

d. The filtrate is neutralised with ammonia and then precipitated with sulphide of ammonium; the precipitate is treated exactly as directed § 85, *b.*; the oxide of zinc obtained, which contains sesquioxide of iron and sesquioxide of manganese, is weighed, and in a weighed portion of it the manganese determined volumetrically (§ 128, 10, *d.*);

the sesquioxide of iron being then ultimately determined by means of solution of permanganate of potassa, after previous reduction by zinc, as directed in § 206.

e. The lime and magnesia are determined in the fluid filtered from the sulphide of zinc, as directed § 127, A.

f. The carbonic acid is determined in a separate portion of the powder, as directed § 110, *b*.

g. If the mineral contains water, this is determined as directed § 19.

B. Zinc blende.

This ore consists of sulphide of zinc, commonly mixed with other metallic sulphides, more especially the sulphides of lead, cadmium, copper, iron, and manganese. Besides these, regard must be had in the analysis to substances from the matrix in which the ore occurs.

The ore is reduced to a very fine powder, which is dried at 212°.

a. If the ore contains no lead, the sulphur in it is determined as directed § 116, II. 1; or, more commonly, as directed § 116, II. 2, *a*. *α*. or *β*.;— if it contains lead, it is treated as directed in § 208.

b. The determination of the bases should always be made in a separate portion of the pulverised ore. If no lead is present, the powder is dissolved in hydrochloric acid, with addition of nitric acid, and the solution treated as directed § 209, A. In presence of lead, the following convenient method, which gives accurate results, may be resorted to. Heat the powder with fuming hydrochloric acid until complete decomposition is effected, evaporate the fluid to the consistence of syrup, and dilute with five or six times its volume of strong alcohol. Let the mixture stand several hours, and then collect the chloride of lead, together with the undissolved mineral substances, on a weighed filter, wash with alcohol, dry, and weigh; treat with boiling water until the chloride of lead is completely removed; dry and weigh the residue: the loss of weight suffered in the last operation gives the quantity of the chloride of lead. Free the filtrate from the alcohol, by distillation or evaporation, and proceed with the hydrochloric acid solution as directed § 209, A.

Appendix to II.

Quantitative estimation of grape or fruit sugar, cane sugar, milk sugar, starch, and dextrine.

The quantitative estimation of these compounds is often called for in the analysis of agricultural and technical products, and also in that of pharmaceutical preparations; it is also of some importance as regards the examination of diabetic urine. I will therefore give in this Appendix some of the best methods by which this is effected.

Setting aside the purely physical processes, which are based either upon the specific gravity of the saccharine solutions, or upon their deportment with polarised light, there are two methods by which the quantitative estimation of grape sugar, and also of the other compounds, which are convertible into grape sugar, may be accomplished, to which I shall confine myself.

A. Methods based upon the reduction of oxide of copper to suboxide.*

§ 210.

If a solution containing sulphate of copper, neutral tartrate of potassa, and solution of soda, *in the proper proportion*, is heated, even to ebullition, it remains unaltered; but if the same solution is heated after addition of grape sugar, suboxide of copper separates. The quantity of the oxide of copper reduced is proportional to the quantity added of the grape sugar: one equivalent of the latter ($C_{12}H_{12}O_{12}$)=2250 reduces ten equivalents of oxide of copper=4960 to the state of suboxide (*Fehling, C. Neubauer*). Therefore, if we know the quantity of oxide of copper reduced, we know also that of grape sugar added.

Upon this principle two methods may be based. Either we may add to a solution of copper of known strength, the exact quantity of grape sugar which, if the grape sugar were perfectly pure, would reduce all the oxide to suboxide; or the solution of copper may be used in excess, and the suboxide which separates determined. The former method is the one most frequently employed; the latter is resorted to in cases in which, from the dark color of the fluid, it is difficult to determine the exact point where the process of reduction and separation is accomplished.

We will now proceed, first to the quantitative estimation of grape sugar, and afterwards to the consideration of the best method of converting cane sugar, starch, &c., into grape sugar.

1. Quantitative estimation of grape sugar in pure or almost pure aqueous solution.

First Method.

Requisites.

a. Solution of copper. Dissolve exactly 40 grammes of pure crystallised sulphate of copper, completely freed from adhering moisture, by pulverising and pressing between sheets of blotting paper, in about 160 grammes of water. Dissolve in another vessel 160 grammes of neutral tartrate of

* Compare *Fehling*, on the quantitative estimation of sugar and starch, by means of sulphate of copper, Ann. d. Chem. u. Pharmacie, Bd. 72, S. 106; and *C. Neubauer*, Archiv der Pharmacie, 2 Reihe, Bd. 72, S. 278.

potassa in a small quantity of water, and add from 600 to 700 grammes of solution of soda of 1·12 sp. gr. Add the first solution gradually to the second, and dilute the deep blue, clear fluid exactly to 1155 c. c.* Every 10 c. c. of this solution contain 0·3463 grm. of sulphate of copper, and correspond exactly to 0·050 grm. of anhydrous grape sugar. Keep the solution in a cool, dark place; before using it, boil 10 c. c. of it for some minutes, by way of trial, with 40 c. c. of water; if this operation produces the least change in the fluid, and causes the separation of even the smallest quantity of suboxide, the solution is unfit for use.

b. Solution of sugar. This must be highly dilute, containing only $\frac{1}{2}$, or, at the most, 1 per cent of sugar. If, therefore, you find, in a first experiment, that the sugar solution is too concentrated, dilute it with a definite quantity of water, and repeat the experiment.

The process.

Put 10 c. c. of the copper solution into a porcelain dish, add 40 c. c. of water, heat to gentle ebullition, and allow the sugar solution to drop slowly and gradually into the fluid, from a burette or pipette, divided into $\frac{1}{5}$° or $\frac{1}{10}$ c. c. After the addition of the first few drops, the fluid shows a greenish-brown tint, owing to the suboxide and hydrated suboxide suspended in the blue solution; in proportion as more of the sugar solution is added, the precipitate becomes more copious, acquires a redder tint, and subsides more speedily. When the precipitate presents a bright red color, remove the lamp, allow the precipitate to subside a little, and give to the dish an inclined position, which will enable you readily to detect the least bluish-green tint. To make quite sure, however, pour a small portion of the clear supernatant fluid into a test tube, add a drop of the sugar solution, and apply heat. If there remains the least trace of salt of copper undecomposed, a yellowish-red precipitate will form, appearing at first like a cloud in the fluid. In that case, pour the contents of the test tube into the dish, and continue adding the solution of sugar until the reaction is complete. The amount used of the solution of sugar contains 0·050 grm. of anhydrous grape sugar. When the operation is terminated, ascertain whether it has fully succeeded, that is, whether the solution really contains neither copper, sugar, nor a brown product of the decomposition of the latter substance. To this end filter off a portion of the fluid still quite hot. This filtrate must be colorless (without the least brownish tinge). Heat a portion of it with a drop of the copper solution; acidify two other portions, and test the one with ferrocyanide of potassium, the other with sulphuretted hydrogen: neither of these tests must produce the slightest alteration. If the fluid contains a perceptible quantity of either oxide of copper or of sugar, this is a proof that too

* *Fehling* dilutes to 1154·4 c. c.; but, as our equivalent for copper slightly differs from his, we make it 1155 c. c.

little or too much of the latter have been added, and the experiment must accordingly be repeated.

The results are constant and very satisfactory.

Second Method.

This requires the same solution as the first. Pour 20 c. c. of the solution of copper and 80 c. c. of water (or a larger quantity of the copper solution diluted with water in the same proportion) into a porcelain dish, add a measured quantity of the dilute sugar solution, but not sufficient to reduce the oxide of copper, and heat for about ten minutes on the water-bath. When the reduction is completed, wash the precipitated suboxide of copper by decantation with boiling water. Pass the decanted fluid through a weighed filter, dried at 212°, lastly place the precipitate also on the filter, dry at 212°, and weigh. Or determine the quantity of the suboxide by *Schwarz's* method (§ 95, 3, *b.*); or ignite the suboxide of copper, with access of air, and then convert it into oxide by treating it with fuming nitric acid.

100 parts of anhydrous grape sugar correspond to 220·5 of oxide of copper,* or 198·2 of suboxide of copper,† or 155·55 of iron converted from the state of sesquichloride to that of protochloride).

In the application of this method, it must be borne in mind that the separated suboxide of copper will gradually redissolve in the supernatant fluid, as soon as this becomes cold, as oxide into which it is reconverted by the oxygen of the atmosphere. Hence the necessity of washing the precipitate by decantation with boiling water.

2. Modification of the preceding methods, and conversion of cane sugar, starch, etc., into grape sugar.

a. The preceding methods may be employed without modification to determine the amount of grape sugar contained in *grape juice, apple juice, and the juices of other fruits,* properly diluted, of course. The same applies also to *diabetic urine.* The other substances contained in the said juices, and in healthy urine, are without action or influence upon the test solution of copper.

b. Vegetable juices of dark color must previously be clarified; this is done by heating a measured quantity of the juice to boiling, and adding a few drops of milk of lime, which usually produces a copious precipitate (of albumen, coloring matter, lime salts, &c.); the fluid is then

* *Fehling* (Annal. d. Chem. und Pharm. Bd. 72, S. 106) obtained, as highest results, 219·4 grammes of oxide of copper.

† *Neubauer* (Archiv der Pharm. 2 Reihe, Bd. 72, S. 278), found in his experiments with starch, that 0·05 of the latter correspond to 0·112 of suboxide of copper. As 90 of starch gives 100 of grape sugar, 0·05 of the former correspond to 0·0555 of the latter. Accordingly 100 of grape sugar gave 201·62 of suboxide of copper, instead of 198·2.

filtered through animal charcoal, the precipitate thoroughly washed, and the washings added to the filtrate, which is then diluted to ten, fifteen, or twenty times its original bulk (*Neubauer*).

c. Cane sugar, or vegetable juices containing cane sugar (the juices of the sugar cane, beetroot, maple, &c.), must first be converted into grape sugar. This is effected by protracted heating with dilute sulphuric acid. Thus, for instance, to prepare beetroot juice for the quantitative estimation of the saccharine matter contained in it, take from 15 to 20 c. c. of the juice treated as directed in *b.*, add twelve drops of dilute sulphuric acid (SO_3, HO+5 water), and boil the mixture from one to two hours, adding water as it evaporates; this operation is conducted best on a water-bath. Neutralise the free acid by means of a dilute solution of carbonate of soda, dilute to ten times the original volume, and examine the fluid as directed in 1.

100 parts of grape sugar ($C_{12}H_{12}O_{12}$) correspond to 95 parts of cane sugar ($C_{12}H_{11}O_{11}$). Accordingly, it takes 0·0475 grm. of cane sugar to decompose 10 c. c. of the copper solution.

d. Starch and *dextrine*, or substances containing either of these bodies, are treated in the same way, but the action of the sulphuric acid is continued much longer than in the conversion of cane sugar into grape sugar. For instance, to convert 1 gramme of starch into grape sugar, proceed as follows: mix the gramme of starch with 10 grammes of water, shake the mixture, apply heat, still shaking, until a paste is formed; add to this 12 drops of dilute sulphuric acid (1 to 5), and apply heat until the fluid becomes thin, boil the fluid now from 6 to 10 hours in an obliquely placed flask on the sand-bath, frequently replacing the evaporated water;* or heat the fluid from 24 to 36 hours in the water-bath. When the conversion into grape sugar is completed, dilute the fluid to 100 or 200 c. c., and proceed as directed in 1. The reaction with tincture of iodine, which has been proposed by several chemists, as a test to ascertain whether the conversion into grape sugar is completed, is not sufficiently reliable. To remove all doubt heat 20 c. c. of the fluid again for several hours, rinse into a measuring tube, dilute to 40 c. c., and proceed again as directed in 1. This second experiment must take exactly double the quantity of solution of copper used in the first; if less is required, this is a proof that an additional quantity of sugar has been formed upon the renewed application of heat.†

* The operation may be greatly facilitated by closing the flask with a perforated cork furnished with a glass tube bent at an obtuse angle, and which leads to a cooling apparatus turned upwards; by this arrangement the evaporating water returns to the flask.

† The complete conversion of starch into sugar may be effected also by making the starch into paste, and digesting this for several hours, at a temperature of from 140° to 158°, with a measured quantity of infusion of malt. If the sugar is now determined in an

100 parts of grape sugar ($C_{12}H_{12}O_{12}$) correspond to 90 parts of starch ($C_{12}H_{10}O_{10}$); or 10 c. c. of the copper solution correspond to 0·045 of starch.

e. Milk sugar reduces a much smaller proportion of oxide of copper than grape sugar; for whilst 1 gramme of the latter decomposes 6·926 of sulphate of copper, 1 part of milk sugar reduces, according to *Neubauer*, 4·331, according to *Mathäi*,* 4·158 parts of oxide of copper; or, in other terms, 10 c. c. of the test solution of copper correspond to 0·08 grm. of milk sugar.

The best way, therefore, to adapt the test solution of copper for the quantitative estimation of milk sugar, is to ascertain in the first place, by means of a solution of milk sugar of known strength, the exact amount to which a given quantity (10 c. c.) of the test solution of copper corresponds.

To determine the milk sugar in milk, the caseine is removed by means of acetic acid, and the whey cleared with a little white of egg and filtered; the filtrate is then mixed with 9 times its volume of water, and the milk sugar determined in the usual way (described in 1), by means of the test solution of copper.

B. Method based upon the decomposition of sugar by alcoholic fermentation.†

§ 211.

1. When a saccharine fluid is exposed, with ferment, or yeast, to the proper temperature, it suffers alcoholic fermentation, in which the elements of one equivalent of anhydrous grape sugar are converted into two equivalents of alcohol and four equivalents of carbonic acid ($C_{12}H_{12}O_{12}$)= $2(C_4H_6O_2 + 4CO_2)$. Accordingly, if the quantity of carbonic acid generated in this way is known, the quantity of sugar decomposed may be calculated from it. 100 parts of anhydrous grape sugar give 51·11 of alcohol and 48·89 of carbonic acid.

2. The carbonic acid escaping in the process is most conveniently determined with the aid of the apparatus illustrated in Fig. 45 (§ 110). The flask A should be rather capacious, B as small as is compatible with the object of the operation. The wax plug on *b* is omitted.

3. The experiment is made with a quantity of the saccharine fluid containing about 2 grammes of anhydrous sugar. If much more is taken, the fermentation lasts too long; if, on the other hand, much less is used, the

equal quantity of infusion of malt, heated for the same time, the difference gives the amount of sugar formed from the starch.

* Archiv der Pharm., 2 Reihe, Bd. 72, S. 293.

† Compare *Krocker* on the quantitative estimation of starch in vegetable aliments, Annal. der Chem. und Pharm., Bd. 58, S. 212.

results are inaccurate, because the quantity of the carbonic acid evolved is in that case too small for correct weighing.

4. As regards the concentration of the fluid, the solution should contain from 4 to 5 parts of water to 1 part of sugar. More highly dilute solutions must therefore be concentrated by evaporation in the water-bath.

5. Pour the sugar solution into the flask A, add a few drops of solution of tartaric acid, and a comparatively large weighed portion of washed yeast (say 20 grammes of fresh, or a corresponding quantity of German yeast.) As yeast generally evolves some carbonic acid from its own constituents, a larger weighed portion of it may be put into another similar apparatus, to determine the carbonic acid evolved from it, which is then calculated for 20 grammes, *i. e.* the quantity used in the fermentation process of the sugar, and the resulting amount deducted from the weight of the carbonic acid obtained in the latter.

6. The apparatus is now accurately weighed, and kept at a pretty constant temperature of 77°. Fermentation soons sets in, and goes on briskly at first, but after a time, more slowly. When no more gas bubbles escape through the sulphuric acid (after 4 or 5 days), the process is terminated. The flask A is now heated, by placing it in a vessel with hot water; it is then taken out, and suction applied to *d*, by means of a perforated cork, to draw out the carbonic acid still lingering in the apparatus; the latter is allowed to cool, and then ultimately weighed again. The loss of weight indicates the amount of carbonic acid which has escaped, and this multiplied by 2·045, gives the corresponding quantity of grape sugar.

7. If it is intended to examine amylaceous substances in this way, the starch in them is converted into grape sugar in the manner directed § 210, 2, *d.*; the fluid is then evaporated in the water-bath to the consistence of syrup, transferred to the flask A, and the free sulphuric acid removed, by adding a highly concentrated solution of neutral tartrate of potassa in sufficient quantity to form sulphate and bitartrate of potassa;)* the fluid is then subjected to the process of fermentation. In the examination of potatoes, from 6 to 8 grammes, in that of the several sorts of flour of the cereals, 3 grammes are used.

* The reaction on litmus paper affords a tolerably safe guide as to the quantity required.

III. ANALYSIS OF THE ASHES OF PLANTS.*

§ 212.

The recent researches and discoveries of agricultural chemistry have fully established the fact, that plants require for their growth and development certain inorganic constituents, which are different for the different classes of plants; the discovery of this fact has created a very natural desire to ascertain *which* inorganic constituents are respectively indispensable for the growth of the several species of plants, and more particularly for that of the cultivated plants, and also for weeds, since the knowledge of the constituents of these latter enables us to infer the nature of the soil in which they grow. This knowledge it was endeavored to attain by the analysis of the ashes remaining upon the combustion of either the entire plants or particular parts of them (the seeds for instance). And, although it is a settled point that perfectly accurate results cannot be so obtained, since the ashes of a plant do not quite truly represent the sum of the inorganic constituents contained in it, still, putting aside a few experiments made in this direction,† we know as yet no better means of obtaining the end in view, and at all events no other means

* As the analysis of the ashes of animal substances is made almost exclusively for the purposes of science, and only rarely for technical purposes, I have omitted in the text a detailed description of it; I will here only remark that the same processes which are given in the text for the incineration of plants and the analysis of the ashes, will equally serve the same purposes for animal substances. Substances which fuse are first heated, according to *H. Rose*, in a platinum dish with stirring, until they have lost their fluidity, and the organic matter is nearly destroyed. The nearly carbonised residue is transferred to a platinum crucible (a common clay crucible will also answer the purpose); the lid is properly closed, and the contents are heated to dull redness. The charcoal obtained is burnt with spongy platinum. *Strecker's* method of incineration which is given in the text, is also well adapted for animal substances. In his paper on the subject (Annal d. Chemie und Pharmacie, 73, 370), he calls attention to the fact that the ashes of animal substances often contain no inconsiderable quantity of cyanates. These salts are destroyed most readily by moistening the ashes with water, and then heating gradually to redness; one moistening usually suffices to convert the cyanates into carbonates. On the subject of the analysis of the ash of animal substances, compare also *F. Verdeil's* paper on the analysis of the ash of the blood of man and several animals (Annal. der Chem. und Pharmacie, 69. 89;—Pharmac. Centralbl., 1849, 198; *Liebig* and *Kopp's* Annual Report, 1849, 367); and *Fr. Keller's* paper on the ash of flesh and broth (Annal der Chem. und Pharmacie, 70, 91;—Pharm. Centrabl., 1849, 581;—*Liebig* and *Kopp's*, Annual Report, 1849, 368).

† *Caillat* states that, by treating grass plants (clover, lucerne, sainfoin) with dilute nitric acid, he succeeded in removing the organic constituents so fully that the readily combustible residuary mass left, upon incineration, for 10 grammes of vegetable used only from 18 to 22 milligrammes of ash consisting of silicic acid and sesquioxide of iron. He states, moreover, that this treatment of the plant gives a larger quantity of the constituents of the ash, more particularly of sulphuric acid, than is obtained by the incineration of the plant. (Compt. rend. XXIX. 137; *Liebig* and *Kopp's* Annual Report, 1849, 418).

equally applicable to the analysis of all vegetable matters. The analysis of the ashes of plants will therefore continue, at least for some time to come, a highly important and interesting branch of analytical chemistry; nay, we may safely presume that this mode of estimating the inorganic constituents of plants will never be abandoned by the agriculturist, since the results which it gives are sufficiently accurate for the purposes of agriculture, though not for those of physiology.

The ashes of plants containing, according to the researches hitherto made, only a limited number of acids and bases, certain widely applicable methods for their analysis have been devised. As these methods present many peculiarities, and are frequently employed, I will here describe those which appear to me the most simple and best adapted for the purpose. A critical discussion of the numerous and essentially different methods proposed would, of course, be out of place in the present work.

The following are the substances generally found in plants:

Bases:

Potassa, soda, lime, magnesia, sesquioxide of iron, sesquioxide of manganese;

Acids and salt-radicals:

Silicic acid, phosphoric acid, sulphuric acid, carbonic acid, chlorine.

Besides these we occasionally find, alumina (which may, however, be regarded as an impurity), fluorine, iodine, bromine, metallic cyanides and cyanates (only in the ashes of bodies abounding in nitrogen), metallic sulphides, and often slight traces of oxide of copper.

Most of these substances were unquestionably constituents of the incinerated plants; as regards some others, it is uncertain whether they were originally present in the vegetable, or whether they owe their formation to the process of incineration; and lastly, some of them, certainly owe their origin entirely to that process. Thus the sulphates and even the carbonates may have been original constituents of the plant; but they also may have been formed in the process of incineration, by the destruction of salts with organic acids, and by the combustion of the sulphur which every plant contains in the unoxidised state; thus the metallic sulphides are formed by the action which the charcoal exercises upon sulphates in the absence of a sufficient supply of air;—thus the metallic cyanides owe their formation to the effect of heat upon nitrogenous charcoal in contact with alkaline carbonates; and the cyanates to the oxidation of the metallic cyanides, &c.

From the variety of these several inorganic substances, and the circumstance that some of them are usually present in very minute quantities only, it is by no means an easy task to devise universally applicable methods; more especially, as it is a great desideratum to unite accuracy with despatch.

The analysis of the ashes of plants is properly divided into four parts, viz. :—

1. The preparation of the ash;
2. The analysis of the ashes;
3. The calculation and statement of the results;
4. The calculation of the percentage proportion which the several ingredients of the ashes respectively bear in the composition of the plant or part of a plant which has furnished them.

A. Preparation of the ash.

§ 213.

In the preparation of the ash for the analytical process, the following conditions must be observed :—

1. The plant or part of a plant to be incinerated, must be free from all adhering impurities.
2. The ash must be as free as possible from unburnt matters.
3. No essential constituents must be lost by the process of incineration.

To satisfy the *first* condition, the plants or parts of plants intended for incineration must be carefully selected and cleaned. It is not always practicable to rub or brush away sand or clay, more especially from small seeds. *H. Rose* gives the following directions for cleaning the latter :

Pour over the seeds in a beaker a moderate quantity of distilled water, stir a few moments with a glass rod, and then place on a sieve with sufficiently wide holes to allow the sand to pass through, whilst retaining the seeds. Repeat this operation several times, but take care never to leave the seeds long in contact with water, otherwise soluble salts might be extracted from them. Finally place the seeds on a linen cloth, and rub them between its folds, which will remove the still adhering fine sand; dry them, to be ready for the process of incineration when required. Seeds cleaned in this manner are almost perfectly free from foreign matters.

For the fulfilment of the *second* and *third* conditions, the principal point to be looked to is that the incineration is effected at the lowest possible temperature (a dull red heat), and with a proper access of air, neither too strong nor too feeble. Too strong a draught is apt to carry away particles of the ash, whilst, on the other hand, with too feeble a draught, the operation lasts too long, and facilities are afforded for processes of reduction to take place. The application of an over-intense heat will cause the fusion of the metallic chlorides and the phosphates of the alkalies, and the fused mass enfolding the carbon will very greatly impede the combustion of the latter; besides, excessive heat may cause the metallic chlorides to volatilise; nay, even phosphoric acid may be lost in this way, since, as *Erdmann* has shown, that acid phosphates of the alkalies, when ignited with carbon, are converted into neutral salts,

with reduction and volatilisation of part of the phosphorus. But, whilst loss of metallic chlorides, phosphoric acid, and sulphuric acid, may be effectually guarded against by properly regulating the heat and the access of air, and, if need be, by mixing baryta or lime with the substance intended for incineration, loss of carbonic acid cannot be avoided. The quantitative estimation of the carbonic acid in the ash will, therefore, never enable us to draw any reliable inference as to the constituents of the incinerated vegetable. It was formerly thought that the presence of carbonates in the ash of a plant containing no carbonates, might be regarded as a proof of the presence of salts with organic acids in the incinerated plant; however, even this assumption has been discovered to rest on error, since, as *Strecker* has shown, alkaline carbonates together with alkaline pyrophosphates are formed when tribasic alkaline phosphates are ignited with a large excess of sugar, or the charcoal of the latter. On the other hand, alkaline pyrophosphates are converted into tribasic phosphates, when strongly ignited in conjunction with alkaline carbonates. With these facts before us, we can readily understand how the detection and estimation of tribasic and bibasic phosphates in an ash may also depend upon the manner in which it has been prepared.

I will now proceed to describe the several methods of incineration.

1. *Incineration in the muffle.*

This method, which was first recommended by *Erdmann*,* and afterwards by *Strecker*,† and which is at present introduced in most laboratories, has almost entirely superseded the old way of burning vegetables substances in hessian crucibles placed in an oblique position.

The muffles which I employ are made of the material of hessian crucibles; they are in internal measurement 28 centimeters long, 11 centimeters wide, and 6 centimeters high. They are placed in furnaces with moveable grates; they have no conducting pipe, and are loosely closed in front with a perforated door. The circulation of air thus created is quite sufficient for the combustion of the charred substance.

The substance which it is intended to incinerate (about 100 grammes) is first dried at 212° or 230°. Succulent roots and fleshy fruits are cut in slices and laid on glass plates. The dried substance is weighed, and then put into a shallow platinum or porcelain dish, or, better still, in a shallow platinum or porcelain capsule, fitting exactly in the muffle; the dish or capsule is introduced into the latter, which is then gradually heated. When the evolution of empyreumatic products ceases, the heat is a little increased, but not beyond a very faint redness not visible in daylight. At this temperature, which is not sufficiently high to fuse either chloride of sodium or pyrophosphate of soda, the carbon burns with feeble incandescence, and 12 hours suffice to produce a quantity of ash free

* Ann. d. Chem. und Pharm., 54, 353. † Ibid, 73, 366

from carbon, sufficient for the purposes of analysis. Substances to which this mode of incineration is unsuited, are charred first at a gentle red heat in a large covered platinum or hessian crucible, and the charred mass is subsequently incinerated in the muffle. As a general rule, the operator had always better refrain from stirring the mass in progress of incineration, since this would tend to diminish the porosity. According to *Strecker*, no chloride of sodium volatilises in this process of incineration.

The ash obtained is weighed, reduced to powder, properly mixed, and kept in a well-stoppered bottle.

2. *Incineration in the dish, with the aid of an artificial current of air.* (*F. Schulze.*)*

Char the organic substance, properly dried at 212° and weighed, in a platinum or hessian crucible, at a gentle red heat, and transfer the charred mass to a shallow platinum dish; put a triangle of platinum wire across the dish, and place on the triangle a common lamp chimney,† which may be secured in position, if desirable, by means of a retort holder. Apply heat by gas or spirit-lamp to the dish. The increased current of air caused by the chimney, and which may be regulated, by taking a longer or shorter one, and placing it higher or lower, suffices to effect the complete incineration, even of the cereal grains, at the temperature of the spirit-lamp.‡) When the incineration is completed, weigh the ash, and proceed as in 1.

3. *Incineration in the muffle, with addition of baryta* (*Strecker*, Annal. der Chem. und Pharm., 73, 366).

Dry the organic substance at 212°, and char it slightly, in a porcelain or platinum dish. Moisten the charred mass with a concentrated solution of pure hydrate of baryta in sufficient quantity to leave after the incineration of the mass, a mixture of about equal parts by weight of ash and baryta. Dry the moistened mass again, and then burn it in the muffle at the lowest possible temperature. The ash is kept from fusion by the baryta; it remains bulky and loose, and thus permits a complete combustion of the carbon.

The residue must still contain a considerable excess of carbonate of baryta. If this is not the case, there is reason to apprehend a loss of sulphur or phosphorus, and it is therefore in that case advisable to incinerate a fresh portion of the vegetable substance with a larger addition of baryta than has been used with the first portion.

Reduce the incinerated residue to a fine powder, mix this intimately, and keep it in a well-stoppered bottle.

* Communicated to me by letter.

† Instead of a chimney a sufficiently wide neck of a retort may be used.

‡ *F. Schulze* employs this method also for the incineration of filters; he places the crucible with the filter in the dish.

4. *Incineration with the aid of spongy platinum* (*H. Rose*).

Char about 100 grammes of the substance, dried at 212°, in a platinum or clay crucible, at a dull red heat; reduce the charred mass to a fine powder by trituration in a porcelain mortar; mix the powder most intimately with from 20 to 30 grammes of spongy platinum; transfer the mixture in portions to a shallow thin platinum dish, and heat over gas or a lamp with double draught. After a short time, and before the mixture is in a state of ignition, every particle of carbon begins to glimmer, and a gray layer speedily covers the surface of the black mixture. By diligent and cautious stirring with a little platinum spatula, the surface is renewed, and the combustion promoted. As long as the mass contains unconsumed carbon, glimmering is observed; but, when the carbon is entirely burnt, all visible incandescence ceases, even though a stronger heat be applied. When the incineration is completed, mix the mass uniformly, dry quickly, and weigh. Deduct from the weight that of the platinum added; the difference expresses the weigbt of the ash.

B. Analysis of the ash.

§ 214.

Before proceeding to the description of the analytical process, I have to remark that of the methods of incineration described in the preceding paragraph, the two first (1 and 2), when properly executed, fully answer the purpose in most cases; as the results obtained are usually inaccurate only in so far as regards carbonic acid and sulphur.* Now the quantitative estimation of the carbonic acid is not more accurate in the other two methods; and the determination of the amount of sulphuric acid in the ash of a vegetable substance is a matter of comparatively little value, as it affords no clue to the sulphur present in the form of sulphuric acid, nor to the total amount of sulphur in the plant. As regards the sulphur, therefore, the safest way is to determine that element in a separate portion of the vegetable substance under examination, in the manner directed § 156.

I have deemed this observation necessary to explain why the analytical process which I am now on the point of describing refers exclusively to ashes prepared by the method 1 or 2, and which accordingly contain no extraneous admixture of baryta or platinum. The modifications which this process may require in cases where the incineration of the vegetable substance has been effected by the method 3 or 4, are only trifling, and such as will readily suggest themselves.

According to their principal constituents, the ashes of plants may be classed under the following heads:

* Compare also *Way* and *Ogston*, *Liebig* and *Kopp's* Annual Report, 1849, 418.

a. Ashes in which *carbonates of the alkalies and alkaline earths* predominate; *e. g.* the ashes of woods, of herbaceous plants, &c.

b. Ashes in which *phosphates of the alkalies and alkaline earths* predominate; to this class belong the ashes of nearly all kinds of seeds.

c. Ashes in which *silicic acid* predominates; *e. g.* those of the stalks of the gramineæ, of the equisetaceæ, &c.

Although it is quite obvious that the limits between the different classes cannot be drawn very strictly, this classification must yet be maintained, in order to impart a certain degree of clearness and simplicity to the analytical methods which I am now going to describe; for the general process requires of course certain modifications according to the class to which the ashes under examination belong.

a. Qualitative analysis.

As the constituents are known which are usually found in the ashes of all plants, a complete qualitative analysis of every kind of ash which may happen to come under the notice of the chemist would be superfluous. A few preliminary experiments suffice to ascertain the presence or absence of the more rarely occurring constituents, and also more particularly to fix the class to which the ash under examination belong. These experiments are as follows:

1. *The ash under examination is heated with concentrated hydrochloric acid, to see whether it is completely decomposed thereby or not.* If the ash strongly effervesces when the acid is poured over it, this may be taken as a proof of its decomposability by that agent. The ashes of the stalks of the gramineæ, &c., which abound in silicic acid, are usually the only kind that resist complete decomposition by hydrochloric acid.

2. If the hydrochloric acid solution of an ash is, after separation of the silicic acid, mixed with an alkaline acetate, or if it is neutralised with ammonia, and free acetic acid is then added, a gelatinous yellowish white precipitate of phosphate of sesquioxide of iron will almost invariably separate. Now, it is necessary to ascertain *whether the ash contains any phosphoric acid besides that in this precipitate*. For this purpose the fluid is filtered from the precipitate, and ammonia in excess added to the filtrate; if this *fails to produce* a precipitate, or if the precipitate produced is red, and consists accordingly of hydrated sequioxide of iron, this is a proof that the ash contains no more phosphoric acid; but if, on the contrary, a white precipitate is formed (phosphate of lime, and phosphate of magnesia and ammonia), this is a positive proof that the ash contains more phosphoric acid than is combined with the sesquioxide of iron present, and is consequently to be classed under the second head.

3. *The ash is tested for manganese*, by mixing a small portion

with carbonate of soda, and exposing the mixture on platinum foil to the outer flame of the blowpipe. (Compare "Elementary instruction in Qualitative Analysis.")

4. The ash is tested for iodine, bromine, fluorine, and other occasional ingredients of vegetable ashes, if it is desirable to ascertain whether traces of them are present. (Compare "Elementary instruction in Qualitative Analysis.")

b. Quantitative analysis.

I. *Ashes in which the carbonates of the alkalies or alkaline earths predominate, and in which the whole of the phosphoric acid present is combined with sesquioxide of iron.*

§ 215.

The ash is divided into three portions, which we will call A, B, and C.

In C we determine the carbonic acid.*

In B the chlorine.

In A the remaining constituents.

A.

1. DETERMINATION OF THE SILICIC ACID, CHARCOAL, AND SAND.

From four to five grammes of the ash are introduced into a flask, and concentrated hydrochloric acid is now added, the flask being held in an oblique position, to preclude the carrying away of small quantities of the fluid by the evolved carbonic acid; a gentle heat is then applied until no more undecomposed ash is visible, with the exception of the carbonaceous and sandy particles which are almost invariably present, and may be readily distinguished. The solution is now carefully transferred to a porcelain dish, and evaporated to dryness on the water-bath; the residue is then heated, with frequent stirring, until all the lumps have crumbled to pieces; the temperature in this process must not be raised above 212° (compare § 111. II. *a.*). If the ash effervesces only feebly when treated with hydrochloric acid, the operator need not use the flask at the commencement of the process, but he may conduct the operation at once in the porcelain dish, taking care simply to cover the latter with a glass plate.

The dry residue is, after cooling, moistened with concentrated hydrochloric acid, which is allowed to act upon it for the space of about thirty minutes; the mass is then heated with a proper quantity of water, to inci-

* The estimation of the carbonic acid, though, as we have seen above, of no great value in itself, is yet necessary to complete the analysis, and thus to supply a certain control.

pient ebullition, and the acid fluid afterwards passed through a tared filter, made of strong paper and dried at 212°.

The silicic acid remains upon the filter, mixed with charcoal and sand, if the ash contains the latter substances. The mass upon the filter is thoroughly washed, carefully dried, and subsequently transferred from the filter to a platinum dish, without injuring the filter. If the powder is perfectly dry, this may be readily accomplished, a few particles of charcoal alone adhering to and coloring the paper. The powder is now boiled for half an hour with a dilute solution of pure soda (free from silicic acid), or with a concentrated solution of carbonate of soda, which gradually effects the total solution of the silicic acid without affecting the sand or charcoal that may be present. The fluid is passed through the same filter as before, and the undissolved residue thoroughly washed and then dried with the filter at 212° until the weight remains constant. The weight of the filter is deducted from that of the residue, which is entered in the calculation of the results as *charcoal* and *sand*.

The filtrate is supersaturated with hydrochloric acid, and the *silicic acid* in it determined as directed § 111, II. *a*.

2. DETERMINATION OF ALL THE REMAINING CONSTITUENTS, WITH THE EXCEPTION OF CHLORINE AND CARBONIC ACID.

The hydrochloric acid solution filtered from the undissolved silicic acid, charcoal, and sand, is most intimately mixed with the rinsing water; the fluid is then divided, by weight or measure, into three, or better still, four parts, since this will leave one part for unforeseen accidents. The best way of proceeding is to filter the fluid into a measuring flask holding 200 c. c., and to fill this up to the mark with the washing water and with pure water, and then to measure off with a pipette three equal portions of 50 c. c. each (the fourth portion being kept in the flask). We will call these three portions respectively *a*. *b*. and *c*.

In *a*. we determine phosphate of sesquioxide of iron, and the alkaline earths, and also the free sesquioxide of iron and the manganese which may be present.

In *b*. the alkalies.

In *c*. the sulphuric acid.

a. Determination of the phosphate of sesquioxide of iron, &c., and of the alkaline earths.

Mix the fluid with ammonia until a persistent precipitate is formed, add acetate of ammonia and a sufficient quantity of free acetic acid to impart a distinctly acid reaction to the fluid; application of a gentle heat will promote the separation of the yellowish-white precipitate, which consists of *phosphate of sesquioxide of iron* ($3\,PO_5$, $2\,Fe_2O_3$, $3\,HO+10$ aq). Filter the fluid from the precipitate, wash the latter with hot water, dry,

ignite, and weigh. Calculate this as phosphate of sesquioxide of iron. The formula of the ignited precipitate is $3\,PO_5$, $2\,Fe_2O_3$, (compare § 72, 4, *c.*).

Saturate the filtrate with ammonia and determine the *lime* and *magnesia* as directed § 122, B. 3. However, should a precipitate of hydrate of sesquioxide of iron form upon the addition of ammonia to the filtrate, this precipitate must first be filtered off and determined; and should the filtrate contain an appreciable quantity of manganese, either alone or with iron, this must first be removed by precipitation with sulphide of ammonium before the estimation of the alkaline earths can be effected. The precipitated sulphide of manganese, if pure, is treated according to § 86, *c.*; if containing iron, according to § 128.

b. Determination of the alkalies.

Evaporate the fluid *b.* on the water-bath until the greater part of the free acid is removed; add baryta-water until the reaction is strongly alkaline; heat, and then filter. This process serves to remove the whole of the sulphuric acid, phosphoric acid, sesquioxide of iron, and magnesia. Wash the precipitate until the last washings produce no longer the least turbidity in solution of nitrate of silver; remove the excess of baryta from the filtrate by means of carbonate of ammonia mixed with ammonia; let the baryta precipitate subside, and filter the fluid; evaporate the filtrate to dryness in a platinum dish, and ignite the residue; redissolve and precipitate again and, if necessary, a third time, with ammonia and carbonate of ammonia.* Evaporate the last filtrate to dryness, ignite the residuary alkaline chlorides gently, weigh, and separate the *soda* and *potassa* as directed § 120, 1, *a.*

N.B. The estimations *a.* and *b.* may also be made with the same portion of the fluid, in which case the phosphate of the sesquioxide of iron is precipitated as directed in *a.* and the filtrate treated exactly as directed § 177, 4, *b.* This method may be resorted to, more especially if the quantity of ash is small.

c. Determination of the sulphuric acid.

Precipitate the fluid *c.* with chloride of barium, and determine the precipitated sulphate of baryta according to the directions of § 105.

B.

DETERMINATION OF THE CHLORINE.

Weigh off a second portion of the ash (from one to two grammes), and treat this with hot water; filter, acidify the filtrate with nitric acid, precipitate with nitrate of silver, and determine the precipitated chloride of silver according to the instructions given in § 112, I. *a.*

* In fact, until the solution of the gently ignited residue is no longer rendered turbid by ammonia and carbonate of ammonia.

C.

DETERMINATION OF THE CARBONIC ACID.

The carbonic acid is determined in a third portion of the ash, according to the directions of § 110, II. *b.* β. (The quantity of ash to be used for this purpose, depends upon the greater or less proportion of carbonic acid which it may contain.)

II. *Ashes decomposable by hydrochloric acid, which contain an additional amount of phosphoric acid, besides that which is combined with sesquioxide of iron.*

§ 216.

The general process is the same as described in I. (§ 215); it requires certain modifications only as regards A. 2, *a.*

When you have thrown down the phosphate of sesquioxide of iron, take care that the phosphate of lime which may have precipitated in conjunction with the iron salt, be completely redissolved by acetic acid; then precipitate the lime from the acid filtrate by means of oxalate of ammonia (§ 81, 2, *b.* β.). Divide the filtrate into two equal parts, and determine in one portion the magnesia, by addition of ammonia and phosphate of soda, in the other the phosphoric acid, by addition of ammonia and solution of sulphate of magnesia mixed with chloride of ammonium. If the phosphoric acid existed in the ash as bibasic salts, the safest manner is to evaporate the portion intended for the estimation of the phosphoric acid, ultimately in a platinum dish, to fuse the residue with carbonate of soda, to dissolve the fused mass in water, and then to determine the phosphoric acid in the solution by addition of ammonia and solution of sulphate of magnesia mixed with chloride of ammonium.

If the ash contain an appreciable quantity of manganese, this simple method cannot well be employed, as the manganese would precipitate partly with the lime, partly with the magnesia. The fluid filtered from the phosphate of sesquioxide of iron (and which still contains alkaline acetate) is, therefore, in such cases, mixed with sesquichloride of iron, until it appears distinctly red, from the acetate of sesquichloride of iron formed; the mixture is boiled for some time, and filtered hot. By this operation, all the phosphoric acid is thrown down, and the maganese, lime, and magnesia, are obtained in solution as chlorides. They are separated as directed § 127. If the precipitate of sulphide of manganese contains iron, as is usually the case, the manganese is separated from the iron as directed § 128.

N.B. If you have only a limited quantity of ash, you may also divide the hydrochloric acid solution of the portion A. into two parts only, *a.* and *b.* Treat *a.* as just now directed; mix *b.* with solution of chloride of

barium in the least possible excess, and determine the sulphuric acid; precipitate the phosphoric acid as directed § 106, I. *c.* γ. (using acetate of ammonia instead of acetate of soda), and determine the alkalies in the filtrate, after previous expulsion of the ammonia salts, and precipitation, first of the magnesia, by means of some milk of lime, then of the lime and baryta, by means of ammonia and carbonate of ammonia. If the basic phosphate of sesquioxide of iron is weighed, this determination may serve to control the one in *a*.

III. *Ashes not decomposable by hydrochloric acid.*

§ 217.

The carbonic acid, which, however, is rarely found in ashes of this class, is determined according to the directions of § 215. The same applies to chlorine. The estimation of the other constituents demands a preliminary decomposition of the ash; this may be effected in several ways, as follows:—

1. Evaporate the ash with pure solution of soda to dryness, in a platinum or silver dish. (The results of many experiments have shown that by this operation the silicates in the ash are completely decomposed, whilst the sand which may be mixed with the ash is left untouched, or, at least, nearly so. The heat must not be raised in the last stage of the process sufficiently high to fuse the mass.) Pour dilute hydrochloric acid over the residue, evaporate, treat again with hydrochloric acid, and proceed with the insoluble residue (silica, charcoal, and sand), as directed in § 215, A. 1; with the solution as directed in § 215, A. 2. The alkalies cannot, of course, be determined in the solution; they are estimated in a separate portion of the ash, which for that purpose is decomposed either by hydrofluoric acid, or by fusion with hydrate of baryta (*Fresenius* and *Will*).

2. *Way* and *Ogston** mix the ash with an equal weight of nitrate of baryta, and fuse the mixture gradually in a large platinum crucible (transferring it to the crucible in small portions at a time). By this process the ash is fully prepared for decomposition by hydrochloric acid, and the charcoal which it may contain is completely destroyed, leaving the ash perfectly white. The silicic acid is separated according to the directions given in § 215, A. 1, and the sulphate of baryta which may be present determined. Of the hydrochloric acid solution, *Way* and *Ogston* use a portion for the estimation of the alkalies, by the method described in § 215, A. 2, *b.*; the remainder they precipitate with sulphuric acid

* Journal of the Royal Agricultural Society, VIII., Part 1.—*Liebig* and *Kopp's* Annual Report, 1849, 600.

slightly in excess.* The filtrate they divide into two portions, determining in one the phosphate of sesquioxide of iron, the lime and the magnesia (§ 216), and in the other the phosphoric acid as directed § 106, I. *c.* γ.

C. Calculation and statement of the results.

§ 218.

It is only recently that chemists have begun to turn their attention seriously to the analysis of the ashes of plants, for the benefit of vegetable physiology and agriculture. The questions which it is intended to solve by the analysis of the ashes of plants, are principally the following:

1. Do plants absolutely require certain quantities of certain constituents? and if so, *what* are these constituents?

2. May some of these inorganic constituents be replaced by others?

3. Has every plant a definite capacity of saturation, that is, in other terms, is the amount of oxygen contained in the bases present invariably the same?

It is quite obvious that a proper and perfectly satisfactory solution of these questions can be expected only from the results of an exceedingly large number of analyses, and that a great many chemists must contribute towards such a solution.

Under these circumstances, it is of the utmost importance that the results of all analyses of vegetable ashes should be invariably arranged and reported in a uniform manner, so that they may be compared readily and without recalculation.

As the manner in which the bases and acids found were originally combined in the plant cannot be inferred from the ash with any degree of certainty, and since, moreover, as I have already had occasion to state, the ashes differ as regards the phosphates, &c., according to the degree of heat employed,—it is unquestionably the most judicious way to enumerate the percentage of the bases and acids separately. The chlorine, however, is put down as chloride of sodium, and, should the quantity of soda present be insufficient, as chloride of potassium; the proportion of sodium contained in the chloride is calculated as soda, and the calculated weight subtracted from the total amount of soda found; since, otherwise, a surplus would be invariably obtained in the analysis, as the chloride of sodium originally present in the ash would be reckoned as chlorine and *soda*, instead of chlorine and *sodium*. The manganese which may be

* As the quantity of nitrate of baryta used is known, an excess over the calculated weight of sulphate of baryta shows that lime has been thrown down together with the baryta; the quantity of sulphate of lime so thrown down is calculated from the excess of the weight of the precipitate.

present is entered as protosesquioxide, since it exists in that form in the ash.

The following analysis of the ash of beech seeds, by *Souchay*, may serve as an illustration:

Potassa	18·13
Soda	7·55
Lime	19·47
Magnesia	9·25
Sesquioxide of iron	2·12
Protosesquioxide of manganese	2·47
Phosphoric acid	16·53
Sulphuric acid	1·75
Chloride of sodium	0·69
Silica	1·49
Carbonic acid	9·11
Charcoal and sand	9·39
	97·95

It is evident, however, that a report of this kind is not sufficiently precise for an accurate comparison of the results with those of another analysis, as we find here enumerated near twenty per cent of substances which are altogether immaterial, viz., carbonic acid, charcoal, and sand. The proportion in which these substances are present in the ashes of plants, nay, it may even be said, their very presence, depends altogether upon accidental circumstances, such as the greater or less care with which the vegetable substances are cleaned previously to incineration, the degree of heat employed, and the longer or shorter duration of the process of ignition.

To render the comparison of the results obtained in several analyses practicable, it is necessary to strike out the unessential constituents, viz: carbonic acid, sand, and charcoal, and to calculate the remaining constituents in percentage parts.

With this correction the results given above, may now be entered as follows:

Potassa	22·82
Soda	9·50
Lime	24·50
Magnesia	11·64
Sesquioxide of iron	2·67
Protosesquioxide of manganese	3·11

Phosphoric acid	20·81
Sulphuric acid	2·20
Chloride of sodium	0·87
Silica	1·88
	100·00

To satisfy all demands, it is best to state the results both ways; the first statement will enable chemists to judge of the degree of accuracy of the analysis, the second will facilitate comparisons. To render his report still more complete, the analyst may also calculate the total amount of oxygen in the several bases.

D. Calculation of the percentage proportion which the several constituents of the ash bear in the composition of the plant, or part of a plant which has furnished it.

§ 219.

The usual way formerly was to incinerate, with proper caution, a small weighed portion of the carefully dried vegetable substance, and to determine the total amount of the ash; and then to incinerate a larger unweighed portion, less carefully dried, and to analyse the ash obtained. A simple calculation then sufficed to find the percentage proportions of the several constituents. For instance grains of wheat left upon incineration 3 per cent of ash, and the ash contained 50 per cent of phosphoric acid: 100 parts of grains of wheat were therefore assumed to contain 1·5 per cent of phosphoric acid; and so for the other ingredients.

This method is unquestionably most convenient; but, unfortunately, it does not give sufficiently accurate results in all cases, since, from the causes stated in § 213, the total amount of the ash is by no means constant, but varies more or less within certain limits, according to the manner, intensity, and duration of the process of ignition. As we can, therefore, in most cases, never be sure that the smaller portion obtained in the determination of the total weight of the ash, corresponds exactly in composition, &c., with the larger portion used in the actual analysis, it is always the safer plan to weigh as I have already recommended in § 213, 1, on the one hand, the total quantity of the (dried) substance intended for incineration and, on the other hand, the total amount of ash obtained and intended for analysis.

If you wish to avoid this, you may also attain the end in view in another manner, viz., by incinerating, a large unweighed portion of the vegetable substance, analysing the ash, and determining thus the relative proportions between the several ingredients; then incinerating a smaller

weighed portion, dried at 212° and determining in the ash one of those ingredients which are not liable to the least change in quantity from the mode of incineration, *lime*, for instance. As both the relative quantity of this substance in the composition of the plant, and the proportion between it and the other ingredients of the ash, are known, it is easy to calculate from these data the percentage proportion also which the other ingredients of the ash bear in the composition of the plant.

IV. ANALYSIS OF SOILS.*

§ 220.

The proposition being fully established that every plant requires for its growth and development certain inorganic matters which are supplied by the soil in which it grows, it is self-evident that the knowledge of the composition of the soil must be a subject of paramount importance to the practical farmer, to enable him both to judge to what kind of plants a given soil will afford the requisite nutriment, and to adapt a soil for the cultivation of a certain plant, by a proper supply of the necessary manure.

But as plants can absorb by their roots substances in a state of solution only, it is not sufficient for their growth and proper development that the ingredients should be present in the soil; but it is necessary, moreover, that they should be present in a form admitting of their absorption. If therefore, the analysis of a soil is to enable the agriculturist to judge of its suitableness for the cultivation of a certain plant, it must inform him not only of the nature of the constituents of the soil, but also of the form, or state in which these constituents are present.

In this sense the inorganic constituents of the soil may be ranged under three heads:

1. Substances which dissolve in water.
2. Substances which, though not dissolving in water, dissolve in dilute acids.
3. Substances which dissolve neither in water nor in dilute acids.

The substances belonging to the first class are supplied directly to the

* I cannot begin this chapter without expressing my warmest thanks to Professor *Otto* for the great benefit which I have derived from his excellent paper on the analysis of soils, in *Sprengel's* Bodenkunde.

plants with the water which they absorb from the soil. The absorption of the substances of the second class is somewhat more difficult, since these are rendered soluble only by the agency of carbonic acid, and of the acid products of decaying organic matters (acids of humus). The substances belonging to the third class require a thorough modification, before they can exercise any influence upon the development of plants; and this they suffer slowly and gradually by progressive disintegration, and decomposition.

The substances which are soluble in water serve therefore for immediate use, whilst those soluble in acids, though exercising a more permanent action, are rendered efficient only by the presence of decaying organic matters; and those, lastly, which are insoluble both in water and dilute acids, afford a prospect of future nourishment, although their nutritive properties are unavailable for the present.

But, besides the inorganic constituents, there are found in most, in fact nearly in all soils, organic substances (vegetable and animal remains, and the products of their decomposition). That these organic substances exercise a material influence on the fertility of the soil, is unquestionable; and, whatever views may be entertained as to the manner of this influence, this much is certain, that it is highly important to obtain a knowledge of the kind and nature of the organic constituents contained in a soil, and of their quantity.

Having thus briefly designated the object which we wish to attain by the analysis of soils, I will now proceed to point out the proper way to attain this object in a simple and satisfactory manner, treating, in the first place, of the analytical process, and in the second place, of the mode of arranging and stating the results obtained. To enter into a minute investigation into the physical and mineralogical condition of soils,* or to draw from the analytical results conclusions for the practical purposes of agriculture, would clearly be altogether beside the purpose of the present work.

The quantitative analysis of a soil is of course always preceded by a qualitative examination. For the processes of the latter I refer to my work on Qualitative Analysis, eighth edition, § 203.

* Ample information on the subject of the physical and mineralogical conditions of soils may be found in *Fr. Schulze's* paper, "Anleitung zur Untersuchung der Ackererden auf ihre wichtigsten physikalischen Eigenschaften und Bestandtheile."—Journal f. prakt. Chem. Bd. 47, 241.

A. The analytical process.

§ 221.

The soil is dried in the air, and then mixed as uniformly as practicable, but not triturated. The processes *a.*, *b.*, and *c.*, are commenced simultaneously, and a portion of the soil is kept in a stoppered bottle to enable the analyst to repeat, if necessary, either of the analytical processes.

a. Determination of the water.

Dry 10 grammes of the soil in the water-bath until the weight remains constant, and determine the loss. (The dried soil is kept for the process *g.*)

b. Determination of the constituents soluble in water.

Prepare an aqueous extract of the soil, either strictly according to the directions of § 204 of *Fresenius's* Qualitative Analysis, or in the following somewhat modified manner,* which requires the use of a three-necked *Woulf's* bottle, provided also with a lateral tubulated orifice in the lower part. A wide glass cylinder open at the top and narrowing towards the lower end (a percolator,) and which holds about 1000 grammes of soil, fits air-tight into the middle neck. Push down into the narrow part of the percolator a loose plug of sponge, spread over this a layer of pure sifted gravel, and cover the latter again with a thick layer of washed fine sand introduce now the portion of the soil intended for the process. Fit a tube connected with a hand air-pump into one of the other two necks, and close the third neck and the lower opening. Moisten the soil with water, pouring on from time to time a fresh quantity, and continuing in this way for 24 hours; then rarify the air in the bottle by means of the hand-pump, which will force the water charged with the soluble parts of the soil more rapidly from the percolator into the bottle. When the latter is nearly full remove the stopper from the third neck, place a vessel under the lower opening to receive the fluid, and then remove the stopper.† The solution so obtained is perfectly clear; the process of extracting may be continued at pleasure, if the layers of gravel and sand are properly disposed.

When the soil ceases to yield to the water a perceptible quantity of soluble matter,‡ measure or weigh the aqueous extract obtained, and

* Professor *Fr. Schulze*—communicated to me by letter.

† If your *Woulf's* bottle is not provided with a lower opening, you must remove the fluid from it with the aid of a syphon.

‡ Total extraction can hardly ever be effected, and least so in the case of soil containing gypsum.

divide it into three parts, α, β, and γ; let the first portion be one-half, the two latter one quarter each.

Evaporate α in a platinum dish, dry the residue at 212°, until it ceases to lose weight, and weigh. Enter this as the *total amount of the constituents soluble in water.* Ignite the residue gently for some time, and weigh again. Put down the loss as *organic substances, nitric acid,* and *ammonia,* if the qualitative analysis has revealed the presence of these bodies.*

Pour a little hydrochloric acid over the residue, evaporate to dryness, redissolve in hydrochloric acid and water, and filter. On the filter remains the *silicic acid,* mixed often with some charcoal, which, however, is destroyed upon ignition.† Mix the filtrate with chlorine water, and add ammonia. If a precipitate forms, this may contain *sesquioxide of iron, sesquioxide of manganese, phosphoric acid,* and, according to circumstances, also *lime* and *magnesia.* Filter, dissolve the precipitate in hydrochloric acid, and, if the quantity of the precipitate was sufficiently large to permit it, separate the sesquioxide of iron, sesquioxide of manganese, &c., by the methods given in § 215 or § 216. The filtrate usually contains still some lime and magnesia, in which case it no longer contains phosphoric acid and is treated as directed § 177, 4, *b.*, to determine the *lime, magnesia, soda,* and *potassa.*

If the filtrate contains no alkaline earths, but *phosphoric acid* in combination with alkalies, treat it as directed § 106, II. *a.*

In β determine the *sulphuric acid* and *chlorine* (§ 135, *b.* 1).

In γ determine the *carbonic acid* which may be present, by evaporating the fluid down to a small bulk, and treating this (the fluid together with the precipitate) as directed § 110, II. *b.* β. If the qualitative analysis has shown the presence of alkaline carbonates in the aqueous extract, it may be necessary to determine the carbonic acid separately in the precipitate and in the fluid.

c. Determination of the constituents soluble in dilute hydrochloric acid.

Treat 25 grammes of the air-dried soil with water in the manner described in the qualitative analysis (preparation of the aqueous extract); transfer to a porcelain dish, and add water until the mass has the consistence of a thin paste; add hydrochloric acid gradually in proper excess (if effervescence ensues, in small portions at a time). Heat it for

* If considerable quantities of salts of ammonia are present, the ammonia is determined in a separate portion of the aqueous extract, in the same way as in a mineral water (see § 177, 8).

† If the aqueous extract was not quite clear, the silicic acid obtained in the process above described is mixed with clay, from which it must be separated by boiling with solution of carbonate of soda.

from one to two hours on the water-bath, filter,* and wash until the water running off has lost, or nearly so, all acid reaction; add the washings of the filtrate, measure the whole fluid, and divide it into five portions.†

Determine in 1 the *sulphuric acid* as directed § 105.

In 2 the *phosphoric acid* according to the directions of § 106, I. *b*. β.

In 3 the *protoxide of iron*‡ according to the directions of § 89, 2, *a*.

In 4 the *total amount of the iron*, according to § 206.

Evaporate 5, with addition of some nitric acid, to dryness, and separate the *silicic acid* (§ 111, II. *a*.); mix the hydrochloric acid solution with chlorine water, then add ammonia, filter, wash the precipitate, and dissolve in hydrochloric acid; add again chlorine water, and then precipitate with a solution of bicarbonate of soda. Wash the precipitate, dry, ignite, and weigh: it contains all the *iron*, in the form of sesquioxide, all the *alumina*, all the *manganese*, in the form of protosesquioxide, and all the phosphoric acid. If you deduct from this weight the joint weight of the sesquioxide of iron and the phosphoric acid, as determined respectively in 2 and 4, you learn the collective weight of the alumina and the protosesquioxide of manganese; and by determining either the former as directed § 128, B. 1, or the latter as directed § 128, B. 10, *c*., you learn the separate weight of each.

In the fluid filtered from the precipitate produced by ammonia, determine the lime, the magnesia, and the alkalies, as directed § 177, 4, *b*. If the fluid filtered from the precipitate produced by bicarbonate of soda contains still traces oflime and magnesia, determine them separately and add to the principal quantities.

A weighed portion of the residuary soil remaining after the treatment with water (see *b*.) is treated according to the directions of § 110, II. *b*. β., to determine the *carbonic acid* contained in the insoluble carbonates in the soil.

d. Determination of those constituents which are insoluble both in water and dilute acids.

Dry the residuary soil left after the treatment with hydrochloric acid (see *c*.); sift the stones from the clay and sand, and treat the mixture of the two latter bodies as directed § 201 or, according to circumstances, § 202.

e. Determination of the acids of humus (ulmic acid, humic acid, geïc acid).

* The best way is to transfer first the large fragments of the undissolved sediment to the filter, and then pour the fluid upon it, otherwise the minute particles suspended in the latter might tend to stop up the pores of the filter.

† If the earth contains organic matters in somewhat considerable quantity, the 25 grammes extracted with water are, previously to the treatment with hydrochloric acid, gently ignited with access of air, until the organic matter is completely destroyed.

‡ This experiment can be made only if the earth has not been ignited previously to the treatment with hydrochloric acid.

Digest from 10 to 100 grammes of the earth (according as the qualitative analysis has shown the presence of a smaller or greater quantity of the acids of humus) for several hours, at from 176° to 194° with a solution of carbonate of soda; filter. Mix the filtrate with hydrochloric acid to slightly acid reaction; the acids of humus will separate in the form of brown flakes. Collect these flakes on a weighed filter, wash until the water begins to appear colored; dry, and weigh. Burn the dry mass, deduct the weight of the ash (after subtracting the filter ash) from that of the dry mass, and put the difference down in the calculation as *acids of humus*.

f. Estimation of the so-called humus coal (*ulmine* and *humine*).

Boil a quantity of the earth equal to that taken in *e.*, in a porcelain dish, for several hours with solution of potassa, replacing the evaporating water from time to time. Dilute, filter,* and wash. Determine the total amount of the acids of humus present in the same manner as in *e.* The difference between the weights obtained respectively in *e.* and *f.*, expresses the quantity of humic acid which has been formed from the ulmine or humine by the process of boiling with potassa; enter it in the calculation as *humus coal.*

g. Determination of the organic matter which has not as yet suffered conversion into humic acid, humus coal, or similar products.

Heat the residuary dry soil left in *a.* (and which corresponds to ten grammes of fresh soil) in a platinum dish, until all organic substances are destroyed; moisten the residue with solution of carbonate of ammonia, evaporate, ignite very gently, and weigh. The loss of weight suffered in the process expresses the total amount of organic matter present in the soil; deduct from this the collective weight of *e.* and *f.* (the humus acids and humus coal), and put the difference down in the calculation as *organic matters.* It is evident that this method of determining the latter cannot give very accurate results, since, of course, the water which the dry earth yields upon ignition goes to swell the apparent quantity of the organic matters. The safer way therefore is, in cases demanding a higher degree of accuracy, to determine the carbon in the soil by the method of organic elementary analysis, in which case either the carbonic acid found in the form of carbonates is deducted from the total amount of carbonic acid obtained, or the carbonates are first completely removed from the earth by treating with dilute hydrochloric acid and thorough washing,† before the combus-

* If the quantity of the humus coal is very considerable, the fluid alone is poured on the filter at first, and the sediment boiled once more with solution of potassa, before it is transferred to the filter.

† The quantity of organic substance dissolved in this process is mostly so trifling that it may safely be disregarded.

tion with oxide of copper is proceeded with. As the oxide of copper need not be very carefully dried, and as the determination of the water is omitted, the process is much simpler than an ordinary elementary analysis. According to *Fr. Schulze*, every 58 parts of carbon correspond on an average to 100 parts of organic matter in the soil, and every 60 parts of carbon to 100 parts of humus substances. *Schulze* determines the carbon in a soil by fusing the earth, freed, if necessary, from carbonates, with bichromate of potassa in excess in a retort, collecting the carbonic acid evolved over water with some oil floating on the surface, and measuring it.

h. Determination of the nitrogen in a soil.

This is effected in strict accordance with the directions of § 155 (determination of nitrogen). The quantity of soil to be subjected to the analytical process depends upon the greater or less proportion of nitrogen present. The weight of the nitrogen being included already in the results of *g.*, it is not enumerated separately in the list.

i. Determination of waxy and resinous substances.

Waxy and resinous substances are found in appreciable quantities in some kinds of soil only. Their determination may be effected in the following manner: dry 100 grammes of the soil in the water-bath, boil repeatedly with strong alcohol, collect the filtrates in a flask, and distil half of the alcohol off. Let the mixture cool, which will cause the wax to separate. Collect this on a weighed filter, wash with cold spirits of wine, and determine the weight. Evaporate the filtrate (in the last stage of the process with addition of water), until the alcohol is completely removed; wash the separated resin with water, dry, and weigh. If the quantity of wax and resin is any way considerable, it must be deducted from the weight of the acids of humus, as the latter have been weighed with the waxy and resinous ingredients.

3. Method of arranging the results.

§ 222.

With respect to the mode of arranging the results of analyses of soils, the following three points seem to me deserving of particular attention.

a. The results of different analyses must readily admit of comparison.

b. They must admit, also, of ready comparison with the results of analyses of vegetable ashes.

c. They should give as perfect and accurate a notion as possible of the nature of the analysed soil.

That any one single method of arranging the results should equally satisfy all these requirements cannot reasonably be expected, three differently arranged statements are required to meet the exigencies of the

case. The additional labor which this may be thought to impose upon the analyst is but trifling in comparison with that bestowed upon the analysis itself, and surely ought not to be considered in comparison with the great advantages to chemical science, which may be expected to accrue from a full and universally intelligible report of the results of all important investigations.

I would therefore propose the following three methods of arranging the results.

I. Soil dried at 212° (direct results).

A. *Inorganic constituents.*

a. Soluble in water.

Potassa.
Soda.
Lime.
Sulphuric acid.
&c.

b. Soluble in dilute hydrochloric acid:

Sesquioxide of iron.
Sesquioxide of manganese.
Alumina.
Lime.
Carbonic acid.
Phosphoric acid.
&c.

c. Insoluble in water and in dilute hydrochloric acid:

Silicic acid.
Lime.
Alumina.
&c.

B. *Organic constituents.*

Humic acids
Humus coal
Other organic matters.

} containing {

Carbon
Nitrogen (inclusive of that which is present in form of ammonia or nitric acid.

II. Soil dried at 212° (calculated results.)*

A. *Inorganic constituents.*

a. Soluble in water:

* The acids and bases are to be associated here according to their relative forces of affinity. Phosphoric acid, silicic acid, and humic, (ulmic, geïc) acid, however, and the bases with which they are assumed to be in combination, are to be entered separately, as we are without sufficiently fixed and definite data respecting the combining proportions of these acids.

Sulphate of lime.
Chloride of potassium.
Chloride of sodium.
Nitrate of magnesia.
&c.

b. Soluble in dilute hydrochloric acid :
Carbonate of lime.
Lime (combined with silicic acid).
Sesquioxide of iron (combined with silicic acid and phosphoric acid).
Phosphoric acid.
Silicic acid.
&c.

c. Insoluble in water and dilute hydrochloric acid :
Lime, Alumina } (combined with silicic acid.)
Silicic acid.
&c.

B. *Organic constituents.*

Humic acids, &c., as above.

III. Air-dried soil.

Soil dried at 212° (say, for instance) . . .	90
Water	10
	100

If the analyst wish to make the last statement more precise, he may determine, by a separate experiment, the quantity of the minute insoluble particles of the soil which may be washed off, and state likewise the results of the microscopic mineralogical examination of the sandy residue; in which case the report would, for instance, run as follows :

Matter removable by elutriation . . .	10
Quarz-sand, detritus of felspar, mica, &c. .	80
Water	10
	100

If the analyst thinks he can dispense with the advantages resulting from a more precise knowledge of the forms and states in which the various constituents exist in the soil, he may save himself much time and labor, by dividing all the ingredients into two classes only, viz., *constituents soluble in water or dilute acids*, and *constituents insoluble both in water and in*

dilute acids; and treating the earth accordingly at once with dilute hydrochloric acid and determining the constituents of the solution by the preceding methods.

V. ANALYSIS OF MANURES.

§ 223.

I SPEAK here simply of the manures supplied by the urine and the excrements of animals. The examination of manures has chiefly a practical object, and demands accordingly simple methods. The value of a manure depends upon the nature and condition of its constituents, of which the following are the most important: organic matters (characterised by their carbon and nitrogen, salts of ammonia, nitrates, phosphates, sulphates, silicates, and chlorides of alkalies or alkaline earths, of potassa, soda, lime, magnesia). Respecting the condition in which the ingredients of manures may be deemed to exercise the most effective and favourable action on the soil, our views are much less clear: and indeed it is obvious that a universally applicable and valid decision cannot well be given in this respect; since the agriculturist sometimes wishes a manure containing most of its constituents in a state of solution, and which will accordingly exercise a speedy fertilising action,* and sometimes a manure which will only gradually supply the soil with the substances required by the plants.

I will here give 1, the outlines of a general method of examining manures, and 2, a method of analysing guano.

A. ANALYSIS OF MANURES IN GENERAL.

§ 224.

Mix the manure uniformly by chopping and crumbling it, and then weigh off successively the several portions required for the various analytical processes.

1. *Determination of the water.*

Dry 10 grammes in the water-bath, and determine the loss of weight

* This sort of manure may, however, prove injurious to tender plants, if applied in too large quantity, without proper dilution with water, and in dry weather.

(§ 18). It is rarely necessary to make a correction on account of the carbonate of ammonia which escapes with the water.*

2. *Determination of the total amount of fixed constituents.*

Incinerate at a gentle heat, a weighed portion of the residue left in 1, in a platinum dish, or in a large platinum crucible placed in an oblique position, and weigh the ash.

3. *Determination of the constituents soluble in water, and also of those insoluble in water.*

Digest 10 grammes of the fresh manure with 300 c. c. of water, pass the liquid through a weighed filter (§ 33), wash the residue, dry at 212° and weigh. The weight found expresses the total quantity of the substances insoluble in water, and the difference gives the amount of the soluble constituents. Incinerate now the insoluble residue, and weigh the ash; the weight of the ash expresses the total amount of the fixed constituents contained in the insoluble part, and from the difference between this and the ash in 2, you learn the total amount of fixed constituents contained in the soluble part.

4. *Separate determination of the several fixed constituents.*

Dry a larger portion of the manure and treat it strictly by one of the methods given for the preparation and analysis of the ashes of plants.

5. *Determination of the total amount of ammonia.*

Treat a weighed portion of the manure by *Schlösing's* method (§ 78, 3)†

6. *Determination of the total amount of nitrogen.*

Moisten a weighed portion of the manure with a dilute solution of oxalic acid in sufficient quantity to impart a feebly acid reaction; dry, and determine the nitrogen either in the entire mass or in a weighed portion of it according to the directions given in § 155. If you deduct from the total amount of nitrogen so found the quantity corresponding to the ammonia and the nitric acid, you learn the quantity of nitrogen contained in the organic substances. It is generally sufficient, however, to total amount of the nitrogen.

7. *Determination of the total amount of carbon.*

Treat a portion of the dried residue of 1 by the process of elementary analysis. If the dried manure contains carbonates, determine the carbonic acid in a separate portion. Deduct this from the total amount obtained in the elementary analysis: the difference shows the quantity of carbonic acid formed from organic substances.

* The determination of the carbonate of ammonia may, if desirable, be effected most simply by boiling a portion of the manure for some time with water in a capacious retort, and collecting the vapors passing over in a receiver containing a definite quantity of sulphuric acid of known strength (compare § 177, 8, *Boussingault's* method.)

† If the quantity of ammonia is only small, a weaker sulphuric acid will answer better than that prepared according to the directions of § 78, 3; it is therefore advisable in such cases to substitute for the latter the acid prepared according to the directions of § 182, and which contains in 10 c. c. 0·4 grm. of sulphuric acid.

8. *Determination of the nitric acid.*

Treat a weighed portion of the manure with water, evaporate the solution to a tolerable consistence, add pure solution of potassa (free from nitric acid), and boil until no more ammoniacal fumes escape. Determine in the residue the nitric acid by *Martin's* method.*

B. Analysis of guano.

§ 225.

Guano, or the dung of sea-fowl, well known for its great fertilising properties, varies very considerably in quality from the sources from which our supplies are derived, and is also often, fraudently adulterated with soil, brick-dust, carbonate of lime, and other matters. This, and the circumstance that guano is an important article of commerce, explains why it is made the object of chemical examination more frequently than other manures.

The guano is mixed as uniformly as possible, and that which is intended for the analytical process is put into a stoppered bottle.

1. *Determination of the water.*

This is effected exactly as in § 224, 1. Genuine guano loses from 17 to 18 per cent.

2. *Determination of the total amount of fixed constituents.*

Incinerate a weighed portion in a porcelain or platinum crucible placed in a slanting position, and weigh the ash. Good guano leaves from 30 to 33 per cent of ash, guano of bad quality from 60 to 80 per cent, a wilfully adulterated article even more. The ash of genuine guano is white or gray. A yellow or reddish color indicates adulteration with loam, sand, soil. In the first stage of the process of incineration, good guano, in its incipient decomposition by heat, emits a strong ammoniacal odor, and white fumes.

3. *Determination of the constituents soluble in water, and also of those insoluble in water.*

Heat 10 grammes of guano with about 200 c. c. of water, pass the solution through a weighed filter, and wash the undissolved sediment with

* This method, which has been published quite recently, is based upon the fact that, if hydrogen in the moment of its disengagement acts upon nitric acid the latter is converted into ammonia ($NO_5+8\,H=NH_3+5\,HO$). According to *Gerhardt* and *Barral* this conversion takes place equivalent for equivalent. The following is the process proposed by *Martin:* introduce newly washed zinc into a glass in the proportion of from 4 to 5 parts to 1 part of nitric acid, supposed to be present, and add the solution of the nitrate, freed previously, if necessary, from ammonia, by boiling with potassa; then add repeatedly small portions of pure dilute sulphuric acid or hydrochloric acid. When the zinc is dissolved, determine by *Schlösing's* method (compare § 224, 5), the quantity of ammonia generated. Compt. rend. 37, 947;—Journ. f. prakt. Chem. 61, 247.

hot water, until the water running off looks no longer yellowish and leaves no perceptible residue when evaporated upon platinum foil; dry the residue and weigh. If you deduct the weight of the water and the insoluble residue from the weight of the guano, you obtain, as difference, the amount of the soluble constituents; and if you incinerate the insoluble part and weigh the ash, you learn from the difference the amount of the fixed soluble salts. With very superior sorts of guano the residue insoluble in water amounts to from 50 to 55 per cent; with inferior sorts to from 80 to 90 per cent. The brown colored aqueous solution of genuine guano upon evaporation evolves ammonia, emits a urinous smell, and leaves a brown saline mass consisting chiefly of sulphates of soda and potassa, chloride of ammonium, oxalate and phosphate of ammonia.

4. *The determination of the several fixed constituents;*

5. *The determination of the total amount of ammonia;*

6. *The determination of the total amount of nitrogen;*

7. *The determination of the total amount of carbon;*

are effected by the methods given in § 224, 4, 5, 6, and 7.

8. *Determination of the carbonic acid.*

Genuine guano contains only a small proportion of carbonates. If therefore a guano effervesces strongly when moistened with dilute hydrochloric acid, this may be regarded as a tolerably conclusive proof of a wilful adulteration with carbonate of lime.

9. *Determination of the uric acid.*

If it is desirable to ascertain the quantity of uric acid which a guano contains, treat the part insoluble in water with a weak solution of soda at a gentle heat, filter, and acidify the filtrate with hydrochloric acid, to precipitate the uric acid. Collect the uric acid on a weighed filter, dry, and weigh.

VI. ANALYSIS OF ATMOSPHERIC AIR.

§ 226.

In the analysis of atmospheric air we usually confine our attention to the following constituents: oxygen, nitrogen, carbonic acid, and aqueous vapor. It is only in exceptional cases that the exceedingly minute quantities of ammonia and other gases (many of which may be assumed to be always present in very minute traces) are also determined.

It does not come within the scope of the present work, to describe all

the methods which have been employed in the excellent investigations made in the last few years by *Brunner*, *Bunsen*, *Dumas* and *Boussingault*, *Regnault* and *Reiset*, and others, and to which we are indebted for a more accurate knowledge of the composition of our atmosphere. Excellent descriptions of these methods will be found in *H. Rose's* Handbuche der analytischen Chemie, Bd. II., S. 853.

I confine myself to those methods which are found most convenient in the analysis of the air for technical, or medical purposes.

A. Determination of the water and the carbonic acid.

§ 227.

The determination of these two constituents of the atmosphere is now always effected by *Brunner's* method, that is, by drawing, by means of an aspirator, a measured volume of air, through accurately weighed apparatus filled with substances having the property of retaining the aqueous vapor and the carbonic acid of the atmosphere; the increase of weight shows the amount of aqueous vapor and carbonic acid contained in the air which has passed through the apparatus. It must be borne in mind, however, that the results obtained can only be relied upon when the air is allowed to pass through the apparatus very slowly to give full time for the complete absorption of the aqueous vapor and carbonic acid.

Fig. 99, represents an aspirator, constructed on *Regnault's* plan, and connected with a complete apparatus for the simultaneous determination of the carbonic acid and the aqueous vapor.

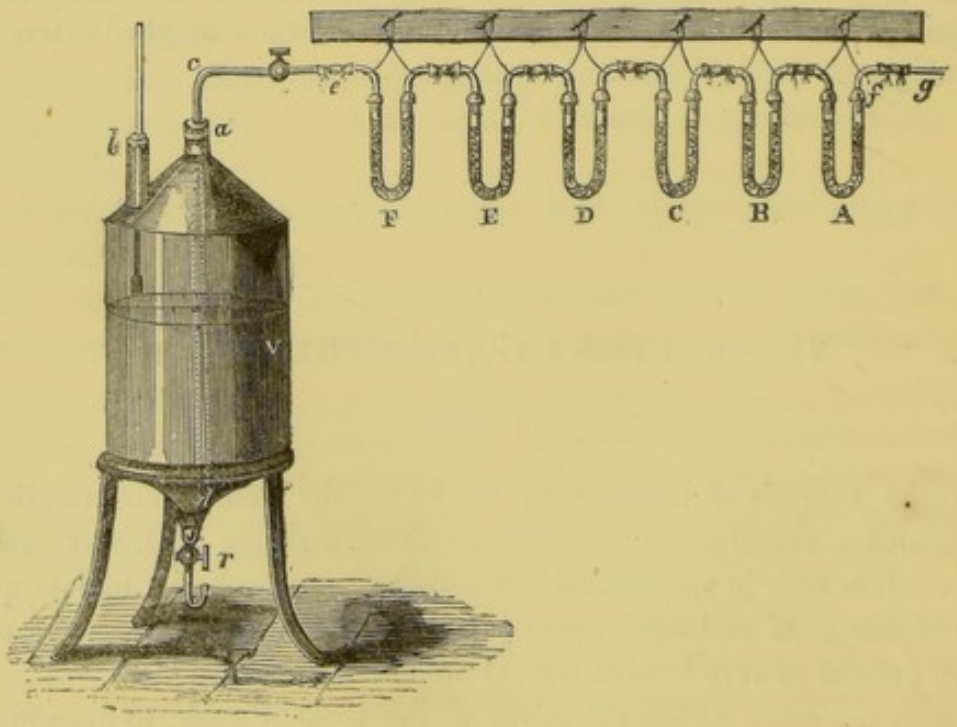


Fig. 99.

The vessel V is made of zinc-plated sheet iron, or of sheet zinc ; it holds from 50 to 100 litres, and stands upon a strong tripod in a trough of sufficient capacity to hold all the water flowing out. At *a* a brass tube, *c*, is firmly fixed in with cement. Into the aperture *b*, which serves also to fill the apparatus, a thermometer reaching down to the middle of V, is fixed air-tight by means of a perforated cork soaked in wax.

The efflux tube, *r*, is bent slightly upward, to guard against the least chance of air entering the vessel from below. The capacity of the vessel is ascertained by filling it completely with water, and then accurately measuring the fluid. The end of the tube *c* is connected air-tight with F, by means of a caoutchouc tube; the tubes A—F are similarly connected. A, B, E, and F are filled with coarsely pounded pumice stone, well moistened with concentrated sulphuric acid; C and D with small lumps of pumice stone, well moistened with concentrated solution of potassa. Finally, A is also connected with a long tube leading to the place from which the air intended for analysis is to be taken. The corks of the tubes are coated over with sealing wax. The tubes A and B are intended to withdraw the moisture from the air; they are weighed together. C, D, and E are also weighed jointly. C and D absorb the carbonic acid ; E the aqueous vapors which the air dried in A and B may take up from the solution of potassa. F need not be weighed; it simply serves to prevent E against the entrance of aqueous vapors from V.

The aspirator is completely filled with water, *c*, and connected with F, thus with the entire system of tubes of which the apparatus consists, and the cock *r* opened a little, just sufficient to cause a slow efflux of water. As the height of the column of water in V is continually diminishing, the cock must from time to time be opened a little wider, to maintain as nearly as possible a uniform flow of water. When V is completely emptied, the height of the thermometer and that of the barometer are noted, and the tubes A and B, and C, D, and E weighed again.

As the increase of weight of A and B gives the amount of water, that of C, D, and E, the amount of carbonic acid in the air which has passed through them; and as the volume of the latter (freed from water and carbonic acid) is accurately known from the ascertained capacity of V,* the calculation is in itself very simple; but it requires, at least in very accurate analyses, the following corrections:

a. Reduction of the air in V, which is saturated with aqueous vapor, to dry air; since the air which penetrated through *c* is dry (see § 166, *γ*.).

* Or from the quantity of water which has flown from V, as the experiment may be altered in this way, that a portion only of the water is allowed to run off, and received into a measuring vessel.

β. Reduction of the volume of dry air so found to 32° and 760 millimeters bar. (§ 166, α. and β.)

When the calculations have been made, the weight of the air which has penetrated into V is readily found (1000 c. c. of dry air at 32° and 760 millimeters bar, weighing 1·2932 grm.); and as the carbonic acid and water have also been weighed, their respective quantities may now be expressed in per cents, by weight or also, calculating the weight in volumes, in per cents by measure, or volume.

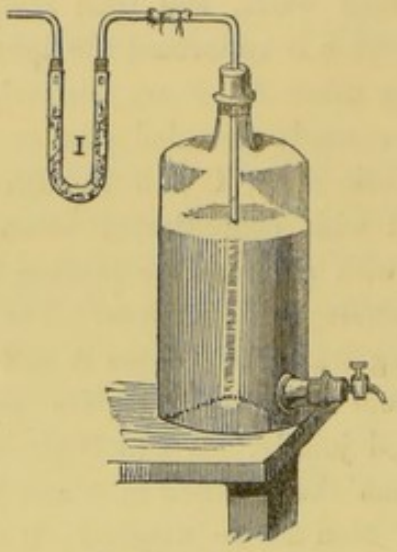


Fig. 100.

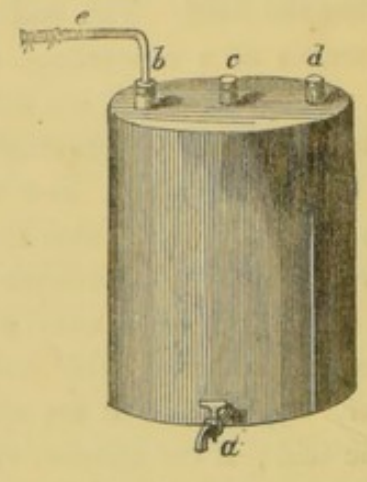


Fig. 101.

Instead of the aspirator V, a flask of the form represented, Fig. 100, or a tin vessel of the form and construction represented Fig. 101, may be used, only it must be borne in mind that sufficiently accurate results can be expected only if at least 25000 c. c. of air are passed through the absorption apparatus.

B. Determination of the nitrogen and oxygen.

The mixture of the nitrogen and oxygen is measured, the oxygen absorbed by an appropriate agent, and the residuary nitrogen gas then again read off: the diminution in the volume shows the amount of the oxygen. In § 177, 12, I have already described the method of removing the oxygen from the air by means of phosphorus; I add here two more methods by which the same end may be attained; I recommend more particularly the former.

I. *Liebig's method.**

§ 228.

This method is based upon the observation made by *Chevreul* and *Döbereiner*, that gallic acid and pyrogallic acid, in alkaline solutions, have a powerful tendency to absorb oxygen.

† Ann. der Chem. und Pharmacie 77, 107.

1. A strong measuring tube holding 30 c. c. and divided into $\frac{1}{5}$ or $\frac{1}{10}$ c. c. is filled to $\frac{2}{3}$ with the air intended for analysis. The remaining part of the tube is filled with mercury, and confined over that agent in a tall cylinder, widened at the top.

2. The volume of air confined is read off (§ 11). If it is intended to determine the carbonic acid—which can be done with sufficient accuracy only if the quantity of the acid amounts to several per cents—the air is dried by means of a ball of chloride of calcium introduced into it (§ 177, 12), and then again measured. If it is not intended to determine the carbonic acid, this operation is omitted. A quantity of solution of potassa of 1·4 specific gravity (1 part of dry hydrate of potassa to 2 parts of water) amounting to from $\frac{1}{40}$ to $\frac{1}{50}$ of the volume of air is then introduced into the measuring tube by means of a pipette with the point bent upward (see Fig. 102,) and spread over the entire inner surface of the tube by shaking the latter (§ 152); when no farther diminution of volume takes place, the decrease is read off. If the air has been dried previously with chloride of calcium, the diminution of the volume expresses exactly the amount of carbonic acid contained in the air; but if it has not been dried with chloride of calcium, the diminution in the volume cannot afford correct information as to the amount of the carbonic acid, since the strong solution of potassa absorbs also aqueous vapor.



Fig. 102.

3. When the carbonic acid has been determined (or simply removed), a solution of pyrogallic acid (containing 1 gramme of the acid in 5 or 6 c. c. of water)* is introduced into the same measuring tube by means of another pipette, similar to the one used in 2 (Fig. 102); the quantity of pyrogallic acid employed should be about half the volume of the solution of potassa used in 2. The mixed fluid (the pyrogallic acid and solution of potassa) is spread over the inner surface of the tube by shaking the latter; and, when no further diminution of volume is observed, the residuary nitrogen is measured.

4. Gallic acid may also be employed instead of pyrogallic acid; the only inconvenience with gallic acid is that the absorption of the oxygen takes from one and a half to two hours, and even a longer time, whilst with pyrogallic acid a few minutes suffice. The gallic acid is em-

* Pyrogallic acid is obtained, according to *Stenhouse* (Ann. der Chem. und Pharmacie, 45, 1), most simply by sublimation (best at 365° F.), from the dry aqueous extract of galls, in the same way as benzoic acid is prepared from benzoin. The quantity of acid obtained amounts to above 10 per cent of the extract used. Brown colored crystallised pyrogallic acid is prepared conveniently by dry distillation of Chinese galls, in small retorts holding about from 150 to 180 grammes in coarse lumps, and evaporation in the water-bath of the concentrated solution of the pyrogallic acid so obtained; this process yields nearly 15 per cent of acid.

ployed in the form of a cold saturated solution of gallate of potassa, either quite neutral, or containing a slight excess of acid. Its property of absorbing oxygen manifests itself only in presence of an excess of alkali. When the gallic acid has mixed with the solution of potassa in the measuring tube, the fluid, in contact with the oxygen of the air, turns of a dark red color; thin layers of it acquire an almost blood-red color, which, after some time, changes to brown. This blood-red color of the fluid moistening the inner surface of the tube, upon shaking, enables the operator closely to watch the progress of the absorption; when this color ceases to make its appearance the operation is terminated. 1 gramme of gallic acid dissolved in strong solution of potassa, absorbs 290 c. c. of oxygen gas (*Chevreul*).

5. The solution of gallic acid or pyrogallic acid mixing with the solution of potassa, of course dilutes it, causing thus an error from the diminution of its tension; but this error is so trifling that it has no appreciable influence upon the results; it may, besides, be readily corrected, by introducing into the tube, after the absorption of the oxygen gas, a small piece of hydrate of potassa corresponding to the amount of water in the solution of the acid.

6. There is another source of error in this method, viz., on account of a portion of the fluid always adhering to the inner surface of the tube the volume of the gas cannot be read off with absolute accuracy. In comparative analyses, the influence of this defect upon the results may be almost entirely neutralised, by taking nearly equal volumes of air in the several analyses.

7. Notwithstanding these several sources of error, the results obtained by this method are very accurate and constant. In eleven analyses which *Liebig* reports, the greatest difference was—with pyrogallic acid—between 20·75 and 21·03; with gallic acid—between 20·52 and 21·35. That the results differ more widely with gallic acid is chiefly owing to the circumstance that the temperature and atmospheric pressure had perceptibly changed in the course of the analytical process;* for the numbers given express the actual and uncorrected results.

II. *Absorption of the oxygen by copper moistened with hydrochloric acid.*

§ 229.

This method is very inferior in accuracy to the one described § 228, I give it here however, because every chemist who may have to make an approximate analysis of atmospheric air may not possess a large quantity of mercury.

* It has already been observed in the text that, with gallic acid, the operation takes from one and a half to two hours, and even longer.

The method is based upon the circumstance that copper moistened with hydrochloric or dilute sulphuric acid rapidly withdraws from atmospheric air the whole of its oxygen. The performance of the process requires only the following apparatus (presupposing always the gaseous mixture consists of oxygen and nitrogen only) :

1. *A graduated tube*, about 30 centimeters long, and from 16 to 20 millimeters in diameter.

2. *A small slip of sheet copper*, somewhat longer than the graduated tube, and of the shape illustrated by the annexed cut.

Copper turnings are tied round this slip in its whole length by means of a piece of string, in such a manner, however, as not to impede its ready introduction into the graduated tube. A slip so prepared answers the purpose better than a smooth piece of copper, as it presents a larger surface, and the string serves to keep the copper turnings moistened with the acid.



Fig. 103.

3. A *glass cylinder*, a few inches taller than the graduated tube, and filled with a mixture of equal parts of hydrochloric acid and water. The cylinder should not be too narrow, and should be widened at the top (see Fig. 104).

4. *A thermometer.*

The performance of the process is exceedingly simple.

The copper slip is introduced into the cylinder, at the bottom of which it is kept fixed by means of the three divergent slips, *a*, *b*, and *c*; the fluid in the cylinder should reach about an inch above the top of the copper. Some time is allowed for the escape of the air contained in the string, and the temperature of the fluid in the cylinder is noted. The graduated tube is about one-third filled with water. The tube is now completely immersed in the fluid in the cylinder (to give the air confined in it the temperature of the dilute hydrochloric acid); it is then raised again until the fluid is on an exact level inside and outside, when the volume of the gas is read off. The tube is now cautiously pushed over the copper-slip,* and pressed down. The annexed cut shows the arrangement of the apparatus.


Fig. 104.

The apparatus is allowed to stand for the space of from one and a half, to two hours, after which the residuary gas is measured; the tube is then once more pushed over the copper-slip, and, after the lapse of half an hour, the residuary gas measured again. If no further decrease has taken place

* The analyst must guard against any escape of air from the tube during the operation; it is on this account that only two-thirds of the tube should be filled with air, otherwise it might be impracticable to prevent loss.

in the interval, the operation is finished. The temperature is now again observed, and if it has not changed, the percentage volumes of the oxygen and nitrogen are found by the following simple calculation:

The first measurement gives the volume of the analysed air, the second that of the nitrogen, and the difference that of the oxygen.

Should the temperature of the fluid have changed during the process, the volume of the nitrogen must of course be corrected first to the original temperature, before this calculation can be made.

Air containing carbonic acid, must be freed from this gas by the method given in § 227, before it is introduced into the measuring tube.

PART III.

EXERCISES FOR PRACTICE.

EXERCISES FOR PRACTICE.

I HAVE given here 70 exercises for practice, viz., 30 of analysis by weight, 30 of analysis by measure and for technical purposes, and 10 of organic elementary analysis. The exercises selected are nearly the same as I have for some sessions past been in the habit of giving to the students in my laboratory; I can therefore safely affirm that all of them may be readily performed, and also that the order of succession in which they are arranged has been found practically useful. In my opinion it is not judicious to occupy students with analyses by measure or with technical analyses before they have acquired some practice and skill in analyses by weight. I think this will be conceded if it be borne in mind that the latter demands, besides great accuracy, considerable patience; students that have once become accustomed to the expeditious processes of volumetrical methods, without having previously passed through a proper training in the more laborious and tedious performances of analyses by weight, will find it difficult afterwards to command the necessary patience in the pursuit of the latter, which after all constitute, and will probably long continue to be, the most essential part of chemical analysis.

The principal point I had in view in the selection of these exercises was that most of them, and more particularly the analyses by weight, should permit an exact control of the results. This is of the utmost importance for the student, since a certain degree of confidence in the correctness of the results of one's own experiments is among the most indispensable requisites for a successful pursuit of quantitative investigations; and a confidence of this kind can, in my opinion, only be attained by affording the student the means of testing and controlling the accuracy of the results obtained in his experiments.

Now, a rigorously accurate control is practicable only in the analysis of pure salts of known composition, or of substances which the analyst himself has previously prepared, and of which he knows the constituents, and the relative proportions in which they are combined. When the student has acquired, in the analysis of such substances, the necessary degree of

confidence in his own abilities, he may gradually proceed to analyses of a somewhat more difficult and intricate nature.

The second point which I had in view in the selection of these exercises for practice, was to make them comprise both the more important analytical methods, and the most important compounds, so as to afford the student proper opportunity to acquire a thorough knowledge of every branch of quantitative analysis. I have therefore not always indicated the most simple methods.

Organic analysis offers far less variety than the analysis of inorganic substances—the exercises relating to the former branch are therefore less numerous here than those relating to the latter. I would advise the student to analyse the same organic substance repeatedly until the results prove quite satisfactory.

In conclusion, I have to remark, that I do not mean to state it is absolutely necessary to go through the whole of these exercises; the time which a student may require to attain proficiency in analysis, depends entirely upon his own abilities. One may be a good analyst without having tried *every* method or analysed *every* compound. I would, however, warn students to guard against prematurely attempting new discoveries. The safest way is to wait until he has acquired a certain degree of proficiency in general chemistry, and more particularly in practical analysis.

EXERCISES.

1. Iron.

Weigh, on a watch-glass, about 0·3 grammes of fine pianoforte wire, and dissolve in hydrochloric acid, with addition of nitric acid. The acids are diluted with a little water.

The solution is effected by boiling in a moderate sized flask covered with a watch-glass. When complete solution has ensued, and the color of the fluid shows that all the iron is dissolved as sesquioxide (if this is not the case some more nitric acid must be added), rinse the watch-glass, dilute the fluid in the flask, heat to incipient ebullition, add ammonia in moderate excess, filter, &c. (Compare § 90, 1.)

The following example will show the best way of entering the results :

Watch-glass + iron	10·3192
,, empty	9·9750
Iron	0·3442
Crucible + sesquioxide of iron . .	17·0673
,, empty	16·5761
	0·4912
Filter-ash No. 2	0·0012
Sesquioxide of iron . .	0·4900 =
Iron . . .	0·343 = 99·65 per cent.

2. Acetate of lead.

Determination of oxide of lead.—Triturate the dry and non-effloresced crystals in a porcelain mortar, and press the powder between sheets of blotting paper until the last sheets are no longer moistened by it.

a. Weigh about 1 gramme, dissolve in water, with addition of a few drops of acetic acid, and proceed exactly as directed § 92, 1, *a. a.*

b. Weigh about 1 gramme, and proceed exactly as directed § 92, 5. (*Dulk's* modification of *Berzelius's* method.)

Pb O . .	1394·64 . . .	111·57 . . .	58·85
$\overline{A}$ . . .	637·50 . . .	51·00 . . .	26·91
3 aq . .	337·50 . . .	27·00 . . .	14·24
	2369·64	189·57	100·00

3. Chloride of sodium.

Fuse pure chloride of sodium in a platinum crucible, pour the fused mass upon a piece of porcelain, break it still hot into pieces, and preserve these in a tightly-corked glass tube.

a. Determination of the chlorine.—Dissolve about 0·4 grm. in water, add nitric acid, and precipitate with solution of nitrate of silver (§ 112, I. *a.*).

b. Determination of the soda.—Convert about 0·3 grm. into *neutral* sulphate of soda, by treating the salt with moderately dilute sulphuric acid (§ 77, 1). The operation may be conducted in a platinum crucible ; to apply a uniform heat to all parts, the crucible is, by means of a platinum triangle, suspended free in a small iron vessel, and heat applied to the latter.

(For the percentage composition, see § 48.)

4. Arsenious acid.

Dissolve about 0·4 grm. of pure arsenious acid in small lumps in a middle-sized flask, with a glass stopper, in some solution of soda, by digesting the mixture on the water-bath; dilute with a little water, add hydrochloric acid in excess, and then nearly fill the flask with sulphuretted hydrogen water. Insert the stopper and shake. If the sulphuretted hydrogen predominates, the precipitation is terminated; if not, conduct sulphuretted hydrogen gas into the fluid until it is saturated; proceed in all other respects exactly as directed § 102, 4.

A_5	937·5	75	75·76
O_3	300·0	24	24·24
	1237·5	99	100·00

5. Potassa alum.

Determination of the alumina.—Press pure triturated potassa alum between sheets of blotting paper; weigh off about 2 grammes, dissolve in water, and determine the alumina as directed § 83, *a*.

KO	588·86	47·11	9·93
Al_2O_3	640·84	51·26	10·81
$4\,SO_3$	2000·00	160·00	33·73
$24\,HO$	2700·00	216·00	45·53
	5929·70	474·37	100·00

6. Carbonate of soda.

Gently ignite anhydrous pure carbonate of soda in a platinum crucible.

a. Determination of the soda.—Convert about 0·5 grm. into chloride of sodium (§ 77, 3).

b. Determination of the carbonic acid.—Determine in from 0·7 to 1 gramme the carbonic acid according to the directions of § 110, II. *b. β. aa.* A small sized apparatus is selected, weighing from 60 to 70 grms. which can be weighed on a delicate balance. The weighing of the carbonate of soda is effected best as follows: from 0·7 to 1 gramme of the recently ignited salt is put into a narrow tube, and the latter then weighed; its contents are cautiously transferred to the flask A, and the exact quantity of carbonate of soda in the flask is then accurately ascertained by reweighing the empty tube.

For the composition, see § 48.

7. Carbonate of lime.

Heat pure carbonate of lime in powder (no matter whether pure calca-

reous spar or artificially prepared carbonate of lime) gently in a platinum crucible.

a. Determination of the lime.—Dissolve in a covered beaker about 1 gramme in dilute hydrochloric acid, and determine the lime as directed § 81, 2, *b*.

b. Determination of the carbonic acid.—Determine in about 0·8 grm. the carbonic acid according to the directions of § 110, II. *b*. *a*.

For the composition, see § 52.

8. Sulphate of copper.

(Complete analysis of sulphate of copper.)

Triturate the pure crystals in a porcelain mortar and press the powder between sheets of blotting paper.

a. Determination of the water of crystallisation.—Weigh an empty bulb tube, and half fill the bulb with sulphate of copper ;* weigh again, and then place it within an air-bath with apertures in its sides (page 37) ; connect one end with a chloride of calcium tube, the other with an aspirator ; heat to from 248 to 284°, and allow the water to flow slowly from the aspirator. When no more water escapes from the sulphate of copper, and repeated weighings of the bulb tube give constant results, the diminution of weight expresses the amount of crystallisation water in the salt.

b. Determination of the water of halhydration.—Proceed with the same experiment, but at a temperature raised to between 482° and 500°. The additional loss of weight of the bulb tube suffered in this process gives the amount of the more strongly combined halhydration water.

c. Determination of the sulphuric acid.—In another portion of the sulphate of copper (about 1·5 grm.) determine the sulphuric acid according to the directions of § 105, I. 1.

d. Determination of the oxide of copper. In about 1·5 grm. determine the oxide of copper as directed § 95, 1, *a*. *a*.

Cu O . . .	496·0 . . .	39·68 . . .	31·83
SO_3	500·0 . . .	40·00 . . .	32·08
HO	112·5 . . .	9·00 . . .	7·22
4 aq . . .	450·0 . . .	36·00 . . .	28·87
	1558·5	124·68	100·00

* This is effected by pushing into one end of the tube down to the bulb a glass rod with paper folded round it, and filling in the salt through the other end. The tube is then restored to a horizontal position, and the bulb gently tapped on the table ; the glass rod is withdrawn, and the ends are, if necessary, cleaned with a feather.

9. Crystallised sulphate of magnesia.

Triturate and dry as directed § 15, *a*.

a. Determination of the magnesia.—Dissolve from 1 to 2 grammes in water, add chloride of ammonium, then ammonia, and precipitate with phosphate of soda (§ 82, 2).

b. Determination of the total amount of water.—Heat about 1 gramme in a porcelain crucible over the lamp to incipient faint ignition, and determine the loss of weight. The residue treated with water, must give a clear solution.

Mg O	250·19	20	16·26
SO_3	500·00	40	32·52
7 aq	787·50	63	51·22
	1537·69	123	100·00

10. Chloride of mercury.

Determination of the mercury.—Dissolve about 0·5 grm. in water, add a few drops of hydrochloric acid, and precipitate with sulphuretted hydrogen (§ 94, 3).

Hg	1250·60	100·05	73·83
Cl	443·28	35·46	26·17
	1693·88	135·51	100·00

11. Sulphide of iron.

Select pure iron pyrites, triturate to a very fine powder, and dry at 212°.

a. Determination of the sulphur.—Treat from 0·5 to 1 gramme as directed § 116, 2, *a*. *α*. or *β*.

b. Determination of the iron.—Dissolve about 0·5 grm. in nitrohydrochloric acid, and precipitate with ammonia (§ 90, 1).

Fe	350	28	46·67
2 S	400	32	53·33
	750	60	100·00

12. Phosphate of lime.

a. Determination of the phosphoric acid.—Ignite, weigh from 0·8 to 1 gramme, put into a flask or beaker, add about 3 grammes (the quantity added must be accurately weighed) of pure metallic tin, and proceed as directed § 106, I. *d*. *a*.

b. Determination of the lime.—Saturate the filtrate of *a.* with ammonia, and precipitate the lime with oxalate of ammonia (§ 81, 2, *b.*).

$3\,CaO$ . . .	1050·00 . . .	84·00 . . .	54·06
PO_5	892·04 . . .	71·36 . . .	45·94
	1942·04	155·36	100·00

13. Bichromate of potassa.

Triturate pure bichromate of potassa, and dry the powder directly over the lamp at a gentle heat.

a. Determination of the chromium.—Dissolve about 1 gramme in water, precipitate with acetate of lead added *slightly* in excess, and determine the precipitated chromate of lead as directed § 104, 1, *b.*

b. Determination of the potassa.—Precipitate from the filtrate of *a.* the lead with sulphuretted hydrogen, and convert the potassa in the filtrate into sulphate of potassa or chloride of potassium (§ 76).

KO . . .	588·86 . . .	47·11 . . .	31·69
$2\,CrO_3$ . .	1269·40 . . .	101·56 . . .	68·31
	1858·26	148·67	100·00

14. Separation of iron from manganese.

Dissolve in hydrochloric acid about 0·5 grm. of fine pianoforte wire and about the same quantity of protosesquioxide of manganese,* previously gently heated; heat the solution with some nitric acid, and separate the two metals by means of carbonate of baryta (§ 128, A. 1.).

15. Separation of lime from magnesia.

Dissolve in dilute hydrochloric acid about 0·5 grm. of pure carbonate of lime, previously gently ignited, and about the same quantity of recently ignited pure magnesia,† and separate the two earths as directed § 122, B. 3, *a.*

16. Separation of magnesia from soda.

Dissolve in dilute hydrochloric acid about 0·5 grm. of pure fused chloride of sodium and about the same quantity of recently ignited pure magnesia, and separate the two substances by means of oxide of mercury (§ 121, A, 1.).

17. Separation of potassa from soda.

Mix weighed quantities of pure chloride of sodium and pure chloride of potassium, and separate the two alkalies.

* For the preparation of protosesquioxide of manganese, see § 86, 1.

† This may be prepared most readily by heating pure oxalate of magnesia (*F. Schulze*).

a. By the direct method described § 120, 1, *a*.
b. By the indirect method described § 120, 3.

18. Separation of sesquioxide of iron from alumina.

Dissolve about 0·3 grm. of pure pianoforte wire in hydrochloric acid, with addition of some nitric acid, add about 1 gramme of pure alum, and separate according to the directions of § 128, B. 10, *a*. (Precipitate the two substances first with ammonia, weigh, dissolve the residue in concentrated hydrochloric acid, and precipitate the iron, after addition of tartaric acid and ammonia, with sulphide of ammonium ; determine the iron as directed § 90, 1, *b*.) Or separate tho two bodies according to the directions of § 128, B. 1, *a*., or of § 128, B. 3, *a*.

19. Separation of cadmium from zinc.

Dissolve about 0·5 grm. of pure oxide of zinc and about the same quantity of pure oxide of cadmium, in 40 c. c. of hydrochloric acid and 100 grammes of water, and separate the two metals by means of sulphuretted hydrogen (§ 130, A.). Treat the sulphide of cadmium as directed § 97, 2, the solution of zinc, after removal of the sulphuretted hydrogen as directed § 85, *a*.

20. Separation of mercury from lead.

Dissolve about 0·5 grm. of pure chloride of mercury, and about 1 gramme of pure crystallised acetate of lead, and separate the two metals as directed § 131, 6, *a*.

21. Separation of magnesia from alumina.

Dissolve about 1 gramme of pure alum and about 1 gramme of pure crystallised sulphate of magnesia in water, add some hydrochloric acid, then a cold prepared saturated solution of bicarbonate of soda, and proceed in all other respects as directed § 124, B. 2, *a*.

22. Separation of sesquioxide of iron and lime from phosphoric acid.

Weigh off about 0·3 grm. of pianoforte wire, dissolve in hydrochloric acid, with addition of nitric acid, and add about 1 gramme of recently ignited phosphate of lime (PO_5, $Ca\,O_3$).

Dilute the solution to about 400 c. c., add cautiously ammonia to incipient alkaline reaction, then acetic acid until the reaction is strongly acid and the precipitated phosphate of lime has redissolved ; the precipitated phosphate of sesquioxide of iron remaining undissolved. Allow it to deposit, wash the precipitate twice by decantation, then on the filter, and dissolve it in hydrochloric acid.

You have now:

a. An hydrochloric acid solution containing all the sesquioxide of iron and a portion of the phosphoric acid; and *b.* a solution, acid from acetic acid, which contains all the lime and the rest of the phosphoric acid.

Mix the solution *a.* with sulphuretted hydrogen in excess, add ammonia, then some sulphide of ammonium, and determine the iron as directed § 90, 1, *b.* Concentrate the filtrate and precipitate the phosphoric acid from it according to the directions of § 106, I. *b.* *a.*

Mix the solution *b.* with ammonia until a persistent precipitate just begins to form, then with a few drops of acetic acid until the fluid has cleared again; add oxalate of ammonia in moderate excess, and determine the lime according to the directions of § 81, 2, *b.* *β.* In the filtrate, concentrated by evaporation, determine the phosphoric acid as directed § 106, I. *b.* *a.* The precipitates of phosphate of magnesia and ammonia thrown down from the filtrates of *a.* and *b.* may be collected on a filter.

23. Separation of iodine from chlorine.

Dissolve about 0·4 grm. of pure iodide of potassium and about the same quantity of pure chloride of sodium in water, and precipitate the solution with solution of silver (§ 112, I. *a.*). When you have weighed the precipitate of chloride and iodide of silver, determine the quantity of the iodide, by igniting a weighed portion of the precipitate in a stream of chlorine and noting the loss of weight consequent upon the conversion of the iodide into chloride of silver (§ 137, 2, *c.*)

24. Analysis of a limestone or dolomite.

This is made exactly according to the directions of § 203.

25. Analysis of natrolite.

The essential constituents of natrolite are: soda, alumina, silicic acid, and water. Besides these, lime and sesquioxide of iron are also occasionally found in this mineral.

Triturate a clean piece of the mineral in an agate mortar to a fine powder, and dry at 212°.

a. Treat about 1·5 grm. with hydrochloric acid and separate the silicic acid exactly as directed § 111, II. *a.*; do not neglect to test the purity of the silicic acid (see page 247).

b. Precipitate the fluid filtered from the silicic acid with carbonate of ammonia and some ammonia, and wash the precipitated alumina first by decantation, then on the filter, &c. (§ 83, *a.*)

c. As the alumina may still contain some silicic acid, and also lime and sesquioxide of iron, digest it, after weighing, for some time with concentrated hydrochloric acid; filter the solution from the undissolved silicic

acid ; ignite and weigh the latter, (do not neglect to test its purity, see page 247). Supersaturate the filtrate with solution of soda, add some carbonate of soda, boil, allow it to deposit, decant through a filter, boil the precipitate which may have formed, again with solution of soda, wash, dissolve in hydrochloric acid, and determine the sesquioxide of iron and the lime as directed § 127, B. 3, *e*. Deduct from the weight of the precipitate produced by carbonate of ammonia, the joint weights of the silicic acid, sesquioxide of iron, and lime found therein : the difference gives the uantity of the alumina.

d. Evaporate the fluid filtered from the first precipitate of alumina (*b*.), finally in a platinum dish, and determine the chloride of sodium in it as directed § 77, 3.

e. Weigh off about 1·5 grm. of the natrolite, dried at 212°, and determine the water by intense ignition.

26. Analysis of brass.

Brass is a compound of from 25 to 35 per cent of zinc and from 65 to 75 per cent of copper. Besides these two essential constituents, it contains usually also small quantities of tin and lead.

Dissolve about 2 grammes in nitric acid. Do not use more of the acid than is absolutely necessary, as the excess must be driven off.

If an insoluble residue remains (binoxide of tin), filter the fluid—after previous dilution with water—from this residue, and add to the filtrate, or, if the quantity of the tin is only very inconsiderable, directly to the solution, about 30 drops of dilute sulphuric acid ; evaporate the mixture to dryness on the water-bath, add 100 c. c. of water, and apply heat. If a residue remains (sulphate of lead), filter, and wash with 50 c. c. of water (as the correct proportion between the acid and the water is of importance in the process, the water must be accurately weighed or measured). Add now 45 c. c. of hydrochloric acid to the 150 c. c. of fluid, and then precipitate the copper with sulphuretted hydrogen gas (not water). When complete precipitation has been effected, and the sulphide of copper has subsided, filter, and wash the precipitate with water mixed with a little sulphuretted hydrogen water. Treat the sulphide of copper as directed in § 95, 1, *c*. Evaporate the filtrate, nearly saturate with solution of soda, and precipitate with carbonate of soda (§ 85, *a*.). If the oxide of zinc obtained contains iron, determine the latter metal by one of the methods given in § 128.

27. Analysis of felspar.

Select a small piece of felspar and triturate it in an agate mortar to a fine powder, add some water, and continue the trituration until all crepi-

tation ceases and the mass is perfectly smooth (see § 14, page 30). Dry the paste in a small porcelain dish at 212°.

a. Fuse about 1·5 grm. with four times the quantity of carbonate of soda and potassa (§ 111, II. *b.* *a.*), and separate the silicic acid as directed § 111, II. *a.*)

b. In the fluid filtered from the silicic acid determine the alumina (and the small quantities of silicic acid and sesquioxide of iron, and also of alkaline earths, which may have been thrown down with it) as directed in the analysis of natrolite (see 25).

c. Treat about 1 gramme of the felspar powder with hydrofluoric acid gas, and decompose the metallic silicofluorides formed, by evaporation with sulphuric acid. When the excess of the latter has been removed and the sulphates formed are dissolved in hydrochloric acid and water, precipitate the sulphuric acid by cautious addition of chloride of barium in very slight excess (should you have added too much of that re-agent, add again a few drops of dilute sulphuric acid to reduce the excess of chloride of barium in the solution to a minimum). Filter and precipitate the filtrate with carbonate of ammonia and ammonia. The precipitate consists of alumina, mixed with some carbonate of baryta and sesquioxide of iron, and also lime and magnesia, in cases where these two latter substances are are present. In the filtrate determine the potassa as chloride of potassium (§ 76, 3). Before the quantity found of the chloride of potassium can be safely taken for correct, you must ascertain whether the solution of the residuary salt remains clear when treated with ammonia and carbonate of ammonia. If you wish to determine the alumina once more, dissolve the precipitate containing it in hydrochloric acid, precipitate the baryta most cautiously with a few drops of dilute sulphuric acid, filter, and then proceed as in the analysis of natrolite (see 25).

28. Analysis of solder (tin, and lead).

Put about 1·5 grm. of the alloy, cut into small pieces into a flask, pour nitric acid over it, and proceed as directed § 101, 1, *a.*, to effect the separation and estimation of the tin

Mix the filtrate in a porcelain dish with pure dilute sulphuric acid, evaporate the nitric acid on the water-bath, and proceed with the sulphate of lead obtained as directed § 92, 2. Test the fluid filtered from the sulphate of lead with sulphuretted hydrogen and sulphide of ammonium for the other metals which the alloy might contain besides tin and lead.

29. Analysis of well or mineral water.

Proceed as directed § 173 or 174.

30. Preparation and analysis of the ash of a plant.

(§ 213—219.)

31. Determination of the specific gravity of hydrochloric acid.

Determine the specific gravity of hydrochloric acid, with the aid of the bottle illustrated in Fig. 92 (§ 177), and calculate from this the strength of the acid, with the aid of Table II. in § 181.

32. Determination of the strength of hydrochloric acid by saturation.

Prepare the test acid and the alkaline test fluid as directed in § 182 (*a.* and *β.*), and then determine by the method described in that paragraph, the strength of the same hydrochloric acid as in 31.

33. Alkalimetry by Mohr's process.

Determine the amount of caustic alkalies and alkaline carbonate in a sample of soda of commerce, by the method described in § 186.

34. Alkalimetry by Descroizilles and Gay-Lussac's method.

Determine the amount of caustic alkali and alkaline carbonate in another portion of the same soda, by the method described in § 185.

35. Determination of ammonia by Schlösing's method.

Weigh off about 0·5 grm. of pure chloride of ammonium, and determine the ammonium in it as directed § 78, 3.

36. Determination of the lime (and the magnesia) in a limestone, by analysis by measure.

Proceed as directed § 204.

37. Determination of the strength of a solution of permanganate of potassa.

Proceed as directed § 89, 2, *a.*; 0·2 grm of pianoforte wire will suffice. Dilute the solution of permanganate of potassa to the extent that from 20 to 30 c. c. of the dilute solution are required for the oxidation of 0·2 grm. of iron, and add from a burette divided in one-tenth c. c. Compare § 206.

38. Determination of iron in an iron stone.

Proceed as directed § 206.

39. Analysis of nitrate of potassa.

Weigh about 0·5 grm. of pure anhydrous nitrate of potassa, and proceed as directed § 117, II. *a*. Before heating to boiling, after the addition of the nitrate of potassa to the solution of protochloride of iron, it is advisable to add some sulphuric acid.

40. Determination of the copper by Schwarz's method.

Weigh about 4 grms. of pure sulphate of copper and dissolve to 200 c. c. Determine the copper in several portions of 50 c. c. each in the manner directed § 95, 3, *b*.

41. Determination of ferricyanide of potassium by De Haen's method.

Dissolve about 0·5 grm. of ferricyanide of potassium in water, and proceed as directed § 198.

42. Separation of ferro- and ferricyanide of potassium.*

Dissolve about 1 grm. of ferricyanide of potassium and about the same quantity of ferrocyanide of potassium in 100 c. c. of water. Determine in one portion of 20 c. c. the ferrocyanide of potassium, and in another portion of 20 c.c. the ferricyanide of potassium, in the manner directed § 198.

43. Preparation of the solutions required in Bunsen's method of determining iodine.

Method described § 114, Appendix. The strength of the solution of iodine to be ascertained by means of bichromate of potassa.

44. Examination of chloride of lime by Bunsen's method.

Method described § 194.

45. Examination of chloride of lime by Penot's method.

Examine a portion of the article used in 44, by the method described § 192.

46. Examination of chloride of lime by means of iron.

Examine another portion of the substance used in 44, by the method described § 193.

* *Mr. Lenssen*, of my laboratory, has devised another method to effect the determination of ferricyanogen, which gives also very good results. It is based upon the fact that, when ferricyanide of potassium, solution of iodide of potassium, and hydrochloric acid are mixed together, an equivalent of iodine (1586) separates for every equivalent of ferricyanide of potassium (4119) $(Cfdy, H_3)+H\,I=2\,(Cfy, H_2)+I$. If the iodine is now determined by *Bunsen's* method, the quantity of the ferricyanide of potassium is learnt with great accuracy. *Lenssen* obtained in four experiments respectively 99·22,—101·7,—102·1,—100·5, instead of 100.

47. Determination of copper by De Haen's method.

Dissolve about 5 grms. of pure sulphate of copper in a sufficient quantity of water to give 500 c. c. of solution. Determine the copper in several portions of 10 c. c. each in the manner described § 107.

48. Examination of manganese ores.

Method described § 196.

49. Determination of manganese in presence of iron.

Dissolve about 0·2 grm. of pianoforte wire and about 0·4 grm. of protosesquioxide of manganese in hydrochloric acid, and determine the two metals as directed § 128, 10, *c*.

50. Determination of silver by Gay-Lussac's method.

Dissolve a small silver coin in nitric acid, and determine the silver as § 91, 5.

51 Determination of chlorine by Liebig's method.

Determine the chlorine in a weighed portion of pure chloride of sodium as directed § 112. I. *c*. *β*.

52. Determination of iodine by Kersting's method.

Determine the iodine in a small weighed portion of pure iodide of potassium as directed § 114, 1, *c*.

53. Determination of sugar by Fehling's method.

Prepare the solution of copper described in § 210, and determine with the aid of this solution the amount of saccharine matter contained in a solution of honey.

54. Examination of starch.

Dry pure starch at 212° and examine it as directed § 210.

55. Determination of caustic soda in presence of carbonate of soda.

Analyse a sample of soda of commerce containing caustic soda, as directed § 188.

56. Examination of manganese ores by Fresenius and Will's method.

Take a fresh portion of the ore used in 46, and examine it by the method described § 195.

57. Determination of the degree of solubility of common salt.

a. At 229·5° (*the boiling point of a saturated solution of common salt in water*). Dissolve perfectly pure pulverised chloride of sodium in distilled water, in a glass flask ; heat the solution to boiling, and keep in ebullition until part of the dissolved salt separates. Pass the fluid now with the greatest expedition into an accurately tared capacious measuring flask, through a funnel surrounded with boiling water and covered with a glass plate. As soon as a few ounces of fluid have passed into the flask, insert the cork, allow the fluid in the flask to cool, and then weigh. Fill the flask now up to the line mark with water, and determine the amount of salt in an aliquot portion of the fluid, by evaporating in a platinum dish ; in this process it is advisable to add some chloride of ammonium, which will, in some measure, prevent the decrepitation that usually attends the ignition of common salt.

b. At 57·2°. Allow the boiling saturated solution to cool down to 57·2° with frequent shaking, and then proceed as in *a*.

100 parts of water dissolve at 229·5° . 40·35° of chloride of sodium.
100 „ „ 57·2° . 35·87° „ „

58. Determination of the degree of solubility of sulphate of lime.

a. In water of 212°.
b. In water of 53·6°.

Digest pure pulverised sulphate of lime for some time with water, in the last stage of the process at a temperature at from 104° to 122° (at which temperature sulphate of lime is most soluble) ; shake the mixture frequently during the process. Decant the clear solution into two flasks, and boil the fluid in one flask for some time ; allow that in the other to cool down to 53·6° (with frequent shaking), and allow it to stand for some time at that temperature. Then filter both solutions, weigh the filtrates, and determine the amount of sulphate of lime respectively contained in them, by evaporating the fluids and igniting the residues.

100 parts of water dissolve at 212° . . 0·217 of anhydrous of sulphate of lime.
100 „ „ 53·6° . . 0·233 „ „

59. Analysis of atmospheric air.

Method I. (§ 228).

O . . .	20·8 vol.
N . . .	79·2 vol.
	100·0

60. Analysis of exhaled air.

Method described § 228. The air is first dried; the carbonic acid is then determined, and finally the oxygen.*

ORGANIC ELEMENTARY ANALYSES.

61. Analysis of cane sugar.

Select perfectly pure white crystals. Triturate and dry at 212°. Burn with oxide of copper, by *Liebig's* method (§ 142 and § 143).

12 C	900·00	72	42·10
11 H	137·50	11	6·44
11 O	1100·00	88	51·46
	2137·50	171	100·00

62. Analysis of crystallised tartaric acid.

Dry the powder of pure crystals of tartaric acid at 212° and burn with oxide of copper, by *Bunsen's* method (§ 144).

4 C	300·0	24	32·0
3 H	37·5	3	4·0
6 O	600·0	48	64·0
	937·5	75	100·0

63. Analysis of oil of turpentine.

Select for the analytical process oil of turpentine which has been recently rectified, and perfectly freed from water by digestion with fused chloride of calcium. Method, § 149.

5 C	375	30	88·24
4 H	50	4	11·76
	425	34	100·00

64. Analysis of starch.

Dry pure starch at 212°, and burn it in a stream of oxygen gas, as directed § 147.

12 C	900	72	44·44
10 H	125	10	6·17
10 O	1000	80	49·39
	2025	162	100·00

65. Determination of the carbon and hydrogen in uric acid.

Dry pure uric acid at 212°, and analyse it by the method described § 151.

* *Liebig* found in exhaled air from 4 to 5·4 carbonic acid, and from 14·95 to 16·36 oxygen.

66. DETERMINATION OF THE NITROGEN IN URIC ACID BY VARRENTRAPP AND WILL'S METHOD.

Method described § 154.

67. DETERMINATION OF THE NITROGEN IN URIC ACID BY PÉLIGOT'S METHOD.

Method described § 155.

68. DETERMINATION OF THE NITROGEN IN URIC ACID BY DUMAS' METHOD.

Method described § 253.

5 C	375	30	35·71
2 N	350	28	33·33
2 H	25	2	2·38
3 O	300	24	28·58
	1050	84	100·00

69. DETERMINATION OF THE SULPHUR IN HORN.

Determine the sulphur in horn filings as directed § 156. (Mulder found 3·4 per cent of sulphur in that substance.)

70. DETERMINATION OF THE DENSITY OF CAMPHOR VAPOR.

Method described § 161. Calculated result, § 172.

APPENDIX.

APPENDIX.

I. ANALYTICAL NOTES.

1. Action of water upon glass and porcelain vessels, in the process of evaporation (to § 24).

A large bottle was filled with water which had been cautiously distilled from a copper steam apparatus with a tin condensing tube. All the experiments in I. were made with this water.

a. 300 c. c. cautiously evaporated in a platinum dish left a residue weighing, after ignition, 0·0005 grm. = 0·0017 per 1000.

b. 600 c. c. were evaporated, boiling, nearly to dryness, in a wide flask of Bohemian glass; the residue was transferred to a platinum dish, and the flask rinsed with 100 c. c. of distilled water, which was added to the residue in the dish, the fluid in the latter was then evaporated to dryness and the residue ignited.

After ignition, the residue weighed . . .	0·0104 grm.
Deducting from this the quantity of fixed matter originally contained in the distilled water, viz. . .	0·0012 „
There remains substance dissolved out of the glass .	0·0092 „

= 0·0153 per 1000.

In three other experiments, made in the same manner, 300 c. c. left, in two 0·0049 grm., in the third 0·0037 grm.; these, calculated for 600 c. c., give an average of . . . . . 0·0090 grm.

And after deduction of . . . . . 0·0012 „

0·0078 „

= 0·013 per 1000.

We may, therefore, assume that 1 litre of water dissolves, upon protracted boiling in glass vessels, about 14 milligrammes of the constituents of the glass.

c. 600 c. c. were evaporated nearly to dryness in a dish of Berlin porcelain, and, in all other respects, treated as in *b*.

The residue weighed	0·0015 grm.
Deducting from this the quantity of fixed matter contained in the distilled water, viz. . . .	0 0012 ,,
There remains substance dissolved out of the porcelain .	0·0003 ,,

= 0·0005 per 1000.

2. ACTION OF HYDROCHLORIC ACID UPON GLASS, AND PORCELAIN VESSELS, IN THE PROCESS OF EVAPORATION (to § 24).

The distilled water used in 1. was mixed with one-tenth of pure hydrochloric acid.

a. 300 grammes, evaporated in a platinum dish, left 0·002 grm. residue.

b. 300 grammes, evaporated first in Bohemian glass nearly to dryness, then in a platinum dish, left 0·0019 residue; the dilute hydrochloric acid, therefore, had not affected the glass.

c. 300 grammes, evaporated in Berlin porcelain, &c., left 0·0036 grm., accordingly after deducting 0·002, 0·0016 = 0·0053 per 1000.

d. In a second experiment made in the same manner as in *c.*, the residue amounted to 0·0034, accordingly after deducting 0·002, 0·0014 = 0·0047 per 1000.

Hydrochloric acid, therefore, affects glass much less than water, whilst in the case of porcelain it is about the same. This shows that the action of the water upon the glass causes the formation of soluble basic silicates.

3. ACTION OF SOLUTION OF CHLORIDE OF AMMONIUM UPON GLASS AND PORCELAIN VESSELS, IN THE PROCESS OF EVAPORATION (to § 24).

In the distilled water of 1, one-tenth of chloride of ammonium was dissolved, and the solution filtered.

a. 300 c. c. evaporated in a platinum dish, left 0·006 grm, of fixed residue.

b. 300 c. c., evaporated first nearly to dryness in Bohemian glass, then to dryness in a platinum dish, left 0·0179 grm.; deducting from this 0·006 grm., there remains 0·0119=0·0397 per 1000 of dissolved constituents of the glass.

c. 300 c. c., treated in the same manner in Berlin porcelain, left 0·0178; deducting from this 0·006, there remains 0·0118=0·0393 per 1000.

Solution of chloride of ammonium, therefore, strongly affects both glass and porcelain in the process of evaporation.

4. ACTION OF SOLUTION OF CARBONATE OF SODA UPON GLASS AND PORCELAIN VESSELS (to § 24).

In the distilled water of 1, one-tenth of pure crystallised carbonate of soda was dissolved.

a. 300 c. c., supersaturated with hydrochloric acid and evaporated to dryness in a platinum dish, &c., left 0·0026 grm. of silicic acid=0·0087 per 1000.

b. 300 c. c. were gently boiled for three hours in a glass vessel, the evaporating water being replaced from time to time; the tolerably concentrated liquid was then treated as in *a.*; it left a residue weighing 0·1376 grm.; deducting from this the 0·0026 grm. left in *a.*, there remains 0·135 grm.=0·450 per 1000.

c. 300 c. c., treated in the same manner as in *b.*, in a porcelain vessel, left 0·0099; deducting from this 0·0026 grm., there remains 0·0073= 0·0243 per 1000.

Which shows that boiling solution of carbonate of soda affects glass very strongly, and porcelain also in a very marked manner.

5. WATER DISTILLED FROM GLASS VESSELS (to § 39, 1).

42·41 grammes of water which had been distilled with extreme caution from a tall glass flask with a LIEBIG's condensing tube, left upon evaporation in a platinum dish, a residue weighing, after ignition, 0·0018 grm., consequently $\frac{1}{23561}$.

6. SULPHATE OF POTASSA AND ALCOHOL (to § 47, *a.*).

a. Ignited pure sulphate of potassa was digested cold with absolute alcohol, for several days, with frequent shaking of the mixture; the fluid was filtered off, the filtrate diluted with water, and then mixed with chloride of barium. It remained perfectly clear upon the addition of this reagent, but after the lapse of a considerable time it began to exhibit a slight opalescence. Upon evaporation to dryness there remained a very trifling residue, which manifested, however, a distinct reaction of sulphuric acid.

b. The same salt treated in the same manner, with addition of some pure concentrated sulphuric acid, gave a filtrate, which upon evaporation in a platinum dish left a clearly perceptible fixed residue of sulphate of potassa.

7. DEPORTMENT OF CHLORIDE OF POTASSIUM IN THE AIR AND AT A HIGH TEMPERATURE (to § 47, *c.*).

0·9727 grm. of ignited (not fused) pure chloride of potassium, heated for ten minutes to dull redness in an open platinum dish, lost 0·0007 grm.;

the salt was then kept for ten minutes longer at the same temperature, when no further diminution of weight was observed. Heated to bright redness and semi-fusion, the salt suffered a further loss of weight to the extent of 0·0009 grm. Ignited intensely and to perfect fusion, it lost 0·0034 grm., in addition to the former 0·0007 and 0·0009 grm.

Eighteen hours exposure to the air produced not the slightest increase of weight.

8. SOLUBILITY OF POTASSIO-BICHLORIDE OF PLATINUM (BICHLORIDE OF PLATINUM AND CHLORIDE OF POTASSIUM) IN ALCOHOL (to § 47, *d.*).

a. In absence of free hydrochloric acid.

α. An excess of perfectly pure, recently precipitated, potassio-bichloride of platinum was digested for six days at from 59° to 68°, with alcohol of 97·5 per cent, in a stoppered bottle, with frequent shaking of the mixture. 72·5 grammes of the perfectly colorless filtrate left upon evaporation in a platinum dish, a residue which, dried at 212°, weighed 0·006 grm. The solution of one part of potassio-bichloride of platinum requires therefore 12083 parts of alcohol of 97·5 per cent.

β. The same experiment was made with spirit of wine of 76 per cent. The filtrate was nearly colorless; upon evaporation, slight blackening ensued, on which account the residue was determined as platinum. 75·5 grammes yielded 0·008 grm. of platinum corresponding to 0·02 grm. of the potassio-bichloride. One part of the latter salt dissolves accordingly in 3775 parts of spirit of wine of 76 per cent.

γ. The same experiment was made with spirit of wine of 55 per cent: the filtrate was distinctly yellowish. 63·2 grammes left 0·0241 grm. of platinum, corresponding to 0·06 grm. of the potassio-bichloride. One part of this latter salt dissolves accordingly in 1053 parts of spirit of wine of 55 per cent.

b. In presence of free hydrochloric acid.

Recently precipitated potassio-bichloride of platinum was digested cold with spirit of wine of 76 per cent, to which some hydrochloric acid had been added. The solution was yellowish; 67 grammes left 0·0146 grm. of platinum, which corresponds to 0·0365 grm. of the potassio-bichloride. One part of the latter salt dissolves accordingly in 1835 parts of spirit of wine of 76 per cent, mixed with hydrochloric acid.

9. SULPHATE OF SODA AND ALCOHOL (to § 48, *a.*).

Experiments made with pure anhydrous sulphate of soda, in the manner described at 6, showed that this salt comports itself both with pure alcohol, and alcohol containing sulphuric acid, exactly like the sulphate of potassa.

10. Deportment of ignited sulphate of soda in the air (to § 48, *a.*).

2·5169 grammes of anhydrous sulphate of soda were exposed in a watch-glass to the open air on a hot summer day. The first few minutes passed without any increase of weight, but after the lapse of five hours an increase of 0·0061 grm. was observed.

11. Experiments with nitrate of soda (to § 48, *b.*).

a. 4·5479 grammes of pure nitrate of soda exposed, in a state of fusion, to the air (in April, in fine weather), exhibited after the lapse of twenty-four hours, an increase of weight of 0·0006 grm.

b. 4·5479 grammes of pure nitrate of soda were dissolved in water, in a platinum dish, and pure nitric acid added to the solution; the mixture was then evaporated to dryness on the water-bath, and the residue cautiously heated until the mass at the bottom of the dish began to fuse. The contents of the dish weighed, after cooling, 4·5503 grammes. It was then again heated to complete fusion, and when cold it weighed 4·5474 grammes.

12. Deportment of chloride of sodium in the air (to § 48, *c.*).

4·3281 grammes of chemically pure, intensely ignited (but not fused) chloride of sodium, which had been cooled under a bell-glass over sulphuric acid, acquired during forty-five minutes exposure to the (somewhat moist) air, an increase of weight of 0·0009 grm.

13. Deportment of chloride of sodium upon ignition both with and without chloride of ammonium (to § 48, *c.*).

4·3281 grammes of chemically pure, ignited chloride of sodium were dissolved in water in a middle-sized platinum dish, and pure chloride of ammonium was added to the solution, which was then evaporated and the residue gently heated until the evolution of chloride of ammonium fumes had apparently ceased. The residue weighed 4·3334 grammes. It was then very gently ignited for about two minutes, and after this reweighed, when the weight was found to be 4·3314 grammes. A few minutes ignition at a red heat reduced the weight to 4·3275 grammes, and two minutes further ignition at a bright red heat (upon which occasion white fumes were seen to escape), to 4·3249 grammes.

14. Deportment of chloride of ammonium upon evaporation and drying (to § 49, *a.*).

0·5625 grm. of pure and perfectly dry chloride of ammonium were dissolved in water in a platinum dish, and the solution was evaporated to dryness in the water-bath; the weight was now found to be 0·5622 grm. (ratio 100 : 99·94). It was again heated for fifteen minutes in the

water-bath, and afterwards reweighed, when the weight was found to be 0·5612 grm. (ratio 100 : 99·77). Exposed once more for fifteen minutes to the same temperature, the residue weighed 0·5608 grm. (ratio 100 : 99·69).

15. Solubility of ammonio-bichloride of platinum (bichloride of platinum and chloride of ammonium) in alcohol (to § 49, *b*.).

a. In the absence of free hydrochloric acid.

α. An excess of perfectly pure, recently precipitated ammonio-bichloride of platinum was digested for six days, at from 59° to 68°, with alcohol of 97·5 per cent., in a stoppered bottle, the action of the alcohol being aided by frequent agitation.

74·03 grammes of the perfectly colorless filtrate left, upon evaporation in a platinum dish, a residue of platinum which, after ignition, weighed 0·0012 grm., corresponding to 0·0028 of the ammonio-bichloride. One part of the latter salt dissolves accordingly in 26535 parts of alcohol of 97·5 per cent.

β. The same experiment was made with spirit of wine of 76 per cent. The filtrate was distinctly yellowish.

81·75 grammes left 0·0257 grm. of platinum, which corresponds to 0·0584 grm. of the ammonio-bichloride. One part of the latter salt dissolves accordingly in 1406 parts of spirit of wine of 76 per cent.

γ. The same experiment was made with spirit of wine of 55 per cent. The filtrate was distinctly yellow. Slight blackening ensued upon evaporation, and 56·5 grammes of the filtrate left 0·0364 grm. of platinum, which corresponds to 0·08272 grm. of the ammonio-bichloride. Consequently one part of the latter salt dissolves in 665 parts of spirit of wine of 55 per cent.

b. In presence of hydrochloric acid.

The experiment described in *β*. was repeated, with this modification, that some hydrochloric acid was added to the spirit of wine. 76·5 grammes left 0·0501 grm. of platinum, which corresponds to 0·1139 grm. of the ammonio-bichloride. 672 parts of the acidified alcohol had therefore dissolved one part of ammonio-bichloride of platinum.

16. Solubility of carbonate of baryta in water (to § 50, *b*.).

a. In cold water. Perfectly pure, recently precipitated carbonate of baryta (Ba O, CO_2) was digested for five days with water of from 60·8 to 68°, with frequent shaking of the mixture. The solution was filtered, and a portion of the filtrate tested with sulphuric acid, and another portion with ammonia; the former reagent immediately produced turbidity in the fluid, the latter only after the lapse of a considerable time. 84·82

grammes of the solution left, upon evaporation, 0·006 of Ba O, CO_2. One part of that salt dissolves consequently in 14137 parts of cold water.

b. In hot water. The same carbonate of baryta being boiled for ten minutes with pure distilled water, gave a filtrate manifesting the same reactions as that prepared with cold water, and remained perfectly clear upon cooling. 84·82 grammes of the hot solution left, upon evaporation, 0·0055 grm. of carbonate of baryta. One part of that salt dissolves therefore in 15421 parts of boiling water.

17. Solubility of carbonate of baryta in water containing ammonia and carbonate of ammonia (to § 50, *b.*).

A solution of chemically pure chloride of barium was mixed with ammonia and carbonate of ammonia in excess, and the mixture gently heated and allowed to stand at rest for twelve hours; the fluid was then filtered off; the filtrate remained perfectly clear upon addition of sulphuric acid; but after the lapse of a very considerable time, a hardly perceptible precipitate separated. 84·82 grammes of the filtrate left, upon evaporation in a small platinum dish, and subsequent gentle ignition of the residue, 0·0006 grm. of carbonate of baryta. One part of this salt had dissolved in 141000 parts of the fluid.

18. Solubility of silico-fluoride of barium in water (to § 50, *c.*).

a. Recently precipitated, thoroughly washed silico-fluoride of barium was digested for four days in cold water, with frequent shaking of the mixture; the fluid was then filtered off, and a portion of the filtrate tested with dilute sulphuric acid, another portion with solution of sulphate of lime; both reagents produced turbidity, the former immediately, the latter after one or two seconds,—precipitates separated from both portions after the lapse of some time. 84·82 grammes of the filtrate left a residue which, after being thoroughly dried, weighed 0·0223 grm. One part of the salt had consequently required 3802 parts of cold water for its solution.

b. Another sample of recently precipitated silico-fluoride of barium was heated with water to ebullition, and the solution allowed to cool (upon which a portion of the dissolved salt separated again). The cold fluid was left for a considerable time longer in contact with the undissolved salt, and was then filtered off. The filtrate showed the same deportment with solution of sulphate of lime as that of *a.* 84·82 grammes of it left 0·025 grm. of silico-fluoride of barium. One part of that salt had accordingly dissolved in 3392 parts of water.

19. Solubility of silico-fluoride of barium in water acidified with hydrochloric acid (to § 50, *c.*).

a. Recently precipitated, pure silico-fluoride of barium was digested for three weeks with cold water acidified with hydrochloric acid, the dissolving action of the water being aided by frequent agitation of the mixture. The filtrate gave with sulphuric acid a rather copious precipitate. 84·82 grammes left 0·1155 grm. of thoroughly dried residue, which, calculated as silico-fluoride of barium, gives 733 parts of fluid to one part of that salt.

b. Recently precipitated, pure silico-fluoride of barium was mixed with water very slightly acidified with hydrochloric acid, and the mixture heated to boiling. 84·82 grammes of the filtrate, cooled down to 53·6°, left a residue of 0·1322 grm., which gives 640 parts of fluid to one part of the salt.

N.B. The solution of silico-fluoride of barium in hydrochloric acid is not effected without decomposition; at least, the residue contained, even after ignition, a rather large proportion of chloride of barium.

20. Solubility of sulphate of strontia in water (to § 51, *a.*).

a. In water of 57·2°.

84·82 grammes of a solution prepared by four days' digestion of recently precipitated sulphate of strontia with water of the common temperature, left 0·0123 grm. of sulphate of strontia. One part of Sr O, SO_3 dissolves consequently in 6895 parts of water.

b. In water of 212°.

84·82 grammes of a solution prepared by boiling recently precipitated sulphate of strontia several hours with water, left 0·0088 grm. of sulphate of strontia. Consequently one part of SrO, SO_3 dissolves in 9638 parts of boiling water.

21. Solubility of sulphate of strontia in water containing hydrochloric acid and sulphuric acid (to § 51, *a.*).

a. 84·82 grammes of a solution prepared by three days' digestion, left 0·0077 grm. of Sr O, SO_3.

b. 42·41 grammes of a solution prepared by four days' digestion, left 0·0036 grm.

c. Pure carbonate of strontia was dissolved in an excess of hydrochloric acid, and the solution precipitated with an excess of sulphuric acid and then allowed to stand in the cold for a fortnight. 84·82 grammes of the filtrate left 0·0066 gram.

In *a.*	1 part of Sr O, SO_3	required	11016 parts.
b.	1 „	„	11780 „
c.	1 „	„	12791 „
		Mean . .	11862

22. Solubility of carbonate of strontia in cold water (to § 51, *b.*).

Recently precipitated, thoroughly washed carbonate of strontia (SrO, CO_2) was digested several days with cold distilled water, with frequent shaking. 84·82 grammes of the filtrate left, upon evaporation, a residue weighing, after ignition, 0·0047 grm. One part of carbonate of strontia requires therefore 18045 parts of water for its solution.

23. Solubility of carbonate of strontia in water containing ammonia and carbonate of ammonia (to § 51, *b.*).

Recently precipitated, thoroughly washed carbonate of strontia was digested for four weeks with cold water containing ammonia and carbonate of ammonia, the operation being aided by frequent shaking. 84·82 grammes of the filtrate left 0·0015 grm. of SrO, CO_2. Consequently one part of the salt requires 56545 parts of this fluid for its solution.

If solution of chloride of strontium is precipitated with carbonate of ammonia and ammonia (§ 80, 2, *a.*), sulphuric acid produces no turbidity in the filtrate, after previous addition of alcohol.

24. Solubility of carbonate of lime in cold water (to § 52, *b.*).

Recently precipitated carbonate of lime was boiled for some time with distilled water, and the fluid then digested cold, for four weeks, with the undissolved residue; the operation being aided by frequent shaking. 84·82 grammes of the filtrate left 0·0080 of CaO, CO_2. One part of the carbonate requires consequently 10601 parts of cold water for its solution.

25. Solubility of carbonate of lime in boiling water (to § 52, *b.*).

Recently precipitated CaO, CO_2 was boiled for some time with distilled water. 42·41 grammes of the filtrate left, upon evaporation and subsequent gentle ignition of the residue, 0·0048 grm. of CaO, CO_2. The solution of one part of carbonate of lime requires consequently 8834 parts of boiling water.

26. Solubility of CaO, CO_2 in water containing ammonia and carbonate of ammonia (to § 52, *b.*).

Pure solution of chloride of calcium was precipitated with carbonate of ammonia and ammonia, and the precipitate allowed twenty-four hours to subside; the fluid was then filtered off. 84·82 grammes of the filtrate

left 0·0013 grm. of Ca O, CO_2. One part of carbonate of lime requires consequently 65246 parts of this fluid for its solution.

27. Deportment of carbonate of lime upon ignition in a platinum crucible (to § 52, *b.*).

0·7955 grm. of perfectly dry carbonate of lime were exposed, in a small and thin platinum crucible, to the gradually increased, and finally most intense heat of a good *Berzelius*' lamp. The crucible was open and placed obliquely (Fig. 37). After the first fifteen minutes the mass weighed 0·6482 grm.,—after half an hour 0·6256 grm.,—after one hour 0·5927 grm., which latter weight remained unaltered after fifteen minutes' additional heating. This corresponds to 74·5 per cent, whilst the proportion of lime in the carbonate is calculated at 56 per cent; there remains therefore evidently still a considerable amount of the carbonic acid.

28. Composition of oxalate of lime dried at 212° (to § 52, *c.*).

0·8510 grm. of pure, thoroughly dry carbonate of lime were dissolved in hydrochloric acid; the solution was precipitated with oxalate of ammonia and ammonia, and the precipitate collected upon a tared filter and dried at 212° until the weight remained constant. The oxalate of lime so produced weighed 1·2461 grm. Calculating this as Ca O, $C_2 O_3$ + aq, the amount found contained 0·4772 of Ca O, which corresponds to 56·07 per cent in the carbonate of lime; the calculated proportion of lime in the latter is 56 per cent.

29. Deportment of sulphate of magnesia in the air and upon ignition (to § 53, *a.*).

0·8135 grm. of perfectly pure, anhydrous MgO, SO_3 in a covered platinum crucible, acquired by exposure on a fine and warm day in June, in half an hour, an increase of weight of 0·004 grm., and in the course of twelve hours, 0·067 grm. Exposed to the air in the open crucible, the salt could not be accurately weighed, owing to its continuous increase.

0·8135 grm., exposed for some time to a very moderate red heat, suffered no diminution of weight; but, after five minutes, exposure to an intense red heat, they were found to have lost 0·0075 grm, and the solution of the residue in water gave no longer a clear fluid.

30. Solubility of the basic phosphate of magnesia and ammonia in pure water (to § 53).

a. Recently precipitated basic phosphate of magnesia and ammonia was thoroughly washed with water, and then digested for twenty-four hours with water of about 59°, with frequent shaking.

84·42 grammes of the filtrate left . . . 0·0047 grm. of pyrophosphate of magnesia.

b. The same precipitate was digested in the same manner for seventy-two hours.

84·42 grammes of the filtrate left . . . 0·0043 grm.

Average 0·0045 grm.

which corresponds to 0·00552 grm. of the anhydrous double salt. One part of that salt dissolves therefore in 15293 parts of pure water.

The cold saturated solution gave with ammonia, after the lapse of a short time, a distinctly perceptible crystalline precipitate ;—on the addition of phosphate of soda, it remained perfectly clear, and even after the lapse of two days no precipitate had formed ;—phosphate of soda and ammonia produced a precipitate as large as that by ammonia.

31. SOLUBILITY OF BASIC PHOSPHATE OF MAGNESIA AND AMMONIA IN WATER CONTAINING AMMONIA (to § 53, *b*.).

a. Pure basic phosphate of magnesia and ammonia was dissolved in the least possible amount of nitric acid ; a large quantity of water was added to the solution, and then ammonia in excess. The mixture was allowed to stand at rest for twenty-four hours, and then filtered ; its temperature was 57·2°. 84·42 grammes of the filtrate left 0·0015 grm. of pyrophosphate of magnesia, which corresponds to 0·00184 grm. of the anhydrous double salt. Consequently one part requires 45880 parts of ammoniated water for its solution.

b. Pure basic phosphate of magnesia and ammonia was digested for four weeks with ammoniated water, the operation being aided by frequent shaking ; the fluid (temperature 57·2°) was then filtered off ; 126·63 grammes of the filtrate left 0·0024 grm. of the pyrophosphate of magnesia, which corresponds to 0·00296 grm. of the double salt. One part of it therefore dissolves in 42780 parts of ammoniated water ; taking the average of *a*. and *b*., one part of the double salt requires 44330 parts of ammoniated water for solution.

32. ANOTHER EXPERIMENT OF THE SAME SUBSTANCE AS 31.

Recently precipitated phosphate of magnesia and ammonia, most carefully washed with water containing ammonia, was dissolved in water acidified with hydrochloric acid, ammonia added to the solution, and the fluid allowed to stand in the cold for twenty-four hours. 169·64 grammes of the filtrate left 0·0031 grm. of pyrophosphate of magnesia, corresponding to 0·0038 of anhydrous phosphate of magnesia and ammonia. One part of the double salt required therefore 44600 parts of the fluid.

33. Solubility of the basic phosphate of magnesia and ammonia in water containing chloride of ammonium (to § 53, *b.*).

Recently precipitated, thoroughly washed basic phosphate of magnesia and ammonia was digested cold with a solution of one part of chloride of ammonium in five parts of water. 18·4945 grammes of the filtrate left 0·002 grm. of pyrophosphate of magnesia, which corresponds to 0·00245 grm. of the double salt. One part of the salt dissolves therefore in 7548 parts of the fluid.

34. Solubility of the basic phosphate of magnesia and ammonia in water containing ammonia and chloride of ammonium (to § 53, *b.*).

Recently precipitated, thoroughly washed phosphate of magnesia and ammonia was digested cold with a solution of one part of chloride of ammonium in seven parts of ammoniated water. 23·1283 grammes of the filtrate left 0·0012 grm. of pyrophosphate of magnesia, which corresponds to 0·00148 grm. of the double salt. One part of the double salt requires consequently 15627 parts of the fluid for its solution.

35. Deportment of acid solutions of pyrophosphate of magnesia with ammonia (to § 53, *c.*).

0·3985 grm. of pyrophosphate of magnesia were treated for several hours, at a high temperature, with concentrated sulphuric acid. This exercised no perceptible action. It was only after the addition of some water that the precipitate dissolved. The fluid heated for some time gave, upon addition of ammonia in excess, a crystalline precipitate. After eighteen hours it was filtered from the latter, which gave 0·3805 grm. of pyrophosphate of magnesia, that is, 95·48 per cent. Phosphate of soda produced in the filtrate a trifling precipitate, which gave 0·0150 grm. of pyrophosphate of magnesia, that is 3·76 per cent. 0·3565 grm. of pyrophosphate of magnesia were dissolved in 3 grammes of nitric acid of 1·2 specific gravity ; the solution was heated, diluted, and precipitated with ammonia : the quantity of pyrophosphate of magnesia reprecipitated amounted to 0·3485 grm., that is, 98·42 per cent ; 0·4975 grm. were treated in the same manner with 7·6 grammes of the same nitric acid : the quantity re-obtained was 0·4935 grm., that is. 99·19 per cent.

0·786 grm., treated in the same manner with 16·2 grammes of nitric acid, gave 0·7765 grm., that is, 98·79 per cent.

Therefore :—

Proportion of the nitric acid to the $2\,MgO, P_2O_5$.	Re-obtained.	Loss.
1 : 9	98·42	1·58
1 : 15	99·19	0·81
1 : 20	98·79	1·21

36. SOLUBILITY OF PURE MAGNESIA IN WATER (to § 53, *d.*).

a. In cold water.

Perfectly pure well crystallised sulphate of magnesia was dissolved in water, and the solution precipitated with carbonate of ammonia and caustic ammonia; the precipitate was thoroughly washed—(and yet, notwithstanding, it retained still a perceptible trace of sulphuric acid)—and then dissolved in pure nitric acid. The solution (which contained no free acid) was then again precipitated with carbonate of ammonia and caustic ammonia, and the precipitate again thoroughly washed. The so prepared perfectly pure basic carbonate of magnesia was ignited in a platinum crucible until the weight remained constant. The residuary pure magnesia was then digested cold for twenty-four hours with distilled water, the operation being aided by frequent shaking. (The distilled water was perfectly free from chlorine, and left no fixed residue upon evaporation.)

α. 84·82 grammes of the filtrate, cautiously evaporated in a platinum dish, left a residue weighing, after ignition, 0·0015 grm. One part of the pure magnesia dissolved therefore in . . . 56546 parts of cold water.

The digestion was continued for forty-eight hours longer, when

β. 84·82 grammes of the filtrate left 0·0016 grm. One part of the magnesia required therefore . . . 53012

γ. 84·82 grammes of the filtrate left 0·0015 grm. One part required 56546

Average 55368

The cold prepared solution of magnesia in water has a feebly yet distinctly alkaline reaction, which is most easily perceived upon the addition of very faintly reddened tincture of litmus; the alkaline reaction of the solution is perfectly manifest also with slightly reddened litmus paper, or with turmeric or dahlia paper, if these test-papers are left for some time in contact with the solution.

Alkaline carbonates fail to render the solution turbid, even upon ebullition. Phosphate of soda also fails to impair the clearness of the solution, but if ammonia is added, and the fluid shaken, the latter becomes speedily turbid, and deposits after some time a perceptible precipitate of basic phosphate of magnesia and ammonia.

b. In hot water.

Upon boiling pure magnesia with water, a solution is obtained which comports itself in every respect like the cold prepared solution of magnesia. A hot prepared solution of magnesia does not become turbid upon cooling,

nor does a cold prepared solution upon ebullition. 84·82 grammes of hot prepared solution of magnesia left 0·0016 grm. of Mg O.

37. Precipitation of alumina by ammonia, etc. (to § 54, *a*.).

a. Ammonia produces in neutral solutions of alumina or of alum, gelatinous precipitates of hydrate of alumina. Upon further addition of ammonia in considerable excess, the precipitate redissolves gradually, without however disappearing altogether.

b. If a drop of a dilute solution of alum is mixed with a copious amount of ammonia, and the mixture shaken, the solution appears almost perfectly clear, but, after standing at rest for some time, slight flakes separate.

c. If a solution of alumina, mixed with a large amount of ammonia is filtered, and

α. The filtrate is boiled for a considerable time, flakes of hydrate of alumina separate gradually as the excess of ammonia escapes.

β. The filtrate is mixed with solution of chloride of ammonium, a very perceptible flocculent precipitate of hydrate of alumina separates immediately; the whole of the hydrated alumina present in the solution will thus separate if the chloride of ammonium be added in sufficient quantity.

γ. The filtrate is mixed with sesquicarbonate of ammonia, the same reaction takes place as in *β*.

δ. The filtrate is mixed with solution of chloride of sodium or chloride of potassium, no precipitate separates, but after several days' standing, slight flakes of hydrate of alumina subside, owing to the decrease of ammonia by evaporation.

d. If a neutral solution of alumina is precipitated with carbonate of ammonia, or a strongly acidified (with hydrochloric or nitric acid) solution with pure ammonia; or if to a neutral solution a sufficient amount of chloride of ammonium is added besides the ammonia, even a considerable excess of the precipitants will fail to redissolve the precipitated alumina, as appears from the continued perfect clearness of the filtrates upon protracted boiling and evaporation.

38. Precipitation of alumina by sulphide of ammonium (to § 54, *a*.).

(*Experiments made by Mr. J. Fuchs, formerly assistant in my laboratory*).

a. 50 c. c. of a solution of pure ammonia-alum, which contained 0·3939 of alumina, were mixed with 50 c. c. of water and 10 c. c. of sulphide of ammonium, and the mixture was filtered after the lapse of ten minutes. The precipitate weighed, after ignition, 0·3825 grm.

b. The same experiment was repeated with 100 c. c. of water; the precipitate weighed 0·3759.

c. The same experiment was repeated with 200 c. c. of water; the precipitated alumina weighed 0·3642.

39. PRECIPITATION OF SESQUIOXIDE OF CHROMIUM BY AMMONIA (to § 55, *a*.).

Solutions of protochloride of chromium and of chrome-alum (concentrated and dilute, neutral and acidified with hydrochloric acid) were mixed with ammonia in excess. All the filtrates drawn off immediately after precipitation appeared red, but when filtered after previous ebullition, they all appeared colorless, if the ebullition had been sufficiently protracted.

40. SOLUBILITY OF THE BASIC CARBONATE OF ZINC IN WATER (to § 56, *a*.).

Perfectly pure, recently (hot) precipitated basic carbonate of zinc was heated with distilled water, and subsequently digested cold for many weeks, the operation being aided by frequent shaking. The clear solution gave no precipitate with sulphide of ammonium, not even after long standing.

84·82 grammes left 0·0014 grm. of oxide of zinc, which corresponds to 0·0019 of basic carbonate of zinc (Zn O assumed = 74 per cent in this salt). One part of the basic carbonate requires therefore 44642 parts of water for solution.

41. DEPORTMENT OF SULPHIDE OF NICKEL WITH SULPHIDE OF AMMONIUM, ETC. (to § 58, *c*.).

A dilute solution of pure sulphate of protoxide of nickel and potassa was mixed with a very slight excess of colorless hydrosulphate of sulphide of ammonium perfectly saturated with sulphuretted hydrogen. The following experiments were then made with the precipitated fluid:

a. One portion was filtered off at once. The filtrate was and remained perfectly clear and colorless.

b. Another portion was digested with an excess of colorless and perfectly saturated hydrosulphate of sulphide of ammonium; and

α. Filtered without previous application of heat. The filtrate presented a hardly perceptible shade of yellow; no precipitate separated, even after long standing.

β. Filtered after previous application of heat. The filtered fluid exhibited a more marked shade of yellow, and deposited some sulphide of nickel, after several days' standing.

c. Another portion was digested with an excess of yellow sulphide of ammonium (prepared by exposing perfectly saturated hydrosulphate of sulphide of ammonium to the action of the air). The filtrate was yellow

without the least shade of brown; after several days' standing, a slight precipitate of sulphide of nickel had separated.

d. Another portion was digested cold with ammoniated water. The filtrate exhibited a faint brownish tint.

e. Another portion was digested with ammonia and colorless hydrosulphate of sulphide of ammonium. The filtrate was of a distinct light brown color. After several days' standing a slight precipitate of sulphide of nickel had separated.

f. Another portion was digested with ammonia and yellow sulphide of ammonium. The filtrate was likewise of a brownish color, and comported itself like the filtrate of *e.*

42. DEPORTMENT OF HYDRATE OF PROTOXIDE OF COBALT PRECIPITATED BY ALKALIES (to § 59, *a.*).

A solution of protochloride of cobalt was precipitated boiling with solution of soda and the precipitate washed with boiling water until the filtrate gave no longer the least indication of presence of chlorine. The dried and ignited residue, heated with water, manifested no alkaline reaction. It was reduced by ignition in hydrogen gas, and the reduced metallic cobalt digested hot with water. The decanted water manifested no alkaline reaction, even after considerable concentration; but the metallic cobalt, brought into contact, moist, with turmeric paper, imparted to the latter a strong brown color.

43. SOLUBILITY OF CARBONATE OF LEAD (to § 62, *a.*).

a. In pure water.

Recently precipitated, pure, and thoroughly washed carbonate of lead was digested for eight days with water at the common temperature, the operation being aided by frequent shaking. 84·82 grammes of the filtrate were evaporated, some pure sulphuric acid being added during the process; the residuary sulphate of lead weighed 0·0019 grm., which corresponds to 0·00167 grm. of carbonate of lead. One part of the latter salt dissolves therefore in 50551 parts of water. The solution, mixed with sulphuretted hydrogen water, remained perfectly colorless, not the least tint being detected in it, even upon looking through it from the top of the test cylinder.

b. In water containing a little acetate of ammonia and also carbonate of ammonia and ammonia.

A highly dilute solution of pure acetate of lead was mixed with carbonate of ammonia and ammonia in excess, and the mixture gently heated and allowed to stand at rest for several days. 84·42 grammes of the filtrate left, upon evaporation with a little sulphuric acid, 0·0041 grm. of sulphate of lead, which corresponds to 0·0036 grm. of the carbonate.

One part of the latter salt requires accordingly 23450 parts of the fluid *b.* for solution. The solution was mixed with sulphuretted hydrogen water ; when looking through the fluid from the top of the test cylinder, a distinct coloration was visible, but when looking through the cylinder laterally this coloration was hardly perceptible. Traces of sulphide of lead separated after the lapse of some time.

c. In water containing a large proportion of nitrate of ammonia, together with carbonate of ammonia and caustic ammonia.

A highly dilute solution of acetate of lead was mixed with nitric acid, and then with carbonate of ammonia and caustic ammonia in excess ; the mixture was gently heated, and allowed to stand at rest for eight days. The filtrate, mixed with sulphuretted hydrogen, exhibited a very distinct brownish color, upon looking through it from the top of the cylinder, but this color appeared very slight only when looking through the cylinder laterally. The amount of lead dissolved was unquestionably more considerable than the quantity dissolved in *b.*

44. Solubility of oxalate of lead (to § 62, *b.*).

A dilute solution of acetate of lead was precipitated with oxalate of ammonia and ammonia, and the mixture allowed to stand at rest for some time, and then filtered. The filtrate, mixed with sulphuretted hydrogen, comported itself exactly like the filtrate of 43, *b.* The same deportment was observed in another similar experiment, in which nitrate of ammonia had been added to the solution.

45. Solubility of sulphate of lead in pure water (to § 62, *d.*)

Thoroughly washed and still moist sulphate of lead was digested for five days with water, at a temperature of from 50° to 59° the operation being aided by frequent shaking. 84·42 grammes of the filtrate (filtered off at 51·8°) left 0·0037 grm. of sulphate of lead. Consequently one part of this salt requires 22816 parts of pure water of 51·8° for solution.

The solution, mixed with sulphuretted hydrogen exhibited a distinct brown color when viewed from the top of the cylinder, but this color appeared very slight upon looking through the cylinder laterally.

46. Solubility of sulphate of lead in water containing sulphuric acid (to § 62, *d.*)

A highly dilute solution of acetate of lead was mixed with an excess of dilute pure sulphuric acid ; the mixture was very gently heated, and the precipitate allowed several days to subside. 80·31 grammes of the filtrate left 0·0022 grm. of sulphate of lead. One part of this salt dissolves

therefore in 36504 parts of water containing sulphuric acid. The solution, mixed with sulphuretted hydrogen, appeared colorless to the eye looking through the cylinder laterally, and very little darker when viewed from the top of the cylinder.

47. Solubility of sulphate of lead in water containing ammoniacal salts and free sulphuric acid (to § 62, *d.*).

A highly dilute solution of acetate of lead was mixed with a tolerably large amount of nitrate of ammonia, and sulphuric acid in excess added. After several days' standing, the mixture was filtered. The filtrate was nearly indifferent to sulphuretted hydrogen water; and, viewed from the top of the cylinder, it looked hardly perceptibly darker than pure water.

48. Deportment of sulphate of lead upon ignition (to § 62, *d.*).

Speaking of the determination of the atomic weight of sulphur, *Erdmann* and *Marchand* (Journal für praktische Chemie, xxxi. s. 385) state that sulphate of lead loses some sulphuric acid upon ignition. To test the correctness of this statement, and to ascertain in how much this loss might impair the accuracy of the method of determining lead as a sulphate, I heated 2·2151 grammes of absolutely pure PbO, SO_3 to the most intense redness, over a spirit-lamp with double draught. I could not perceive the slightest decrease in the weight of the ignited compound; at all events, the decrease did not amount to 0·0001 grm.

49. Deportment of solutions of lead with sulphuretted hydrogen (to § 62, *f.*).

It is a well known fact that solutions of lead which contain much free acid are not precipitated by sulphuretted hydrogen unless diluted with water. *Triboulet* (Archiv. der Pharmacie, xxix. s. 234) maintains that sulphuretted hydrogen fails to precipitate the whole of the lead from solutions of lead mixed with solution of acetate of potassa; but that the lead will completely precipitate if ammonia is added. To test the correctness of this statement, I added to a concentrated solution of acetate of potassa, mixed with solution of neutral acetate of lead, and acidified with a drop of acetic acid; *a.* sulphuretted hydrogen water in excess; *b.* sulphuretted hydrogen gas in excess. In both cases, the precipitation was so complete that the filtrates drawn off after vigorous agitation of the mixture suffered not the least alteration upon addition of ammonia and sulphide of ammonium. It is *certain*, therefore, that *Triboulet's* statement is erroneous, and *probable* that this error was caused by the presence of iron in the fluid upon which this chemist operated.

50. Deportment of metallic mercury at the common temperature and upon ebullition with water (to § 63, *a*.).

To ascertain in what manner loss of metallic mercury occurs upon drying, and likewise upon boiling with water, and to determine which is the best method of drying, I made the following experiments:

I placed 6·4418 grammes of perfectly pure mercury upon a watch-glass, poured distilled water over the metal, removed the water again as far as practicable (by decantation and finally by means of blotting-paper), and weighed. I found the weight to be 6·4412 grammes, which after several hours' exposure to the air were reduced to 6·4411 grammes. I placed these 6·4411 grammes under a bell-jar over sulphuric acid, the temperature being about 62° or 63°. After the lapse of twenty-four hours the weight had not altered in the least. I introduced the 6·4411 grammes of mercury into a flask, poured a copious quantity of distilled water over it, and strongly boiled the mixture for fifteen minutes. I then placed the mercury again upon the watch-glass, dried it most carefully with blotting-paper, and weighed. The weight was now 6·4402 grammes. Finding that a trace of mercury had adhered to the paper, I repeated the same experiment with the 6·4402 grammes. After fifteen minutes' boiling with water, the mercury had again lost 0·0004 grm. The remaining 6·4398 grammes were exposed to the air for six days (in summer, during very hot weather), after which they were found to have lost only 0·0005 grm.

51. Deportment of sulphide of mercury with potassa, sulphide of ammonium, etc. (to § 63, *c*.).

a. If pure recently precipitated sulphide of mercury is boiled with pure solution of potassa, not a trace of it dissolves in that fluid; hydrochloric acid produces no precipitate, nor even the least coloration, in the filtrate.

b. If sulphide of mercury is boiled with solution of potassa in conjunction with some sulphuretted hydrogen water, sulphide of ammonium, or sulphur, complete solution is effected.

c. Digestion of sulphide of mercury with sulphide of ammonium (no matter whether colorless or yellow) fails to dissolve the least trace of the mercurial sulphide—cyanide of potassium also fails to dissolve it. Hydrochloric acid produced in the sulphide of ammonium filtrate a pure white turbidity or precipitate, and in the cyanide of potassium filtrate not the least turbidity.

d. Thoroughly washed sulphide of mercury, moistened with water, suffers no alteration upon exposure to the air; at least, the fluid which I obtained by washing sulphide of mercury which had been thus exposed to the air for twenty-four hours, did not manifest acid reaction, nor did it contain mercury or sulphuric acid.

52. Deportment of oxide of copper upon ignition (to § 64, *a.*).

Pure oxide of copper (prepared from nitrate of copper) was ignited in a platinum crucible, then cooled under a bell-jar over sulphuric acid, and finally weighed. The weight was 3·542 grammes. The oxide was then most intensely ignited for five minutes, over a *Berzelius'* lamp, cooled and reweighed, when the weight was found unaltered; the oxide was then once more ignited for five minutes, but with the same result.

53. Deportment of oxide of copper in the air (to § 64, *a.*).

A platinum crucible containing 4·3921 grammes of gently ignited oxide of copper, prepared from the nitrate, was placed for ten minutes (covered with the lid) in a warm room (in winter); the weight of the oxide of copper was found to have increased to 4·3939 grammes.

The oxide of copper was then intensely ignited over a spirit-lamp; after ten minutes' standing in the covered crucible, the weight had not perceptibly increased—after twenty-four hours it had increased by 0·0036 grm.

54. Deportment of sulphide of cadmium with ammonia, etc. (§ to 66, *c.*).

Pure recently precipitated sulphide of cadmium was diffused through water, and the following experiments were made with the fluid.

a. A portion was digested cold with ammonia in excess, and the fluid filtered. The filtrate remained perfectly clear upon addition of hydrochloric acid.

b. Another portion was digested hot with excess of ammonia, and the fluid filtered. This filtrate likewise remained perfectly clear upon addition of hydrochloric acid.

c. Another portion was digested for some time with solution of cyanide of potassium, and the fluid filtered. This filtrate also remained perfectly clear upon addition of hydrochloric acid.

d. Another portion was digested with hydrosulphate of sulphide of ammonium, and the fluid filtered. The turbidity which hydrochloric acid imparted to this filtrate was of a pure white color.

(A remark made by *Wackenroder*, in *Buchner's* Repertorium der Pharmacie, xlvi. s. 226, induced me to make these experiments.)

55. Determination of soda in salts with organic acids (to § 77, 4.).

1·154 grm. of paratartrate of soda gave, upon intense ignition, after deduction of 0·004 grm. of charcoal, 0·63 grm. of NaO, CO_2, which corresponds to 0·3698 of NaO = 32·05 per cent (calculated 32·04 per cent); this gives 99·7 instead of 100.

56. Determination of baryta by precipitation with carbonate of ammonia (to § 79, 2. *a.*).

0·7553 grm. of pure ignited chloride of barium were precipitated according to the directions of § 79, 2, *a.*; the precipitate of Ba O, CO_2 weighed 0·7142 grm., which corresponds to 0·554719 of Ba O = 73·44 per cent (100 parts of Ba Cl ought to have given 73·59 parts). The result accordingly was 99·79 instead of 100.

57. Determination of baryta in organic salts (to § 79, 2, *b.*).

0·686 grm. of paratartrate of baryta [2 (Ba O, R) + 5 aq], treated according to the directions of § 79, 2, *b.*, gave 0·408 grm. of carbonate of baryta = 0·3168936 of Ba O = 46·20 per cent (calculated 46·36 per cent), which gives 99·61 instead of 100.

58. Determination of strontia as sulphate of strontia (to § 80, 1.).

a. An aqueous solution of 1·2398 grm. of SrCl was precipitated with SO_3 in excess, and the precipitated sulphate of strontia washed with water. It weighed 1·4113 grm., which corresponds to 0·795408 grm. of Sr O = 64·15 per cent (calculated 65·38 per cent); this gives 98·12 instead of 100.

b. 1·1510 grm. of Sr O, CO_2 was dissolved in hydrochloric acid in excess, the solution diluted, and then precipitated with SO_3; the precipitated Sr O, SO_3 was washed with water; it weighed 1·4024 grm. = 0·79039 Sr O = 68·68 per cent (calculated 70·07 per cent); this gives 98·02 instead of 100.

59. Determination of strontia as sulphate, with correction (to § 80, 1.).

The *filtrate* obtained in the experiment described 58, *b.*, weighed 190·84 grammes. According to experiment No. 21, 11862 parts of water containing sulphuric acid dissolve one part of sulphate of strontia. 190·84 grammes of the filtrate contain therefore 0·0161 grm. of that salt in solution. The *washing water* weighed 63·61 grammes. According to experiment No. 20, 6895 parts of water dissolve one part of Sr O, SO_3; the 63·61 grammes of washing water contain therefore 0·0092 grm.

Adding 0·0161 and 0·0092 gramme to the 1·4024 gramme of precipitated sulphate of strontia, we find the total amount = 1·4277 gramme, which corresponds to 0·80465 of Sr O = 69·91 per cent in Sr O, CO_2 (calculated 70·07 per cent); this gives 99·77 instead of 100.

60. Determination of strontia as carbonate of strontia (to § 80, 2.).

1·3104 of chloride of strontium, precipitated according to the direc-

tions of § 80, 2, gave 1·2204 grm. of Sr O, CO_2, containing 0·8551831 of Sr O = 65·26 per cent (calculated 65·38), which gives 99·82 instead of 100.

61. Determination of lime as sulphate of lime, by precipitation (to § 81, 1, *a.*).

(In the experiments described from 61 to 65, chemically pure air-dried carbonate of lime was used, in a portion of which the amount of anyhdrous carbonate had been determined by very cautious heating. 0·7647 grm. of the heated carbonate left 0·7581 grm., which weight remained unaltered upon further (most gentle) ignition of the carbonate; the air-dried carbonate contains accordingly 55·516 per cent of lime).

1·186 grm. of the said air-dried carbonate of lime was dissolved in hydrochloric acid, and the solution precipitated with sulphuric acid in conjunction with alcohol (see § 81, 1, *a.*). The precipitated sulphate of lime weighed 1·5949 grm., containing 0·65598 of Ca O = 55·31 per cent (calculated at 55·51), which gives 99·64 instead of 100.

62. Determination of Ca O as Ca O, CO_2, by precipitation with carbonate of ammonia and washing of the precipitate with pure water (to § 81, 2, *a.*).

An hydrochloric acid solution of 1·1437 grm. of the air-dried carbonate of lime of 61, gave upon precipitation with carbonate of ammonia (§ 81, 2, *a.*) 1·1243 grm. of anhydrous carbonate of lime, corresponding to 0·629608 of Ca O = 55·05 per cent (calculated 55·51 per cent), which gives 99·17 instead of 100.

63. Determination of Ca O as Ca O, CO_2, by precipitation with oxalate of ammonia from alkaline solutions (to § 81, 2, *b.* *a.*).

1·1734 grm. of the air-dried carbonate of lime of 61, dissolved in hydrochloric acid, and treated as stated § 81, 2, *b.* *a.*, gave 1·1632 grm. of Ca O, CO_2 (reaction not alkaline), containing 0·651392 of Ca O = 55·513 per cent (calculated 55·516 per cent), which gives 99·99 instead of 100.

64. Determination of lime as oxalate (to § 81, 2, *b.* *a.*).

0·857 grm. of the air-dried carbonate of lime of 61 were dissolved in hydrochloric acid; the solution was precipitated with oxalate of ammonia and ammonia, the precipitate washed, and then dried at 212° until the weight remained constant. The precipitate (Ca O, O + aq) weighed 1·2461 grm. containing 0·477879 of Ca O = 55·76 per cent (calculated 55·516 per cent), which gives 100·45 instead of 100.

65. DETERMINATION OF Ca O, AS Ca O, CO_2 BY PRECIPITATION AS Ca O, $\overline{C}$ FROM ACID SOLUTION (to § 81, 2, *b.* β.).

0·857 grm. of the dry carbonate of lime of 61, dissolved in hydrochloric acid and precipitated from this solution according to the directions of § 81, 2, *b.* β., gave 0·8476 grm. of carbonate of lime (which did not manifest alkaline reaction, and the weight of which did not vary in the least upon evaporation with carbonate of ammonia) containing 0·474656 of Ca O = 55·39 per cent (calculated 55·51), which gives 99·78 instead of 100.

66. DETERMINATION OF MAGNESIA AS 2 MgO, PO_5 (to § 82, 2).

a. A solution of 1·0587 grm. of pure anhydrous sulphate of magnesia in water, precipitated according to 82·2, gave 0·9834 of pyrophosphate of magnesia, containing 0·3533944 of magnesia = 33·38 per cent (calculated 33·35 per cent), which gives 100·09 instead of 100.

b. 0·9672 grm. of sulphate of magnesia gave 0·8974 2 Mg O, P O_5 = 33·34 per cent of Mg O (calculated 33·35 per cent which gives 99·97 instead of 100.

67. PRECIPITATION OF ACETATE OF ZINC BY SULPHURETTED HYDROGEN (to § 85, *b.*).

a. A solution of pure acetate of zinc was treated with sulphuretted hydrogen in excess, and the mixture allowed to stand at rest for some time, and then filtered. The filtrate was mixed with ammonia; it remained perfectly clear at first, and even after long standing, a few, hardly visible flakes only had separated.

b. A solution of acetate of zinc to which a tolerably large amount of acetic acid had been added previously to the precipitation with sulphuretted hydrogen, showed exactly the same deportment.

68. DETERMINATION OF MERCURY IN THE METALLIC STATE IN THE MOIST WAY BY MEANS OF PROTOCHLORIDE OF TIN (to § 94, 1, *b.*)

201 grammes of perchloride of mercury gave 1·465 grm. of metallic mercury=72·88 per cent (calculated 73·83 per cent), which gives 98·71 instead of 100. (*Schaffner.*)

69. PRECIPITATION OF NITRATE OF BISMUTH BY CARBONATE OF AMMONIA (to § 96, *a.*)

If a solution of nitrate of bismuth, no matter whether containing much or little free nitric acid, is mixed with water, precipitated with carbonate of ammonia and ammonia, and filtered without applying heat, the filtrate acquires upon addition of sulphuretted hydrogen water, a blackish-brown color. But if the mixture before filtering is heated for a short time, nearly to boil-

ing, sulphuretted hydrogen fails to impart this color to the filtrate, or, at all events, the change of color is hardly visible to the eye looking through the top of the test-tube filled with it to the brim.

70. Determination of phosphoric acid as pyrophosphate of magnesia (to § 106.)

In the following experiments I used perfectly pure air-dried crystallised phosphate of soda, the amount of water of which I had most carefully determined by heating and ignition.

1·3123 grm. of the substance left 0·4899 grm. of pyrophosphate of soda. This shows a percentage amount of water = 62·67. The formula 2 Na O, PO_5, HO + 24 aq. requires 62·71 per cent.

a. 1·9847 grm. of the air-dried crystallised phosphate of soda was dissolved in water, and the solution precipitated with sulphate of magnesia, chloride of ammonium, and ammonia, as directed § 106, I. *b*, *a*. The precipitate was thoroughly washed with ammoniated water. It yielded, after ignition, and after deducting for the filter-ash, 0·6336 grm. of pyrophosphate of magnesia, which corresponds to 0·3945328 of phosphoric acid. This shows the amount of phosphoric acid in the crystallised phosphate of soda = 19·87 per cent.—the above given formula demands 19·9—and corrected to the amount of water found, 19·91 per cent.

b. 3·0676 grammes of the same sample of crystallised phosphate of soda were dissolved in water; the solution was mixed with hydrochloric acid, then with sesquichloride of iron and solution of alum, and tartaric acid added, and finally ammonia, until the precipitate which had formed at first was completely redissolved. The mixture was then precipitated with sulphate of magnesia, and allowed to stand at rest for twelve hours, when it was filtered and the precipitate washed with ammoniated water, so thoroughly, that a drop of the last washings left not the least residue of evaporation on a platinum plate; and yet, nevertheless, the precipitate was not white; but it retained a faint shade of yellow, and turned upon ignition slightly blackish throughout the whole mass. It weighed, after deduction of 0·0026 grm. filter-ash, 0·9786 grm. which corresponds to 0·6181 of phosphoric acid = 20·14 per cent, (calculated 19·91 per cent). The 0·23 per cent surplus was owing to the presence of a trace of charcoal and a minute amount of sesquioxide of iron; the charcoal separated subsequently upon the solution of the residue in hydrochloric acid; the sesquioxide of iron was detected distinctly in the solution upon testing with sulphocyanide of potassium.

71. Separation of magnesia from soda (to § 121, B. 4, *a*. *a*.).

1·1864 grm. of pure ignited chloride of sodium and 1·4252 grm. of pure anhydrous sulphate of magnesia were dissolved in water, the solution was

heated to 212°, and mixed with water of baryta in excess. The fluid was filtered from the precipitate formed, and the excess of baryta removed from the filtrate by means of carbonate of ammonia. The filtrate was then evaporated with sulphuric acid: it gave 1·4371 grm. of neutral sulphate of soda, containing 0·4694 of sodium. The precipitate produced by the water of baryta was washed, then heated with dilute hydrochloric acid, the solution filtered from the undissolved sulphate of baryta, and the filtrate evaporated with addition of sulphuric acid (which produced a small precipitate of sulphate of baryta). The gently ignited residue weighed 1·4308 grm. It was treated with water, and the undissolved sulphate of baryta filtered off and determined; its weight was 0·0889 grm. There remained therefore for the sulphate of magnesia 1·4308 grm. which corresponds to 0·48668 of Mg O.

This gives in 100 parts of the mixture,

	found.	calculated.
Na	17·34	17·86
Mg O	18·63	18·56

Now, although these numbers correspond pretty closely, yet the result of the analysis would have been more satisfactory had the amount of magnesia found been somewhat too low, and that of sodium somewhat too high. From the results which I obtained, I was led to conclude that the precipitate produced by the water of baryta had not been thoroughly washed, and I was indeed able to detect the presence of a trace of soda in the separated sulphate of magnesia.

72. Chlorimetrical Experiments (to § 189, &c.).

10 grammes of chloride of lime were triturated with water to one litre of fluid, with which the following experiments were made:

a. Examination by *Gay-Lussac's* method (§ 191), result 23·42—23·52 per cent.

b. Examination by *Penot's* method (§ 192), result 23·5—23·5 per cent.

c. Examination by means of iron (§ 193, modification *a*.), result 23·6 per cent.

d. Examination by *Bunsen's* method (§ 194), result 23·6—23·6 per cent.

I have mentioned these experiments to show that more accurate results are obtained with dilute solution of chloride of lime (1 : 100) than with more concentrated solutions.

II. TABLES FOR THE CALCULATION OF ANALYSES.

TABLE I.

EQUIVALENTS OF THE ELEMENTS WHICH OCCUR IN THE PRESENT WORK.*

		O = 100	H = 1	
Aluminium, *a*	Al	170·42	13·63	(Berzelius)
Antimony	Sb	1612·90	129·00	„
Arsenic, *b*	As	937·50	75·00	(Pelouze, Berzelius)
Barium, *c*	Ba	857·32	68·59	(Marignac)
Bismuth	Bi	2599·95	208·00	(Schneider)
Boron, *d*	B	138·05	11·04	(Berzelius)
Bromine	Br	999·62	79·97	(Marignac[a])
Cadmium	Cd	696·77	55·74	(Stromeyer)
Calcium	Ca	250·00	20·00	(Dumas, Erdmann and Marchand)
Carbon	C	75·00	6·00	„ „
Chlorine	Cl	443·28	35·46	(Marignac[a])
Chromium, *e*	Cr	334·70	26·78	(Moberg, Wildenstein)
Cobalt, *f*	Co	368·65	29·49	(Rothoff)
Copper	Cu	396·00	31·68	(Erdmann & Marchand)
Fluorine	Fl	237·50	19·00	(Louyet)
Gold	Au	2458·33	196·67	(Berzelius)
Hydrogen	H	12·50	1·00	(Dumas)
Iodine	I	1586·00	126·88	(Marignac[a])
Iron	Fe	350·00	28·00	(Erdmann & Marchand)
Lead	Pb	1294·65	103·57	(Berzelius)
Lithium, *g*	Li	83·01	6·64	„
Magnesium	Mg	150·19	12·00	(Marchand and Scheerer)
Manganese	Mn	344·68	27·57	(Berzelius)
Mercury	Hg	1250·60	100·05	(Erdmann & Marchand)
Nickel, *h*	Ni	369·33	29·55	(Rothoff)
Nitrogen	N	175·06	14·00	(Marignac[a])

[a] Revised by Berzelius.

* These equivalent numbers are calculated from the best and most precise investigations; some of them have not yet been established by recent experiment, but are calculated from others so determined. It became necessary, therefore, to adjust the results of the original experiments to the corrected equivalent numbers. I have done this, and I add the necessary explanations by way of appendix; the small letters by the side of the elements in question refer to these explanations. The names of the chemists who have furnished the analytical results are likewise stated.

		O = 100	H = 1	
Oxygen	O	100·00	8·00	
Palladium	Pd	665·48	53·24	(Berzelius)
Phosphorus	P	392·04	31·36	„
Platinum	Pt	1236·75	98·94	(Andrews)
Potassium	K	488·86	39·11	(Marignac[a])
Silicon	Si	185·18*	14·81	(Berzelius)
Silver	Ag	1349·66	107·97	(Marignac[a])
Sodium, *i*	Na	287·44	23·00	(Pelouze)
Strontium, *k*	Sr	545·93	43·67	(Stromeyer)
Sulphur	S	200·00	16·00	(Erdmann & Marchand)
Tin	Sn	735·30	58·82	(Berzelius)
Zinc	Zn	406·59	32·53	(Axel Erdmann)

* Revised by Berzelius.

Zirconium Zr 312·5 25· (Pierre)
Uranium Ur 742·87 59·4 (Ebelmen)

EXPLANATORY NOTES TO THE FOREGOING TABLE.

a. EQUIVALENT OF ALUMINIUM.

100 parts of anhydrous sulphate of alumina left, after expulsion of the acid by intense ignition, 29·934 parts of alumina. Consequently, 100 parts of sulphuric acid are saturated by 42·7227 parts of alumina (*Berzelius*).

$$100 : 42{\cdot}7227 :: 1500 \text{ (3 equ. of } SO_3) : x$$

$$x \text{ (equivalent of } Al_2O_3) = 640{\cdot}8405$$

$$640{\cdot}8405 - 300 = 340{\cdot}8405 \text{ (2 Al)}$$

$$\frac{340{\cdot}8405}{2} = 170{\cdot}42$$

b. EQUIVALENT OF ARSENIC.

1. The number in the Table (937·5) is the same which *Pelouze* obtained by precipitating protochloride of arsenic with solution of silver (Compt. rend. xx. p. 1047). But the calculation is based upon *Marignac's* equivalent of silver (1349·01) and chlorine (443·2). If we substitute for these numbers 1349·66 and 443·28, as corrected by *Berzelius*, we find that the real equivalent of arsenic found by *Pelouze* is 938·348.

2. 2·203 grammes of arsenious acid, heated with sulphur, gave 1·069 grm. of SO_2, which contains 0·5345 O (*Berzelius*). 2·203 grammes of $As\,O_3$ consist accordingly of 0·5345 O and 1·6685 As.

$$5345 : 16685 :: 300 : x$$

$$x = 936{\cdot}48$$

The mean of the two numbers is 937·4, instead of which I have given in the Table 937·5, to avoid unnecessary deviations.

* 185·18 is two-thirds of the number given by *Berzelius*, viz., 277·778, as I have regarded silicic acid as $Si\,O_2$.

c. Equivalent of barium.

Marignac found that 96·365 of chloride of barium are precipitated by 100 of silver.

$$100 : 96{\cdot}365 :: 1349{\cdot}66 : x;$$
$$x = 1300{\cdot}5998$$
$$1300{\cdot}5998 - 443{\cdot}28 = 857{\cdot}32$$

d. Equivalent of boron.

100 of borax gave 47·1 per cent of water (*Berzelius*).

$$47{\cdot}1 : 100 :: 1125 : x$$
$$x = 2388{\cdot}53$$

2388·53 — 2112·44 (viz. the sum of one equivalent of Na O=387·44, 10 equivalents of H O = 1125·0, and six equivalents of O=600)= 276·09

$$\frac{276{\cdot}09}{2} = 138{\cdot}05$$

e. Equivalent of chromium.

Moberg (Journal f. prakt. Chemie, 43, 119) obtained in his determination of the equivalent of chromium, 334·769 as the mean result of his experiments.

Wildenstein (Journal f. prakt. Chemie, 59, 27) decomposed chloride of barium with neutral chromate of potassa; the mean result of 32 experiments showed that 100 of chromate of baryta correspond to 81·70 of chloride of barium.

$$81{\cdot}7 : 100 :: 1300{\cdot}60 : x;$$
$$x = 1591{\cdot}92$$
$$1591{\cdot}92 - 1257{\cdot}32 \text{ (\textit{i. e.} the sum of Ba O}+3\text{ O)}=334{\cdot}60$$

The numbers found by the two chemists agree accordingly pretty closely; I have taken the mean, viz. 334·7.

f. Equivalent of cobalt.

269·2 parts of Co O, converted into neutral protochloride and precipitated with nitrate of silver, gave 1029·9 parts of Ag Cl (*Rothoff*).

$$1029{\cdot}9 : 269{\cdot}2 :: 1792{\cdot}94 \text{ (equivalent of Ag Cl)} : x$$
$$x = 468{\cdot}65$$
$$468{\cdot}65 - 100{\cdot}00 = 368{\cdot}65$$

g. Equivalent of lithium.

1·874 of Li O, SO_3 gave 3·9985 grms. of Ba O, SO_3 (*Berzelius*).

$$3{\cdot}9985 : 1{\cdot}874 :: 1457{\cdot}32 : x$$
$$x = 683{\cdot}01$$
$$683{\cdot}01 - 600\ (SO_3 + O) = 83{\cdot}01.$$

h. Equivalent of nickel.

188 of Ni O, converted into neutral protochloride gave 718·2 of Ag Cl (*Rothoff*).

718·2 : 188 : : 1792·94 (equ. of Ag Cl) : x

33 x = 469·33

469·33 — 100 = 369·33

i. EQUIVALENT OF SODIUM.

730·37 of chloride of sodium were precipitated by 1349·01 of silver (*Pelouze*).

1349·01 : 730·37 : : 1349·66 (the corrected equ. of silver) : x

x = 730 72

730·72 — 443·28 = 287·44

k. EQUIVALENT OF STRONTIUM.

100 Sr Cl gave 181·25 of Ag Cl (*Stromeyer*)

181·25 : 100 : : 1792·94 : x

x = 989·21

989·21 — 443·28 = 545·93

TABLE II.

COMPOSITION OF THE BASES AND OXYGEN ACIDS.

a. BASES.

GROUP I.	Potassa	K . . .	488·86	39·11	83·02
		O . . .	100·00	8·00	16·98
		KO . . .	588·86	47·11	100·00
...	Soda	Na . . .	287·44	23·00	74·19
		O . . .	100·00	8·00	25·81
		Na O . .	387·44	31·00	100·00
...	Lithia	Li . . .	83·01	6·64	45·36
		O . . .	100·00	8·00	54·64
		LiO . .	183·01	14·64	100·00
...	Ammonia	NH_4 . .	225·06	18·00	69·23
		O . . .	100·00	8·00	30·77
		NH_4O . .	325·06	26·00	100·00
GROUP II.	Baryta	Ba . . .	857·32	68·59	89·55
		O . . .	100·00	8·00	10·45
		Ba O . .	957·32	76·59	100·00
...	Strontia	Sr . . .	545·93	43·67	84·52
		O . . .	100·00	8·00	15·48
		Sr O . .	645·93	51·67	100·00
...	Lime	Ca . . .	250·00	20·00	71·43
		O . . .	100·00	8·00	28·57
		Ca O . .	350·00	28·00	100·00
...	Magnesia	Mg . .	150·19	12·00	60·03
		O . . .	100·00	8·00	39·97
		Mg O . .	250·19	20·00	100·00
GROUP III	Alumina	Al_2 . . .	340·84	27·26	53.19
		O_3 . . .	300·00	24·00	46·81
		$Al_2 O_3$ . .	640·84	51·26	100 00

GROUP III.	Chromium sesquioxide	Cr_2	669·40	53·56	69.05
		O_3	300·00	24·00	30·95
		$Cr_2 O_3$	969·40	77·56	100·00
GROUP IV.	Zinc, oxide	Zn	406·59	32.53	80 26
		O	100·00	8·00	19·74
		Zn O	506·59	40·53	100·00
...	Manganese, protoxide	Mn	344·68	27·57	77·51
		O	100·00	8·00	22·49
		Mn O	444·68	35·57	100·00
...	Manganese, sesquioxide	Mn_2	689·36	55·14	69·67
		O_3	300·00	24·00	30·33
		$Mn_2 O_3$	989·36	79·14	100·00
...	Nickel, protoxide	Ni	369·33	29·55	78·69
		O	100·00	8·00	21·31
		Ni O	469·33	37·55	100·00
...	Cobalt, protoxide	Co	368·65	29·49	78·66
		O	100·00	8·00	21·34
		Co O	468·65	37·49	100·00
...	Cobalt, sesquioxide	Co_2	737·30	58·98	71·08
		O_3	300·00	24·00	28·92
		$Co_2 O_3$	1037·30	82·98	100·00
...	Iron, protoxide	Fe	350·00	28·00	77·78
		O	100·00	8·00	22·22
		Fe O	450·00	36·00	100·00
...	Iron, sesquioxide	Fe_2	700·00	56·00	70·00
		O_3	300·00	24·00	30·00
		$Fe_2 O_3$	1000·00	80·00	100·00
GROUP V.	Silver, oxide	Ag	1349·66	107·97	93·10
		O	100·00	8·00	6·90
		Ag O	1449·66	115·97	100·00
...	Lead, oxide	Pb	1294·65	103·57	92·83
		O	100·00	8·00	7·17
		Pb O	1394·65	111·57	100·00

Group V.	Mercury, suboxide	Hg_2	2501·20	200·10	96·16
		O	100·00	8·00	3·84
		Hg_2O	2601·20	208·10	100·00
...	Mercury, oxide	Hg	1250·60	100·05	92·59
		O	100·00	8·00	7·41
		Hg O	1350·60	108·05	100·00
...	Copper, suboxide	Cu_2	792·00	63·36	88·79
		O	100·00	8·00	11·21
		Cu_2O	892·00	71·36	100·00
...	Copper, oxide	Cu	396·00	31·68	79·84
		O	100·00	8·00	20·16
		Cu O	496·00	39·68	100·00
...	Bismuth, oxide	Bi	2599·95	208·00	89·655
		O_3	300·00	24·00	10·345
		$Bi O^3$	2899·95	232·00	100·000
...	Cadmium, oxide	Cd	696·77	55·74	87·45
		O	100·00	8·00	12·55
		Cd O	796·77	63·74	100·00
Group VI.	Gold, teroxide	Au	2458·33	196·67	89·12
		O_3	300·00	24·00	10·88
		$Au O_3$	2758·33	220·67	100·00
...	Platinum, oxide	Pt	1236·75	98·94	86·08
		O_2	200·00	16·00	13·92
		$Pt O_2$	1436·75	114·94	100·00
...	Antimony, teroxide	Sb	1612·90	129·00	84·32
		O_3	300·00	24·00	15·68
		$Sb O_3$	1912·90	153·00	100·00
...	Tin, protoxide	Sn	735·30	58·82	88·02
		O	100·00	8·00	11·98
		Sn O	835·30	66·82	100·00
...	Tin, binoxide	Sn	735·30	58·82	78·62
		O_2	200·00	16·00	21·38
		$Sn O_2$	935·30	74·82	100·00

GROUP VI.	Arsenious acid	As	937·50	75·00	75·76
		O_3	300·00	24·00	24·24
		$As O_3$	1237·50	99·00	100·00
...	Arsenic acid	As	937·50	75·00	65·22
		O_5	500·00	40·00	34·78
		$As O_5$	1437·50	115·00	100·00

b. ACIDS.

...	Chromic acid	Cr	334·70	26·78	52·74
		O_3	300·00	24·00	47·26
		$Cr O_3$	634·70	50·78	100·00
...	Sulphuric acid	S	200·00	16·00	40·00
		O_3	300·00	24·00	60·00
		$S O_3$	500·00	40·00	100·00
...	Phosphoric acid	P	392·04	31·36	43·95
		O_5	500·00	40·00	56·05
		$P O_5$	892·04	71·36	100·00
...	Boracic acid	B	138·05	11·04	31·51
		O_3	300·00	24·00	68·49
		$B O_3$	438·05	35·04	100·00
...	Oxalic acid	C_2	150·00	12·00	33·33
		O_3	300·00	24·00	66·67
		$C_2 O_3$	450·00	36·00	100·00
...	Carbonic acid	C	75·00	6·00	27·27
		O_2	200·00	16·00	72·73
		$C O_2$	275·00	22·00	100·00
...	Silicic acid	Si	185·18	14·81	48·08
		O_2	200·00	16·00	51·92
		$Si O_2$	385·18	30·81	100·00
...	Nitric acid	N	175·06	14·00	25·93
		O	500·00	40·00	74·07
		$N O_5$	675·06	54·00	100·00
...	Chloric acid	Cl	443·28	35·46	46·99
		O_5	500·00	40·00	53·01
		$Cl O_5$	943·28	75·46	100·00

TABLE III.

METHOD OF ASCERTAINING THE AMOUNT OF ONE OF THE CONSTITUENTS OF A COMPOUND PRODUCED, BY SIMPLE MULTIPLICATION OR DIVISION.

This Table contains some of the more frequently occurring compounds only, the formulæ preceded by ! give perfectly accurate results.

FOR INORGANIC ANALYSIS.

CARBONIC ACID.

! Carbonate of lime × 0·44 = Carbonic Acid.

CHLORINE.

Chloride of silver × 0·24724 = Chlorine.

COPPER.

Oxide of copper × 0·79839 = Copper.

IRON.

! Sesquioxide of iron × 0·7 = 2 Iron.
! Sesquioxide of iron × 0·9 = 2 Protoxide of Iron

LEAD.

Oxide of lead × 0·92830 = Lead.

MAGNESIA.

Pyrophosphate of magnesia × 0·35936 = 2 Magnesia.

MANGANESE.

Protosesquioxide of manganese × 0·72107 = 3 Manganese.
Protosesquioxide of manganese × 0·9303 = 3 Protoxide of Manganese.

PHOSPHORIC ACID.

Pyrophosphate of magnesia × 0·6406 = Phosphoric Acid.

POTASSA.

Chloride of potassium × 0·52445 = Potassium.
Sulphate of potash × 0·54080 = Potassa.
Potassio-bichloride of platinum × 0·30507
or
$\frac{\text{Potassio-bichloride of platinum}}{3{\cdot}278}$
= Chloride of Potassium.

$$\left.\begin{array}{l}\text{Potassio-bichloride of platinum} \times 0{\cdot}19272 \\ \text{or} \\ \dfrac{\text{Potassio-bichloride of platinum}}{5{\cdot}188}\end{array}\right\} = \text{Potassa.}$$

SODA.

Chloride of sodium × 0·5302 = Soda.
Sulphate of soda × 0·43658 = Soda.

SULPHUR.

Sulphate of baryta × 0·13724 = Sulphur.

✓ Ba 68·6 = S 16·002184
instead of 16·0000

SULPHURIC ACID.

Sulphate of baryta × 0·34309 = Sulphuric Acid.

✓ Ba 68·6 = S 16·0021
instead of 16·0000

FOR ORGANIC ANALYSIS.

CARBON.

$$\left.\begin{array}{l}\text{Carbonic acid} \times 0{\cdot}2727 \\ \text{or} \\ \dfrac{\text{Carbonic acid}}{3{\cdot}666} \\ \text{or} \\ \dfrac{\text{Carbonic acid} \times 3}{11}\end{array}\right\} = \text{Carbon.}$$

HYDROGEN.

$$\left.\begin{array}{l}\text{Water} \times 0{\cdot}1111 \\ \text{or} \\ \dfrac{\text{Water}}{9}\end{array}\right\} = \text{Hydrogen.}$$

NITROGEN.

Ammonio-bichloride of platinum × 0·06271 = Nitrogen.
Platinum × 0·1415 = Nitrogen.

TABLE

Showing the amount of the

number of the compound

Elements.	Found.	Sought.	1
Aluminium	Alumina $Al_2 O_3$	Aluminium Al_2	0·53186
Ammonium	Chloride, ammonium $N H_4, Cl$	Ammonia $N H_3$	0·31804
	Ammonio-bichloride of platinum $N H_4 Cl, Pt Cl_2$	Oxide of ammonium $N H_4, O$	0·11644
	Ammonio-bichloride of platinum $N H_4 Cl, Pt Cl_2$	Ammonia $N H_3$	0·07614
Antimony	Teroxide of antimony $Sb O_3$	Antimony Sb	0·84317
	Antimony Sb	Teroxide of antimony $Sb O_3$	1·18600
	Tersulphide of antimony $Sb S_3$	Teroxide of antimony $Sb O_3$	0·86443
	Antimonious acid $Sb O_4$	Teroxide of antimony $Sb O_3$	0·95032
Arsenic	Arsenious acid. $As O_3$	Arsenic As	0·75758
	Arsenic acid $As O^5$	Arsenic As	0·65217
	Arsenic acid $As O_5$	Arsenious acid $As O_3$	0·86087
	Sulpharsenious acid $As S_3$	Arsenious acid $As O_3$	0·80488
	Sulpharsenious acid $As S_3$	Arsenic acid $As O_5$	0·93496
Barium	Baryta Ba O	Barium Ba	0·89554
	Sulphate of baryta $Ba O, S O_3$	Baryta Ba O	0·65690
	Carbonate of baryta $Ba O, C O_2$	Baryta Ba O	0·77684
	Silico-fluoride of barium $Ba Fl, Si Fl_2$	Baryta Ba O	0·54548
Bismuth	Teroxide of bismuth $Bi O^3$	Bismuth Bi	0·89655
Boron	Boracic acid. $B O_3$	Boron B	0·31515
Bromine	Bromide of silver Ag Br	Bromine Br	0·42550
Cadmium	Oxide of cadmium Cd O	Cadmium Cd	0·87449
Calcium	Lime Ca O	Calcium Ca	0·71429
	Sulphate of lime $Ca O, S O_3$	Lime Ca O	0·41176
	Carbonate of lime $Ca O, C O_2$	Lime Ca O	0·56000

IV.

constitutent sought for every

found, from 1—9.

2	3	4	5	6	7	8	9
1·06373	1·59559	2·12746	2·65932	3·19118	3·72305	4·25491	4·78678
0·63608	0·95413	1·27217	1·59021	1·90825	2·22629	2·54433	2·86237
0·23288	0·34932	0·46576	0·58220	0·69864	0·81508	0·93152	1·04796
0·15228	0·22842	0·30456	0·38070	0·45684	0·53299	0·60913	0·68527
1·68634	2·52951	3·37268	4·21585	5·05902	5·90219	6·74536	7·58853
2·37200	3·55800	4·74400	5·93000	7·11600	8·30200	9·48800	10·67400
1·72886	2·59329	3·45772	4·32215	5·18659	6·05102	6·91545	7·77988
1·90064	2·85096	3·80128	4·75160	5·70192	6·65224	7·60256	8·55288
1·51516	2·27274	3·03032	3·78790	4·54548	5·30306	6·06064	6·81822
1·30435	1·95652	2·60870	3·26087	3·91304	4·56522	5·21739	5·86957
1·72174	2·58261	3·44348	4·30435	5·16521	6·02608	6·88695	7·74782
1·60975	2·41463	3·21951	4·02439	4·82927	5·63415	6·43902	7·24390
1·86992	2·80488	3·73984	4·67480	5·60975	6·54471	7·47967	8·41463
1·79108	2·68662	3·58216	4·47770	5·37325	6·26879	7·16433	8·05987
1·31380	1·97070	2·62760	3·28450	3·94140	4·59830	5·25520	5·91210
1·55369	2·33053	3·10737	3·88421	4·66106	5·43790	6·21474	6·99158
1·09096	1·63644	2·18192	2·72740	3·27288	3·81836	4·36384	4·90932
1·79310	2·68965	3·58620	4·48275	5·37930	6·27586	7·17240	8·06895
0·63029	0·94544	1·26058	1·57573	1·89088	2·20602	2·52117	2·83631
0·85100	1·27650	1·70200	2·12750	2·55300	2·97850	3·40400	3·82950
1·74898	2·62347	3·49796	4·37245	5·24694	6·12143	6·99592	7·87041
1·42857	2·14286	2·85714	3·57143	4·28571	5·00000	5·71429	6·42857
0·82353	1·23529	1·64706	2·05882	2·47059	2·88235	3·29412	3·70588
1·12000	1·68000	2·24000	2·80000	3·36000	3·92000	4·48000	5·04000

TABLE IV.

Elements.	Found.	Sought.	1
Carbon	Carbonic acid $C O_2$	Carbon C	0·27273
	Carbonate of lime $Ca O, C O_2$	Carbonic acid $C O_2$	0·44000
Chlorine	Chloride of silver Ag Cl	Chlorine Cl	0·24724
	Chloride of silver Ag Cl	Hydrochloric acid Cl H	0·25421
Chromium	Sesquioxide of chromium $Cr_2 O_3$	Chromium Cr_2	0·69053
	Sesquioxide of chromium $Cr_2 O_3$	Chromic acid $2 Cr O_3$	1·30947
	Chromate of lead $Pb O, Cr O_3$	Chromic acid $Cr O_3$	0·31276
Cobalt	Cobalt Co	Protoxide of cobalt Co O	1·27126
Copper	Oxide of copper Cu O	Copper Cu	0·79839
Fluorine	Fluoride of calcium Ca Fl	Fluorine Fl	0·48718
	Fluoride of silicon $Si Fl_2$	Fluorine 2 Fl	0·71950
Hydrogen	Water H O	Hydrogen H	0·11111
Iodine	Iodide of silver Ag I	Iodine I	0·54025
	Iodide of palladium Pd I	Iodine I	0·70443
Iron	Sesquioxide of iron $Fe_2 O_3$	Iron Fe_2	0·70000
	Sesquioxide of iron $Fe_2 O_3$	Protoxide of iron 2 Fe O	0·90000
Lead	Oxide of lead Pb O	Lead Pb	0·92830
	Sulphate of lead $Pb O, S O_3$	Oxide of lead Pb O	0·73609
	Chloride of lead Pb Cl	Oxide of lead Pb O	0·80248
	Chloride of lead Pb Cl	Lead Pb	0·74494
	Sulphuret of lead Pb S	Oxide of lead Pb O	0·93309
Magnesium	Magnesia Mg O	Magnesium Mg	0·60030
	Sulphate of magnesia $Mg O, S O_3$	Magnesia Mg O	0·33350
	Pyrophosphate of magnesia $P O_5$ 2 Mg O	Magnesia 2 Mg O	0·35936
Manganese	Protoxide of manganese Mn O	Manganese Mn	0·77512
	Protosesquioxide of manganese $Mn O + Mn_2 O_3$	Manganese Mn^3	0·72107

$Mn^3 O^4$ = Mn O

$Mn^3 O^4$ = $Mn O^2$ 1·139[illegible]

continued.

2	3	4	5	6	7	8	9
0·54546	0·81818	1·09091	1·36364	1·63636	1·90909	2·18181	2·45455
0·88000	1·32000	1·76000	2·20000	2·64001	3·08000	3·52000	3·96000
0·49448	0 74172	0·98896	1·23620	1·48344	1·73068	1·97792	2·22516
0·50842	0·76263	1·01684	1·27105	1·52526	1·77947	2·03368	2·28789
1·38106	2·07159	2·76212	3·45265	4·14318	4·83371	5·52424	6·21477
2·61894	3·92841	5·23788	6·54735	7·85681	9·16628	10·47575	11·78522
0·62552	0·93828	1·25104	1·56380	1·87657	2·18933	2·50209	2·81485
2·54252	3·81388	5·08504	6·35630	7·62756	8·89882	10·17008	11·44134
1·59677	2·39516	3·19355	3·99193	4·79032	5·58871	6·38710	7·18548
0·97436	1·46154	1·94872	2·43590	2·92307	3·41027	3·89743	4·38461
1·43900	2·15850	2·87800	3·59750	4·31700	5·03650	5·75600	6·47550
0·22222	0·33333	0·44444	0·55555	0·66667	0·77778	0·88889	1·00000
1·08050	1·62075	2·16100	2·70125	3·24150	3·78175	4·32200	4·86225
1·40886	2·11329	2·81772	3·52215	4·22658	4·93101	5·63544	6·33987
1·40000	2·10000	2·80000	3·50000	4·20000	4·90000	5·60000	6·30000
1·80000	2·70000	3·60000	4·50000	5·40000	6·30000	7·20000	8·10000
1·85660	2·78490	3·71320	4·64150	5·56980	6·49810	7·42640	8·35470
1·47219	2·20829	2·94438	3·68048	4·41658	5·15268	5·88878	6·62487
1·60495	2·40743	3·20990	4·01238	4·81486	5·61734	6·41982	7·22229
1·48987	2·23480	2·97974	3·72468	4·46962	5·21455	5·95949	6·70442
1·86619	2·79928	3·73238	4·66547	5·59856	6·53166	7·46475	8·39785
1·20061	1·80091	2·40121	3·00151	3·60182	4·20212	4·80242	5·40273
0·66700	1·00051	1·33401	1·66751	2·00101	2·33451	2·66802	3·00152
0·71872	1·07808	1·43744	1·79680	2·15616	2·51552	2·87488	3·23424
1·55024	2·32536	3·10048	3·87560	4·65072	5·42585	6·20096	6·97608
1·44214	2·16321	2·88428	3·60535	4·32641	5·04748	5·76855	6·48962

TABLE IV.

Elements.	Found.	Sought.	1
Manganese	Sesquioxide of manganese $Mn_2 O_3$	Manganese Mn_2	0·69678
	Sulphate of protoxide of manganese $Mn O, S O_3$	Protoxide of manganese $Mn O$	0·47072
Mercury	Mercury Hg_2	Suboxide of mercury $Hg_2 O$	1·03998
	Mercury Hg	Oxide of mercury $Hg O$	1·07996
	Subchloride of mercury $Hg_2 Cl$	Mercury Hg_2	0·84945
	Subsulphide of mercury $Hg S$	Mercury Hg	0·86213
Nickel	Protoxide of nickel $Ni O$	Nickel Ni	0·78693
Nitrogen	Ammonio-bichloride of platinum $N H_4 Cl, Pt Cl_2$	Nitrogen N	0·06071
	Platinum Pt	Nitrogen N	0·14155
	Sulphate of baryta $Ba O, S O_3$	Nitric acid $N O_5$	0·46322
	Cyanide of silver $Ag, C_2 N$	Cyanogen $C_2 N$	0·19410
	Cyanide of silver $Ag, C_2 N$	Hydrocyanic acid $C_2 N, H$	0·20156
Oxygen	Alumina $Al_2 O_3$	Oxygen O_3	0·46814
	Teroxide of antimony $Sb O_3$	Oxygen O_3	0·15683
	Arsenious acid $As O_3$	Oxygen O_3	0·24242
	Arsenic acid $As O_5$	Oxygen O_5	0·34783
	Baryta $Ba O$	Oxygen O	0·10446
	Oxide of lead $Pb O$	Oxygen O	0·07170
	Oxide of Cadmium $Ca O$	Oxygen O	0·12551
	Lime $Ca O$	Oxygen O	0·28571
	Sesquioxide of chromium $Cr_2 O_3$	Oxygen O_3	0·30947
	Sesquioxide of iron $Fe_2 O_3$	Oxygen O_3	0·30000
	Protoxide of iron $Fe O$	Oxygen O	0·22222
	Potassa $K O$	Oxygen O	0·16982
	Silicic acid $S O_2$	Oxygen O_2	0·51923
	Protoxide of cobalt $Co O$	Oxygen O	0·21338

continued.

2	3	4	5	6	7	8	9
1·39356	2·09034	2·78712	3·48390	4·18068	4·87746	5·57424	6·27102
0·94144	1·41217	1·88289	2·35361	2·82433	3·29505	3·76578	4·23650
2·07996	3·11994	4·15992	5·19990	6·23988	7·27986	8·31984	9·35982
2·15992	3·23988	4·31984	5·39980	6·47977	7·55973	8·63969	9·71965
1·69890	2·54836	3·39781	4·24726	5·09672	5·94617	6·79562	7·64508
1·72425	2·58638	3·44850	4·31063	5·17275	6·03488	6·89701	7·75913
1·57386	2·36079	3·14772	3·93465	4·72158	5·50851	6·29544	7·08237
0·12542	0·18812	0·25083	0·31354	4·37625	0·43896	0·50166	0·56437
0·28310	0·42464	0·56619	0·70774	0·84929	0·99084	1·13238	1·27393
0·92644	1·38966	1·85288	2·31610	2·77932	3·24254	3·70576	4·16898
0·38820	0·58239	0·77640	0·97050	1·16460	1·35870	1·55280	1·74690
0·40312	0·60468	0·80624	1·00780	1·20936	1·41092	1·61248	1·81404
0·93627	1·40441	1·87254	2·34068	2·80882	3·27695	3·74509	4·21322
0·31366	0·47049	0·62732	0·78415	0·94098	1·09781	1·25464	1·41147
0·48484	0·72726	0·96968	1·21210	1·45452	1·69694	1·93936	2·18178
0·69565	1·04348	1·39130	1·73913	2·08696	2·43478	2·78261	3·13043
0·20892	0·31338	0·41784	0·52230	0·62675	0·73121	0·83567	0·94013
0·14340	0·21510	0·28680	0·35850	0·43020	0·50190	0·57360	0·64530
0·25102	0·37653	0·50204	0·62755	0·75306	0·87857	1·00408	1·12959
0·57143	0·85714	1·14286	1·42857	1·71429	2·00000	2·28571	1·57143
0·61894	0·92841	1·23788	1·54735	1·85682	2·16629	2·47576	2·78523
0·60000	0·90000	1·20000	1·50000	1·80000	2·10000	2·40000	2·70000
0·44444	0·66667	0·88889	1·11111	1·33333	1·55555	1·77777	1·99999
0·33964	0·50946	0·67928	0·84910	1·01892	1·18874	1·35856	1·52838
1·03846	1·55769	2·07692	2·59615	3·11538	3·63461	4·15384	4·67307
0·42676	0·64014	0·85352	1·06690	1·28028	1·49366	1·70704	1·92042

TABLE IV.

Elements.	Found.	Sought.	1
Oxygen	Oxide of copper Cu O	Oxygen O	0·20161
	Magnesia Mg O	Oxygen O	0·39970
	Protoxide of manganese Mn O	Oxygen O	0·22488
	Protosesquioxide of manganese Mn O + Mn_2 O	Oxygen O_4	0·27893
	Sesquioxide of manganese Mn_2 O_3	Oxygen O_3	0·30322
	Soda Na O	Oxygen O	0·25810
	Protoxide of nickel Ni O	Oxygen O	0·21307
	Oxide of mercury Hg O	Oxygen O	0·07404
	Suboxide of mercury Hg O	Oxygen O	0·03844
	Oxide of silver Ag O	Oxygen O	0·06898
	Strontia Sr O	Oxygen O	0·15482
	Water H O	Oxygen O	0·88889
	Teroxide of bismuth Bi O_3	Oxygen O_3	0·10345
	Oxide of zinc Zn O	Oxygen O	0·19740
	Binoxide of tin Sn O_2	Oxygen O	0·21384
Phosphorus	Phosphoric acid P O_5	Phosphorus P.	0·43949
	Pyrophosphate of magnesia P O_5, 2 Mg O,	Phosphoric acid P O_5	0·64064
	Phosphate of sesquioxide of iron 3 P O_5, 2 Fe_2 O_3	Phosphoric acid 3 P O_5	0·57229
	Phosphate of sesquioxide of iron Fe_2 O_3, P O_5	Phosphoric acid P O_5	0·47147
	Phosphate of silver P O_5, 3 Ag O	Phosphoric acid P O_5	0·17020
	Pyrophosphate of silver P O_5, 2 Ag O	Phosphoric acid P O_5	0·23528
Potassium.	Potassa K O	Potassium K	0·83018
	Sulphate of potassa K O, S O_3	Potassa K O	0·54080
	Nitrate of potassa K O, N O_5	Potassa K O	0·46590
	Chloride of potassium K Cl	Potassium K	0·52445
	Chloride of potassium K Cl	Potassa K O	0·63173

continued.

2	3	4	5	6	7	8	9
0·40323	0·60484	0·80645	1·00807	1·20968	1·41129	1·61290	1·81452
0·79939	1·19909	1·59879	1·99849	2·39818	2·79788	3·19758	3·59727
0·44976	0·67464	0·89952	1·12440	1·34928	1·57416	1·79904	2·02392
0·55786	0·83679	1·11572	1·39465	1·67359	1·95252	2·23145	2·51038
0·60644	0·90966	1·21288	1·51610	1·81932	2·12254	2·42576	2·72898
0·51621	0·77431	1·03242	1·29052	1·54863	1·80673	2·06484	2·32294
0·42614	0·63921	0·85228	1·06535	1·27842	1·49149	1·70456	1·91763
0·14808	0·22212	0·29616	0·37021	0·44425	0·51829	0·59233	0·66637
0·07688	0·11533	0·15377	0·19221	0·23066	0·26910	0·30754	0·34599
0·13796	0·20694	0·27592	0·34490	0·41388	0·48286	0·55184	0·62082
0·30964	0·46446	0·61928	0·77410	0·92892	1·08374	1·23856	1·39338
1·77778	2·66667	3·55556	4·44445	5·33333	6·22222	7·11111	8·00000
0·20690	0·31035	0·41380	0·51725	0·62070	0·72415	0·82760	0·93105
0·39480	0·59220	0·78960	0·98700	1·18440	1·38180	1·57920	1·77660
0·42768	0·64152	0·85536	1·06920	1·28304	1·49688	1·71072	1·92456
0·87898	1·31847	1·75796	2·19745	2·63694	3·07643	3·51592	3·95541
1·28128	1·92192	2·56256	3·20320	3·84384	4·48448	5·12512	5·76576
1·14459	1·71688	2·28918	2·86147	3·43376	4·00506	4·57835	5·15065
0·94294	1·41441	1·88588	2·35735	2·82882	3·30029	3·77176	4·24323
0·34040	0·51060	0·68080	0·85101	1·02121	1·19141	1·36161	1·53181
0·47056	0·70584	0·94112	1·17640	1·41168	1·64696	1·88224	2·11752
1·66036	2·49054	3·32072	4·15090	4·98108	5·81126	6·64144	7·47162
1·08161	1·62241	2·16321	2·70402	3·24482	3·78563	4·32643	4·86723
0·93179	1·39769	1·86359	2·32949	2·79539	3·26129	3·72719	4·19309
1·04890	1·57335	2·09780	2·62225	3·14669	3·67114	4·19559	4·72004
1·26346	1·89519	2·52692	3·15865	3·79037	4·42210	5·05383	5·68556

TABLE IV.

Elements.	Found.	Sought.	1
Potassium	Potassio-bichloride of platinum K Cl, Pt Cl_2	Potassa K O	0·19272
	Potassio-bichloride of platinum K Cl, Pt Cl_2	Chloride of potassium K Cl	0·30507
Silicon	Silicic acid Si O_2	Silicon Si	0·48077
Silver	Chloride of silver Ag Cl	Silver Ag	0·75276
	Chloride of silver Ag Cl	Oxide of silver Ag O	0·80854
Sodium	Soda Na O	Sodium Na	0·74190
	Sulphate of soda Na O, S O_3	Soda Na O	0·43658
	Nitrate of soda Na O, N O_5	Soda Na O	0·36465
	Chloride of sodium Na Cl	Soda Na O	0·53022
	Chloride of sodium Na Cl	Sodium Na	0·39337
	Carbonate of soda Na O, C O_2	Soda Na O	0·58487
Strontium	Strontia Sr O	Strontium Sr	0·84518
	Sulphate of strontia Sr O, S O_3	Strontia Sr O	0·56367
	Carbonate of strontia Sr O, C O_2	Strontia Sr O	0·70139
Sulphur	Sulphate of baryta Ba O, S O_3	Sulphur S	0·13724
	Tersulphuret of arsenic As S_3	Sulphur S_3	0·39024
	Sulphate of baryta Ba O, S O_3	Sulphuric acid S O3	0·34309
Tin	Binoxide of tin Sn O_2	Tin Sn	0·78616
	Binoxide of tin Sn O_2	Protoxide of tin Sn O	0·89308
Zinc	Oxide of zinc Zn O	Zinc Zn	0·80260

continued.

2	3	4	5	6	7	8	9
0·38545	0·57817	0·77090	0·96362	1·15634	1·34907	1·54179	1·73452
0·61015	0·91522	1·22030	1·52537	1·83044	2·13552	2·44059	2.74567
0·96154	1·44231	1·92308	2·40385	2·88462	3·36539	3·84616	4·32693
1·50552	2·25828	3·01104	3·76380	4·51656	5·26932	6·02208	6·77484
1·61708	2·42562	3·23416	4·04270	4·85124	5·65978	6·46832	7·27686
1·48379	2·22569	2·96758	3·70948	4·45137	5·19327	5·93516	6·67706
0·87316	1·30975	1·74633	2·18291	2·61949	3·05607	3·49265	3·92924
0·72930	1·09395	1·45860	1·82325	2·18789	2·55254	2·91719	3·28184
1·06043	1·59065	2·12086	2·65108	3·18130	3·71151	4·24173	4·77194
0·78673	1·18009	1·57346	1·96683	2·36019	2·75356	3·14692	3·54029
1·16974	1·75460	2·33947	2·92434	3·50921	4·09407	4·67894	5·26381
1·69036	2·53554	3·38072	4·22590	5·07108	5·91626	6·76144	7·60662
1·12734	1·69101	2·25469	2·81836	3·38204	3·94571	4·50938	5·07305
1·40278	2·10417	2·80556	3·50695	4·20834	4·90973	5·61112	6·31251
0·27447	0·41171	0·54894	0·68618	0·82342	0·96066	1·09789	1·23513
0·78049	1·17073	1·56097	1·95122	2·34146	2·73170	3·12194	3·51219
0·68619	1·02929	1·37238	1·71548	2·05857	2·40167	2·74476	3·08786
1·57232	2·35848	3·14464	3·93080	4·71696	5·50312	6·28928	7·07544
1·78616	2·67924	3·57232	4·46540	5·35848	6·25156	7·14464	8·03772
1·60520	2·40780	3·21040	4·01300	4·81560	5·61820	6·42080	7·22340

TABLE V.

SPECIFIC GRAVITY AND ABSOLUTE WEIGHT OF SEVERAL GASES.

	Specific gravity, atmospheric air = 1·0000.	1 litre (1000 cubic centimeters) of gas at 0° C. and 0·76 metre bar. pressure weighs Grammes.
Atmospheric air . . .	1·0000	1·29363
Oxygen	1·10563	1·43028
Hydrogen . . .	0·06910	0·08939
Water, vapor of . . .	0·62192	0·80453
Carbon, vapor of . . .	0·82922	1·07270
Carbonic acid . . .	1·52024	1·96663
Carbonic oxide . . .	0·96743	1·25150
Phosphorus, vapor of . .	4·33452	5·60727
Sulphur, vapor of . .	6·63378	8·58165
Hydrosulphuric acid . .	1·17475	1·51969
Iodine, vapor of . . .	8·76760	11·34203
Bromine, vapor of . .	5·52605	7·14866
Chlorine	2·45052	3·17007
Nitrogen	0·96776	1·25192
Ammonia . . .	0·58753	0·76005

TABLE VI.

COMPARISON OF THE DEGREES OF THE MERCURIAL THERMOMETER WITH THOSE OF THE AIR THERMOMETER.

According to Dulong and Petit.

Degrees of the mercurial thermometer.	Degrees of the air thermometer.	Degrees of the mercurial thermometer.	Degrees of the air thermometer.
105	104·8	220	216·2
110	109·6	230	225·9
120	119·5	240	235·4
130	129·2	250	245·0
140	139·0	260	254·6
150	148·7	270	264·0
160	158·4	280	273·5
170	168·0	290	283·2
180	177·7	300	292·7
190	187·4	320	311·6
200	197·0	340	330·5
210	206·7	350	340·0

According to Magnus.

Degrees of the mercurial thermometer.	Degrees of the air thermometer.
100	100·00
150	148·74
200	197·49
250	245·39
300	294·51
330	320·92

According to Regnault.

Air thermometer.	Mercurial thermometer.
0	0
50	50·2
100	100·0
150	150·0
200	200·0
250	250·3
300	301·2
325	326·9
350	353·3

TABLE

FOR THE CONVERSION OF DEGREES INTO DEGREES OF

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
—50°	—58°·0	—3°	26°·6	44°	111°·2	91°	195°·8
—49	—56·2	—2	28·4	45	113·0	92	197·6
—48	—54·4	—1	30·2	46	114·8	93	199·4
—47	—52·6	0	32·0	47	116·6	94	201·2
—46	—50·8	+1	33·8	48	118·4	95	203·0
—45	—49·0	2	35·6	49	120·2	96	204·8
—44	—47·2	3	37·4	50	122·0	97	206·6
—43	—45·4	4	39·2	51	123·8	98	208·4
—42	—43·6	5	41·0	52	125·6	99	210·2
—41	—41·8	6	42·8	53	127·4	100	212·0
—40	—40·0	7	44·6	54	129·2	101	213·8
—39	—38·2	8	46·4	55	131·0	102	215·6
—38	—36·4	9	48·2	56	132·8	103	217·4
—37	—34·6	10	50·0	57	134·6	104	219·2
—36	—32·8	11	51·8	58	136·4	105	221·0
—35	—30·0	12	53·6	59	138·2	106	222·8
—34	—29·2	13	55·4	60	140·0	107	224·6
—33	—27·4	14	57·2	61	141·8	108	226·4
—32	—25·6	15	59·0	62	143·6	109	228·2
—31	—23·8	16	60·8	63	145·4	110	230·0
—30	—22·0	17	62·6	64	147·2	111	231·8
—29	—20·2	18	64·4	65	149·0	112	233·6
—28	—18·4	19	66·2	66	150·8	113	235·4
—27	—16·6	20	68·0	67	152·6	114	237·2
—26	—14·8	21	69·8	68	154·4	115	239·0
—25	—13·0	22	71·6	69	156·2	116	240·8
—24	—11·2	23	73·4	70	158·0	117	242·6
—23	— 9·4	24	75·2	71	159·8	118	244·4
—22	— 7·6	25	77·0	72	161·6	119	246·2
—21	— 5·8	26	78·8	73	163·4	120	248·0
—20	— 4·0	27	80·6	74	165·2	121	249·8
—19	— 2·2	28	82·4	75	167·0	122	251·6
—18	— 0·4	29	84·2	76	168·8	123	253·4
—17	+ 1·4	30	86·0	77	170·6	124	255·2
—16	3·2	31	87·8	78	172·4	125	257·0
—15	5·0	32	89·6	79	174·2	126	258·8
—14	6·8	33	91·4	80	176·0	127	260·6
—13	8·6	34	93·2	81	177·8	128	262·4
—12	10·4	35	95·0	82	179·6	129	264·2
—11	12·2	36	96·8	83	181·4	130	266·0
—10	14·0	37	98·6	84	183·2	131	267·8
— 9	15·8	38	100·4	85	185·0	132	269·6
— 8	17·6	39	102·2	86	186·8	133	271·4
— 7	19·4	40	104·0	87	188·6	134	273·2
— 6	21·2	41	105·8	88	190·4	135	275·0
— 5	23·0	42	107·6	89	192·2	136	276·8
— 4	24·8	43	109·4	90	194·0		

VII.

ON THE CENTIGRADE THERMOMETER

FAHRENHEIT'S SCALE.

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
137	278·6	183	361·4	229	444·2	275	527·0
138	280·4	184	363·2	230	446·0	276	528.8
139	282·2	185	365·0	231	447·8	277	530·6
140	284·0	186	366·8	232	449·6	278	532·4
141	285·8	187	368·6	233	451·4	279	534·2
142	287·6	188	370·4	234	453·2	280	536·0
143	289·4	189	372·2	235	455·0	281	537·8
144	291·2	190	374·0	236	456·8	282	539·6
145	293·0	191	375·8	237	458·6	283	541·4
146	294·8	192	377·6	238	460·4	284	543·2
147	296·6	193	379·4	239	462·2	285	545·0
148	298·4	194	381·2	240	464·0	286	546·8
149	300·2	195	383·0	241	465·8	287	548·6
150	302·0	196	384·8	242	467·6	288	550·4
151	303·8	197	386·6	243	469·4	289	552·2
152	305·6	198	388·4	244	471·2	290	554·0
153	307·4	199	390·2	245	473·0	291	555·8
154	309·2	200	392·0	246	474·8	292	557·6
155	311·0	201	393·8	247	476·6	293	559·4
156	312·8	202	395·6	248	478·4	294	561·2
157	314·6	203	397·4	349	480·2	295	563·0
158	316·4	204	399·2	250	482·0	296	564·8
159	318·2	205	401·0	251	483·8	297	566·6
160	320·0	206	402·8	252	485·6	298	568·4
161	321·8	207	404·6	253	487·4	299	570·2
162	323·6	208	406·4	254	489·2	300	572·0
163	325·4	209	408·2	255	491·0	301	573·8
164	327·2	210	410·0	256	492·8	302	575·6
165	329·0	211	411·8	257	494·6	303	577·4
166	330·8	212	413·6	258	496·4	304	579·2
167	332·6	213	415·4	259	498·2	305	581·0
168	334·4	214	417·2	260	500·0	306	582·8
169	336·2	215	419·0	261	501·8	307	584·6
170	338·0	216	420·8	262	503·6	308	586·4
171	339·8	217	422·6	263	505·4	309	588·2
172	341·6	218	424·4	264	507·2	310	590·0
173	343·4	219	426·2	265	509·0	311	591·8
174	345·2	220	428·0	266	510·8	312	593·6
175	347·0	221	429·8	267	512·6	313	595·4
176	348·8	222	431·6	268	514·4	314	597·2
177	350·6	223	433·4	269	516·2	315	599·0
178	352·4	224	435·2	270	518·0	316	600·8
179	354·2	225	437·0	271	519·8	317	602·6
180	356·0	226	438·8	272	521·6	318	604·4
181	357·8	227	440·6	273	523·4	319	606·2
182	359·6	228	442·4	274	525·2	320	608·0

TABLE VIII.

WEIGHTS AND MEASURES.

GRAMMES.		GRAINS.	DECIGRAMMES.		GRAINS.
1	=	15·4346	1	=	1·5434
2	...	30·8692	2	...	3·0869
3	...	46·3038	3	...	4·6304
4	...	61·7384	4	...	6·1738
5	...	77·1730	5	...	7·7173
6	...	92·6076	6	...	9·2607
7	...	108·0422	7	...	10·8042
8	...	123·4768	8	...	12·3476
9	...	138·9114	9	...	13·8911

CENTIGRAMMES.		GRAINS.	MILLIGRAMMES.		GRAINS.
1	=	·1543	1	=	·0154
2	...	·3086	2	...	·0308
3	...	·4630	3	...	·0463
4	...	·6173	4	...	·0617
5	...	·7717	5	...	·0771
6	...	·9260	6	...	·0926
7	...	1·0804	7	...	·1080
8	...	1·2347	8	...	·1234
9	...	1·3891	9	...	·1389

METRES.		INCHES.	DECIMETRES.		INCHES.
1	=	39·37	1	=	3·937
2	...	78·74	2	...	7·874
3	...	118·11	3	...	11·811
4	...	157·48	4	...	15·748
5	...	196·85	5	...	19·685
6	...	236·22	6	...	23·622
7	...	275·59	7	...	27·559
8	...	314·96	8	...	31·496
9	...	354·33	9	...	35·433

CENTIMETRES.		INCHES.	MILLIMETRES.		INCHES.
1	=	·3937	1	=	·03937
2	...	·7874	2	...	·07874
3	...	1·1811	3	...	·11811
4	...	1·5748	4	...	·15748
5	...	1·9685	5	...	·19685
6	...	2·3622	6	...	·23622
7	...	2·7559	7	...	·27559
8	...	3·1496	8	...	·31496
9	...	3·5433	9	...	·35433

One kilogramme	=	15434 grains.
One cubic centimeter	=	0·0610 cubic inch.
One litre	=	61·0271 cubic inches.

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ERRATA.

Page 105, line 17 from top, *for* is, *read* or.

— 120, line 3 from bottom, *for* paratartaric, *read* tartaric.

— 123, line 11 and 12 from top, *for* tersulphide of arsenic is weighed either as arseniate of lead or as arsenic, *read* arsenic is weighed either as tersulphide of arsenic or as arseniate of lead.

Page 301, line 8 from top, *for* sulphide, *read* sulphite.

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