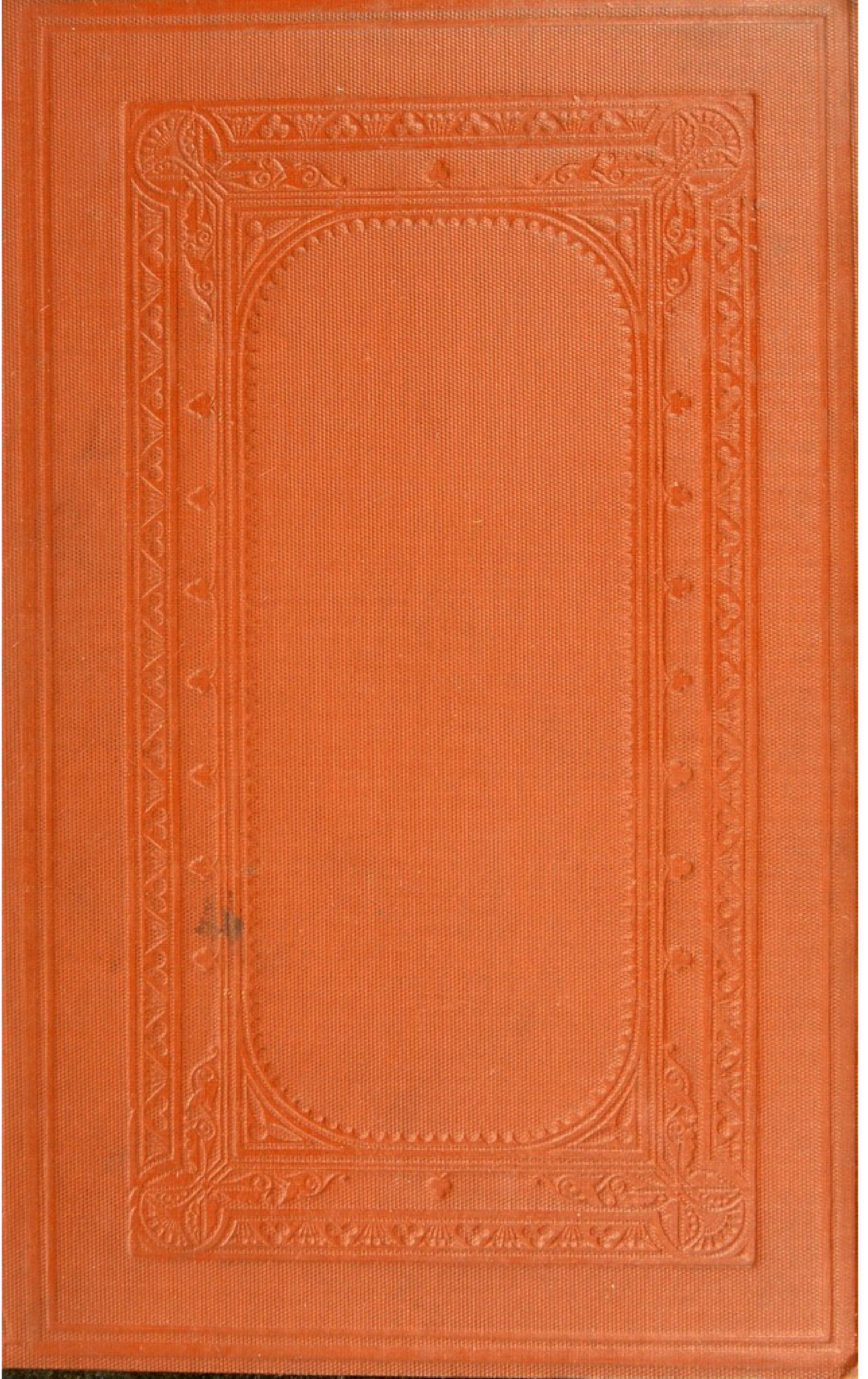
**A systematic handbook of volumetric analysis, or, The quantitative estimation of chemical substances by measure, applied to liquids, solids, and gases / by Francis Sutton.**



16/-

# A SYSTEMATIC HANDBOOK
OF
# VOLUMETRIC ANALYSIS.

A

# SYSTEMATIC HANDBOOK

OF

# VOLUMETRIC ANALYSIS;

OR,

## THE QUANTITATIVE ESTIMATION OF CHEMICAL SUBSTANCES BY MEASURE, APPLIED TO LIQUIDS, SOLIDS, AND GASES.

ADAPTED TO THE REQUIREMENTS OF PURE CHEMICAL RESEARCH,
PATHOLOGICAL CHEMISTRY, PHARMACY, METALLURGY, MANUFACTURING
CHEMISTRY, PHOTOGRAPHY, ETC., AND FOR THE VALUATION
OF SUBSTANCES USED IN COMMERCE, AGRICULTURE, AND THE ARTS.

BY

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# PREFACE.

The literature of chemical analysis published throughout the Continent and in America during the last three or four years has been very voluminous, and in my opinion very satisfactory, as manifesting the true liberal spirit of Science—namely, the desire to impart any discovery or improvement to any one who is anxious to learn. Nevertheless it has its drawbacks in the publication of many useless processes, but this is probably more than compensated for, by here and there a really good thing.

This may certainly be said of the department of analysis to which this book belongs; to wit, the valuable experiments of R. T. Thompson on the Indicators for use in Alkalimetry and Acidimetry; the development of technical gas analysis and the verification and improvement in older methods, which naturally arises from the observation and practice of a large variety of operators. The difficulty is to keep a work like this within reasonable bounds, so that it may continue what it professes to be—a Handbook.

No pains or time have been spared in consulting the contributions of a host of writers in the journals of various countries and languages, combined with practical verification of methods, in order to keep the book abreast of the times. Nevertheless I am conscious of many shortcomings, due to the fact that the examination of processes under all sorts of conditions is no light demand on the time and patience of any one man.

It will be noticed that some parts of the previous editions have been excluded, as being of little value, among which may be mentioned the systematic analysis of soils and manures by volumetric methods; also that of indigo, a really good process for which has still to be found.

Other new methods have been added, and the whole has undergone complete revision, together with an enlargement of the index, so that I indulge the hope that the book may still continue to be as acceptable as it has hitherto been.

The French translation of the fourth edition, by Dr. Méhu of Paris, was published in 1883, and has had a satisfactory reception.

I have again to thank my friend Mr. W. Thorp, B. Sc., for the revision of some of the proof-sheets, not so many, however, as I could wish, owing to the demand for the book necessitating its rapid passage through the press.

There must inevitably be some errors, but I hope and believe, thanks to a careful printer's reader, that they will be few and unimportant.

FRANCIS SUTTON.

NORWICH,
*October*, 1886.

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| Name. | Symbol. | Exact Atomic Weight, as found by the latest researches. | Atomic Weight adopted in this Edition. |
|---|---|---|---|
| Aluminium | Al | 27·3 | 27·3 |
| Antimony | Sb | 119·6 | 120·0 |
| Arsenic | As | 74·9 | 75·0 |
| Barium | Ba | 136·8 | 136·8 |
| Bismuth | Bi | 208·0 | 210·0 |
| Bromine | Br | 79·75 | 80·0 |
| Cadmium | Cd | 111·6 | 111·6 |
| Calcium | Ca | 39·9 | 40·0 |
| Carbon | C | 11·97 | 12·0 |
| Cerium | Ce | 141·2 | 141·2 |
| Chlorine | Cl | 35·37 | 35·37 |
| Chromium | Cr | 52·4 | 52·4 |
| Cobalt | Co | 58·6 | 59·0 |
| Copper | Cu | 63·18 | 63·0 |
| Gold | Au | 196·2 | 196·5 |
| Hydrogen | H | 1·0 | 1·0 |
| Iodine | I | 126·5 | 126·5 |
| Iron | Fe | 55·88 | 56·0 |
| Lead | Pb | 206·4 | 206·4 |
| Magnesium | Mg | 23·94 | 24·0 |
| Manganese | Mn | 55·0 | 55·0 |
| Mercury | Hg | 199·8 | 200·0 |
| Molybdenum | Mo | 95·8 | 95·8 |
| Nickel | Ni | 58·6 | 59·0 |
| Nitrogen | N | 14·01 | 14·0 |
| Oxygen | O | 15·96 | 16·0 |
| Phosphorus | P | 30·96 | 31·0 |
| Platinum | Pt | 196·7 | 196·7 |
| Potassium | K | 39·04 | 39·0 |
| Silver | Ag | 107·66 | 107·66 |
| Sodium | Na | 22·99 | 23·0 |
| Strontium | Sr | 87·2 | 87·2 |
| Sulphur | S | 31·98 | 32·0 |
| Tin | Sn | 117·8 | 118·0 |
| Tungsten | W | 184·0 | 184·0 |
| Uranium | Ur | 239·8 | 240·0 |
| Vanadium | Va | 51·2 | 51·2 |
| Zinc | Zn | 64·9 | 65·0 |

## **Abbreviations and Explanations.**

The formulæ are constructed on the basis $H=1$. $O=16$. $H^2O=18$.

The normal temperature for the preparation and use of standard solutions is 16° C., or about 60° Fahr.

c.c. denotes cubic centimeter.

gm. ,, gram=15·43235 grains English.

grn. ,, grain.

dm. ,, decem=10 fluid grains.

1 liter=1000 c.c. at 16° C.

1 c.c.=1 gm. distilled water at 16° C.

1 dm.=10 grn.

Distilled water is to be used in all the processes, unless otherwise expressed.

Normal Solutions are those which contain one gram atom of re-agent (taken as monobasic), or an equivalent in some active constituent (*e.g.* oxygen) in the liter (see p. 22).

Decinormal Solutions are one-tenth of that strength $=\frac{N}{10}$.

Centinormal, one hundredth $=\frac{N}{100}$.

Empirical Standard Solutions are those which contain no exact atomic proportion of re-agent, but are constructed generally so that 1 c.c.=0·01 gm. (one centigram) of the substance sought.

A Titrated Solution (from the French word *titre*, title or power) denotes a solution whose strength or chemical power has been accurately found by experiment.

When a chemical substance or solution is directed to be *titrated*, the meaning is, that it is to be quantitatively tested for the amount of pure substance it contains by the help of standard or titrated solutions. The term is used in preference to *tested* or *analyzed*, because these expressions may relate equally to qualitative and quantitative examinations, whereas titrations can only apply to quantitative examination.

*J. C. S.* denotes Journal of the Chemical Society (Transactions only).

*J. S. C. I.* ,, Journal of the Society of Chemical Industry.

*Z. a. C.* ,, Zeitschrift für Analytische Chemie.

*C. N.* ,, Chemical News.

Other book-references are given in full.

# VOLUMETRIC ANALYSIS
OF
# LIQUIDS AND SOLIDS.

## PART I.

### GENERAL PRINCIPLES.

§ 1. QUANTITATIVE analysis by weight, or gravimetric analysis, consists in separating out the constituents of any compound, either in a pure state or in the form of some new substance of known composition, and accurately weighing the products. Such operations are frequently very complicated, and occupy a long time, besides requiring in many cases elaborate apparatus, and the exercise of much care and experimental knowledge. Volumetric processes, on the other hand, are, as a rule, quickly performed; in most cases are susceptible of extreme accuracy, and need much simpler apparatus. The leading principle of the method consists in submitting the substance to be estimated to certain characteristic reactions, employing for such reactions solutions of known strength, and from the volume of solution necessary for the production of such reaction, determining the weight of the substance to be estimated by aid of the known laws of chemical equivalence.

Volumetric analysis, or quantitative chemical analysis by measure, in the case of liquids and solids, consequently depends upon the following conditions for its successful practice:—

1. A solution of the re-agent or test, the chemical power of which is accurately known, called the "standard solution."

2. A graduated vessel from which portions of it may be accurately delivered, called the burette.

3. The decomposition produced by the test solution with any given substance must either in itself or by an indicator be such, that *its termination is unmistakable to the eye*, and thereby the quantity of the substance with which it has combined accurately determined.

Suppose, for instance, that it is desirable to know the quantity of pure silver contained in a shilling. The coin is first dissolved in nitric acid, by which means a bluish solution, containing silver, copper, and probably other metals, is obtained. It is a known fact that chlorine combines with silver in the presence of other metals to form silver chloride, which is insoluble in nitric acid. The proportions in which the combination takes place are 35·37 of chlorine to every 107·66 of silver; consequently, if a standard solution of pure sodic chloride is prepared by dissolving in water such a weight of the salt as will be equivalent to 35·37 grains of chlorine (= 58·37 grains NaCl) and diluting to the measure of 1000 grains; every single grain measure of this solution will combine with 0·10766 grain of pure silver to form silver chloride, which is precipitated to the bottom of the vessel in which the mixture is made. In the process of adding the salt solution to the silver, drop by drop, a point is at last reached when the precipitate ceases to form. Here the process must stop. On looking carefully at the graduated vessel from which the standard solution has been used, the operator sees at once the number of grain measures which has been necessary to produce the complete decomposition. For example, suppose the quantity used was 520 grain measures; all that is necessary to be done is to multiply 520 by the coefficient for each grain measure, viz. 0·10766, which shows the amount of pure silver present to be 55·98 grains.

This method of determining the quantity of silver in any given solution occupies scarcely a quarter of an hour, whereas the estimation by weighing could not be done in half a day, and even then not so accurately as by the volumetric method. It must be understood that there are certain necessary precautions in conducting the above process which have not been described; those will be found in their proper place; but from this example it will at once be seen that the saving of time and trouble, as compared with the older methods of analysis, is immense; besides which, in the majority of instances in which it can be applied, it is equally accurate, and in many cases much more so.

The only conditions on which the volumetric system of analysis are to be carried on successfully are, that the greatest care is exercised with respect to the graduation of the measuring instruments, the strength and purity of the standard solutions, and the absence of other matters which would interfere with the accurate estimation of the particular substance sought.

The fundamental distinction between gravimetric and volumetric analysis is, that in the former method, the substance to be estimated must be completely isolated in the purest possible state or combination, necessitating in many instances very patient and discriminating labour; whereas, in volumetric processes, such complete separation is very seldom required, the processes being so contrived as to admit of the presence of half a dozen or more other substances which have no effect upon the particular chemical reaction required.

The process just described for instance, the estimation of silver in coin, is a case in point. The alloy consists of silver and copper, with small proportions of lead, antimony, tin, gold, etc. None of these things affect the amount of salt solution which is chemically required to precipitate the silver, whereas, if the metal had to be determined by weight it would be necessary to first filter the nitric acid solution to free it from insoluble tin, gold, etc.; then precipitate with a slight excess of sodic chloride; then to bring the precipitate upon a filter, and wash repeatedly with pure water until every trace of copper, sodic chloride, etc., is removed. The pure silver chloride is then carefully dried, ignited separately from the filter, and weighed; the filter burnt, residue as reduced metallic silver and filter ash allowed for, and thus finally the amount of silver is found by the balance with ordinary weights.

On the other hand the volumetric process has been purely chemical, the burette or measuring instrument has taken the place of the balance, and theoretical or atomic weights have supplanted ordinary weights.

The end of the operation in this method of analysis is in all cases made apparent to the eye. In alkalimetry it is the change of colour produced in litmus, turmeric, or other sensitive colouring matter. The formation of a permanent precipitate, as in the estimation of cyanogen. A precipitate ceasing to form, as in chlorine and silver determination. The appearance of a distinct colour, as in iron analysis by permanganate solution, and so on.

I have adopted the classification of methods used by Mohr and others, namely:—

1. Where the determination of the substance is effected by saturation with another substance of opposite properties—generally understood to include acids and alkalies, or alkaline earths.

2. Where the determination of a substance is effected by a reducing or oxidizing agent of known power, including most metals, with their oxides and salts; the principal oxidizing agents being potassic permanganate, potassic bichromate, and iodine; and the corresponding reducing agents, ferrous and stannous compounds, and sodic thiosulphate.

3. Where the determination of a substance is effected by precipitating it in some insoluble and definite combination, an example of which occurs in the estimation of silver described above.

This classification does not rigidly include all the volumetric processes that may be used, but it divides them into convenient sections for describing the peculiarity of the reagents used, and their preparation. If strictly followed out, it would in some cases necessitate the registration of the body to be analyzed under two or three heads. Copper, for instance, can be determined residually by potassic permanganate ; it can also be determined by precipitation with sodic sulphide. The estimation of the same metal by potassic cyanide, on the other hand, would not come under any of the heads.

It will be found, therefore, that liberties have been taken with the arrangement ; and for convenient reference all analytical processes applicable to a given body are included under its name.

It may be a matter of surprise to some that several distinct volumetric methods for one and the same substance are given ; but a little consideration will show that in many instances greater convenience, and also accuracy, may be gained in this way.

The operator may not have one particular reagent at command, or he may have to deal with such a mixture of substance as to preclude the use of some one method ; whereas another may be quite free from such objection : the choice in such cases of course requires judgment, and it is of the greatest importance that the operator shall be acquainted with the qualitative composition of the matters with which he is dealing, and that he should ask himself at every step why such and such a thing is done.

It will be apparent from the foregoing description of the volumetric system, that it may be successfully used in many instances by those who have never been thoroughly trained as analytical chemists ; but we can never look for the scientific development of the system in such hands as these.

In the preparation of this work an endeavour has been made to describe all the operations and chemical reactions as simply as possible, purposely avoiding abstruse mathematical expressions, which, though they may be more consonant with the modern study of chemical science, are hardly adapted to the technical operator.

# THE INSTRUMENTS AND APPARATUS.

## THE BALANCE.

§ 2. Strictly speaking, it is necessary to have two balances in order to carry out the volumetric system completely; one to carry about a kilogram in each pan, and turn when loaded with about five milligrams. This instrument is used for graduating flasks, or for testing them, and for weighing large amounts of pure reagents for standard solutions. The second balance should be light and delicate, and to carry about fifty grams, and turn easily and quickly when loaded with one or two-tenths of a milligram. This instrument serves for weighing small quantities of substances to be tested, many of which are hygroscopic, and need to be weighed quickly and with great accuracy; it also serves for testing the accuracy of pipettes and burettes.

For all technical purposes, however, a moderate sized balance of medium delicacy is quite sufficient, especially if rather large quantities of substances are weighed and brought into solution—then further subdivided by means of measuring flasks and pipettes.

The operator also requires, besides the balance and the graduated instruments, a few beakers, porcelain basins, flasks, funnels, stirring rods, etc., as in gravimetric analysis; above all he must be practically familiar with proper methods of filtration, washing of precipitates, and the application of heat.

## VOLUMETRIC ANALYSIS WITHOUT WEIGHTS.

§ 3. This is more a matter of curiosity than of value; but, nevertheless, one can imagine circumstances in which it might be useful. In carrying it out, it is necessary only to have (1) a correct balance, (2) a pure specimen of substance to use as a weight, (3) an accurate burette filled with the appropriate solution. It is not necessary that the strength of this should be known; but the state of concentration should be such as to permit the necessary reaction to occur under the most favourable circumstances.

If a perfectly pure specimen of substance, say calcic carbonate, be put into one scale of the balance, and be counterpoised with an impure specimen of the same substance, and both titrated with the same acid, and the number of c.c. used for the pure substance be called 100, the number of c.c. used for the impure substance will correspond to the percentage of pure calcic carbonate in the specimen examined.

The application of the process is, of course, limited to the use of such substances as are to be had pure, and whose weight is not variable by exposure; but where even a pure substance of one kind cannot be had as a weight, one of another kind may be used as a substitute, and the required result obtained by calculation. For instance, it is required to ascertain the purity of a specimen of sodic carbonate, and only pure calcic carbonate is at hand to use as a weight; equal weights of the two are taken, and the impure specimen titrated with acid. To arrive at the required answer, it is necessary to find a coefficient or factor by which to convert the number of c.c. required by the sodic carbonate, weighed on the calcic, into that which should be required if weighed on the sodic, basis. A consideration of the relative molecular weights of the two bodies will give the factor thus—

$$\frac{\text{Calcic carbonate } 100}{\text{Sodic carbonate } 106} = 0{\cdot}9434$$

If, therefore, the c.c. used are multiplied by this number, the percentage of pure sodic carbonate will be obtained. The method may be extended to a number of substances, on this principle, with the exercise of a little ingenuity.

## VOLUMETRIC ANALYSIS WITHOUT BURETTES OR OTHER GRADUATED INSTRUMENTS.

§ 4. This operation consists in weighing the standard solutions on the balance instead of measuring them. The influence of variation in temperature is, of course, here of no consequence. The chief requisite is a delicate flask, fitted with a tube and blowing ball, as in the burette, fig. 5, or an instrument known as Schuster's alkalimeter may be used. A special burette has been devised for this purpose by Casamajor (*C. N.* xxxv. 98). The method is capable of very accurate results, if care be taken in preparing the standard solutions and avoiding any loss in pouring the liquid from the vessel in which it is weighed. It occupies much more time than the usual processes of volumetric analysis, but at great extremes of temperature it is far more accurate.

## THE BURETTE.

§ 5. This instrument is used for the delivery of an accurately measured quantity of any particular standard solution. It invariably consists of a long glass tube of even bore, throughout the length of which are engraved, by means of hydrofluoric acid, certain divisions corresponding to a known volume of fluid.

It may be obtained in a great many forms, under the names of their respective inventors, such as Mohr, Gay Lussac, Binks, etc., but as some of these possess a decided superiority over others, it is not quite a matter of indifference which is used, and therefore a slight description of them may not be out of place here. The burette, with glass stop-cock or india-rubber tube and clip, contrived by Mohr, shown in figs. 1 and 2, has the preference above all others for general purposes.

The advantages possessed by this instrument are, that its constant

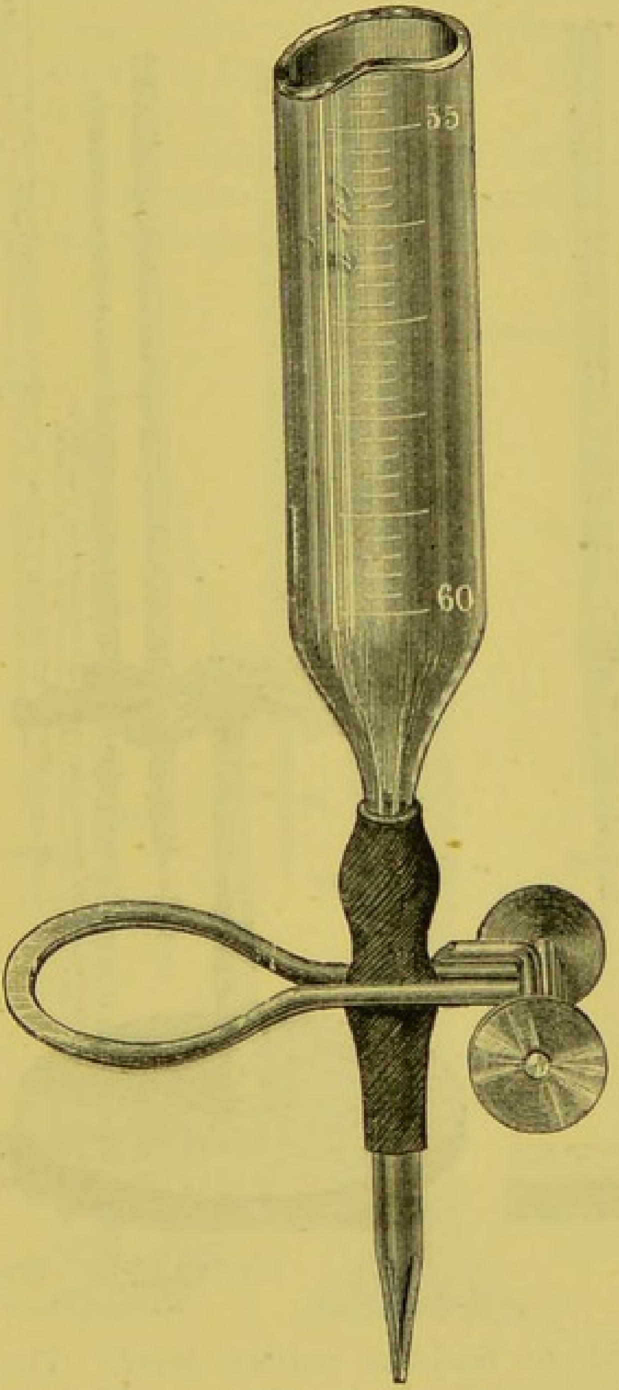

Fig. 1.

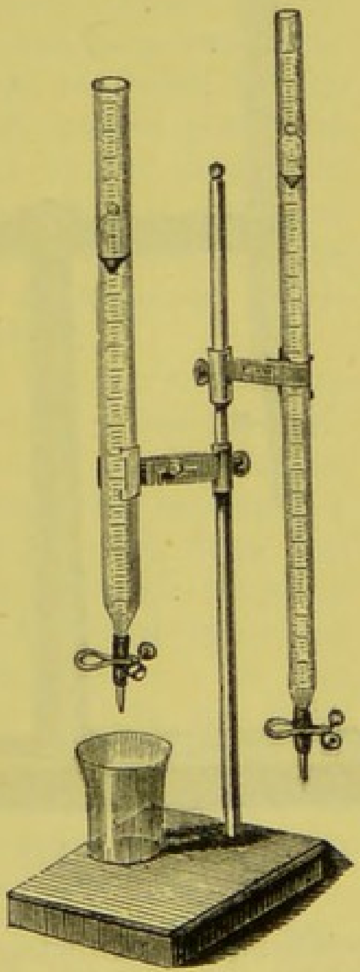

Fig. 2.

upright position enables the operator at once to read off the number of degrees of test solution used for any analysis. The quantity of fluid to be delivered can be regulated to the greatest nicety by the pressure of the thumb and finger on the spring clip or by the tap; and the instrument not being held in the hand, there is no chance of increasing the bulk of the fluid by the heat of the body, and thus leading to incorrect measurement, as is the case with Binks' or Gay Lussac's form of instrument. The principal disadvantage, however, of these two latter forms of burette is, that a correct reading can only be obtained by placing them in an upright position, and allowing the fluid to find its perfect level. The preference should, therefore, unhesitatingly be given to Mohr's burette, wherever it can be used; the greatest drawback to its original form is, that it cannot be used for permanganate in consequence of its india-rubber tube, which decomposes the solution. This, however, can be entirely obviated by the use of the same kind of burette fitted with a delicate glass stop-cock, as shown in fig. 4. This tap burette is very serviceable, as it can be used not only for permanganate but for all other solutions, and may also

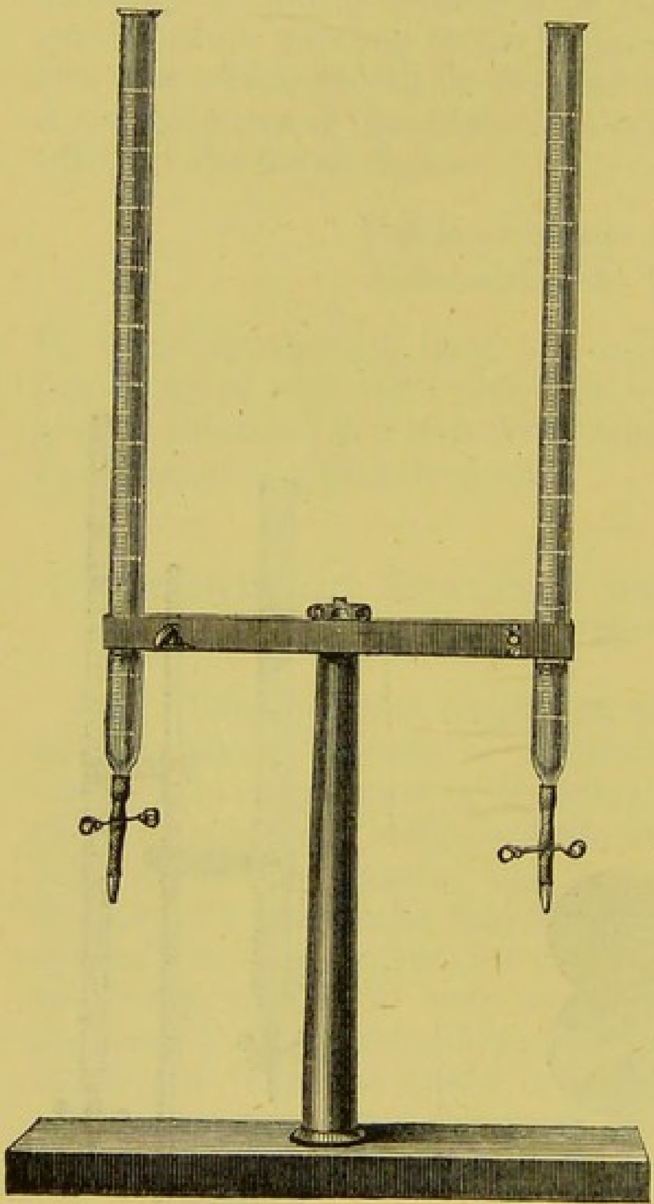

Fig. 3.

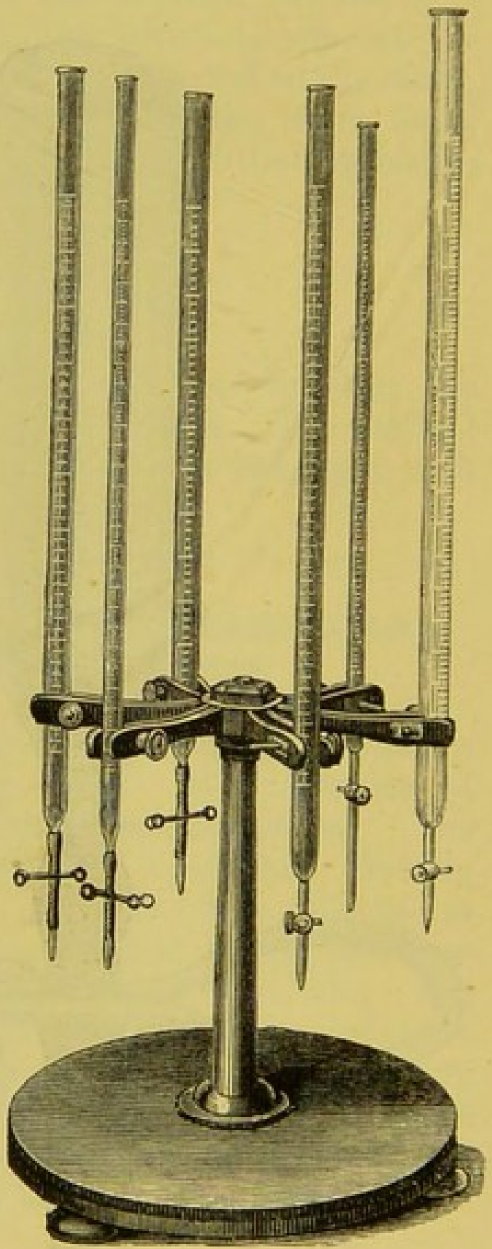

Fig. 4.

be arranged so as to deliver the solution in drops, leaving both the hands of the operator disengaged. The tap should be ground very accurately, and the end of the plug should have a collar of india-rubber or buckskin fastened on it, so as to prevent the plug from slipping out of its place. Owing to the action of caustic alkalies upon glass, such a burette does not answer well for strong solutions of potash or soda, unless emptied and washed immediately after use. Two convenient forms of stand for Mohr's burettes are shown in figs. 3 and 4; in the latter, the arms carrying the burettes revolve.

We are indebted to Mohr for another form of instrument to avoid the contact of permanganate and india-rubber, viz., the foot burette, with elastic ball, shown in fig. 5.

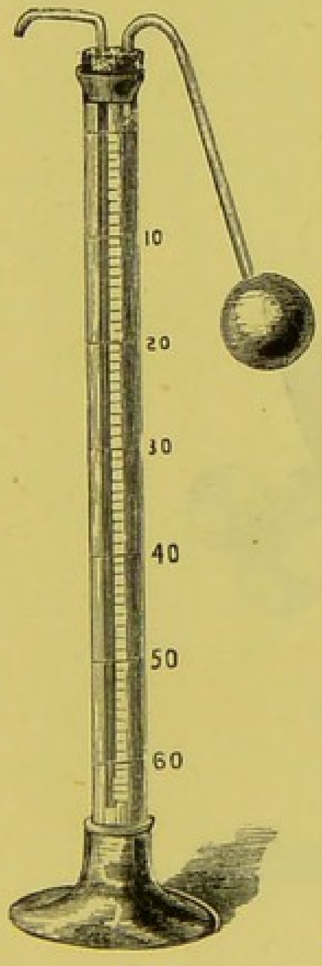

Fig. 5.

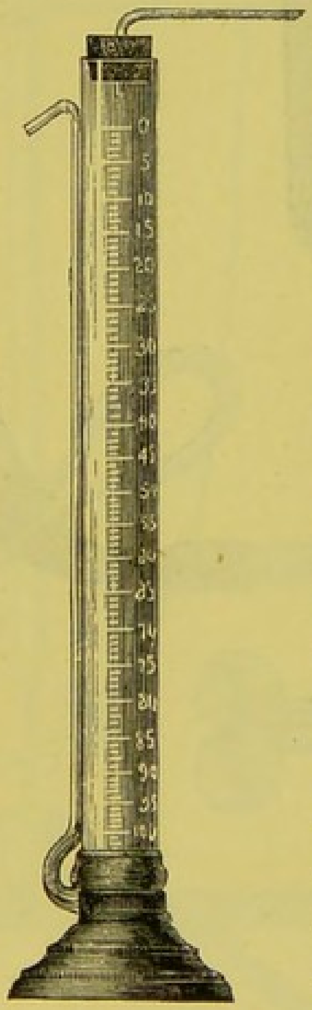

Fig. 6.

The flow of liquid from the exit tube can be regulated to a great nicety by pressure upon the ball which should be large, and have two openings,—one cemented to the tube with marine glue, and the other at the side, over which the thumb is placed when pressed, and on the removal of which it refills itself with air.

Gay Lussac's burette, supported in a wooden foot, may be used instead of the above form, by inserting a good fitting cork into the open end, through which a small tube bent at right angles is passed. If the burette is held in the right hand, slightly inclined towards the beaker or flask into which the fluid is to be measured, and the mouth applied to the tube, any portion of the solution may be emptied out by the pressure of the breath, and the disadvantage of holding the instrument in a horizontal position, to the great danger of spilling the contents, is avoided; at the same time the beaker or flask can be held in the left hand and shaken so as to mix the fluids, and by this means the end of the operation be more accurately determined (see fig. 6).

There is an arrangement of Mohr's burette which is extremely serviceable, when a series of analyses of the same character have to be made, such as in alkali works, assay offices, etc. It consists in having a T piece of glass tube inserted between the lower end of the burette and the spring clip, which communicates with a reservoir of the standard solution, placed above so that the burette may be filled as often as emptied, by a syphon, and in so gradual a manner that no air bubbles occur, as in the case of filling it with a funnel, or pouring in liquid from a bottle; beside which, this plan prevents evaporation or dust in the standard solution either in the burette or reservoir.

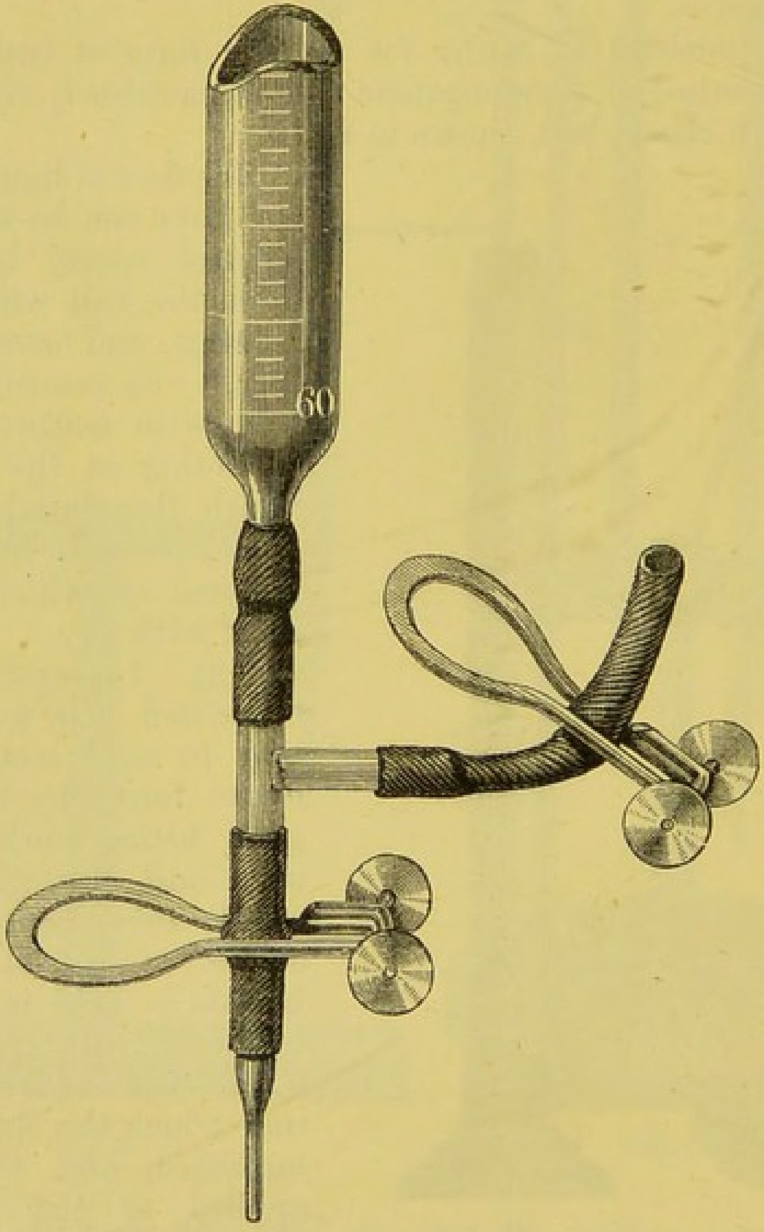

Fig. 7.

Figs. 7 and 8 show this arrangement in detail.

It sometimes happens that a solution requires titration at a hot or even boiling temperature, such as the estimation of sugar by copper solution: here the ordinary arrangement of Mohr's burette will

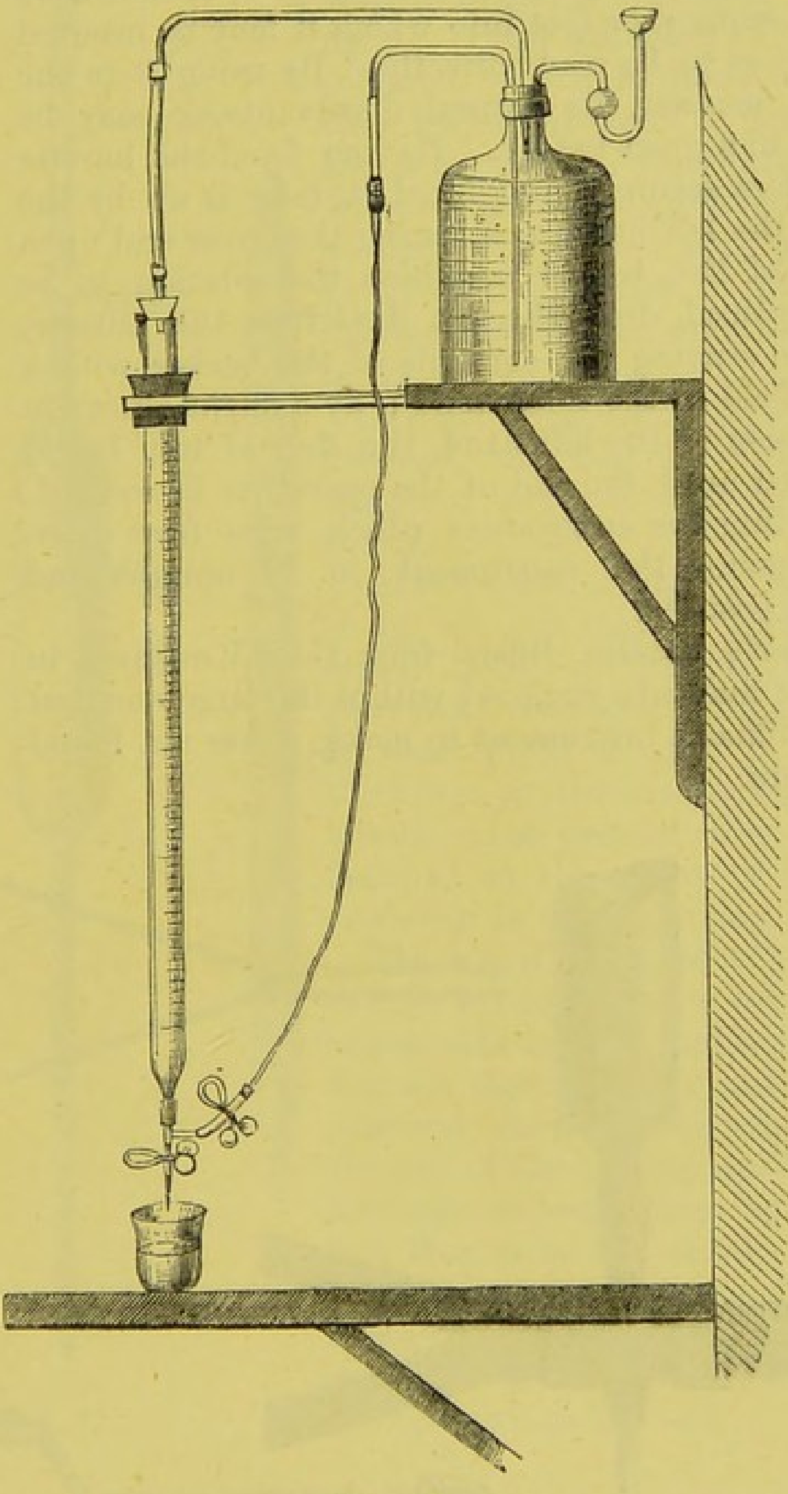

Fig. 8.

not be available, since the steam rising from the liquid heats the burette and alters the volume of fluid. This may be avoided by using a much longer piece of india-rubber tube, so that the burette stands at the side of the capsule or beaker being heated, and the elastic tube is brought over its edge; the pinch-cock is fixed midway; no heat can then reach the body of fluid in the burette, since there can be no conduction past the pinch-cock. If this plan is not adopted, a Gay Lussac or ball burette should be used.

Gay Lussac's burette, shown in fig. 9, should have a wooden support or foot into which it may be inserted (fig. 6), so as to be read correctly. By using it in the following manner, its natural disadvantages may be overcome to a great extent. Having fixed the burette into the foot securely, and filled it, take it up by the foot with the left hand, and resting the upper end upon the edge of the beaker in which the solution to be tested is placed, drop the test fluid from the burette, meanwhile stirring the contents of the beaker with a glass rod held in the right hand; by a slight elevation or depression of the left hand, the flow of test liquid is regulated until the end of the operation is secured, thus avoiding the annoyances which arise from alternately placing the instrument in an upright and horizontal position.

Geissler's burette differs from Gay Lussac's in having the fine tube enclosed within the large one, but as it is a difficult instrument to make, it has not found much favour.

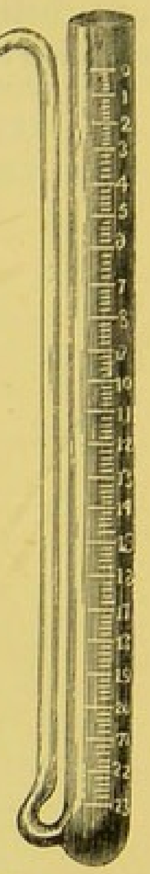

Fig. 9.

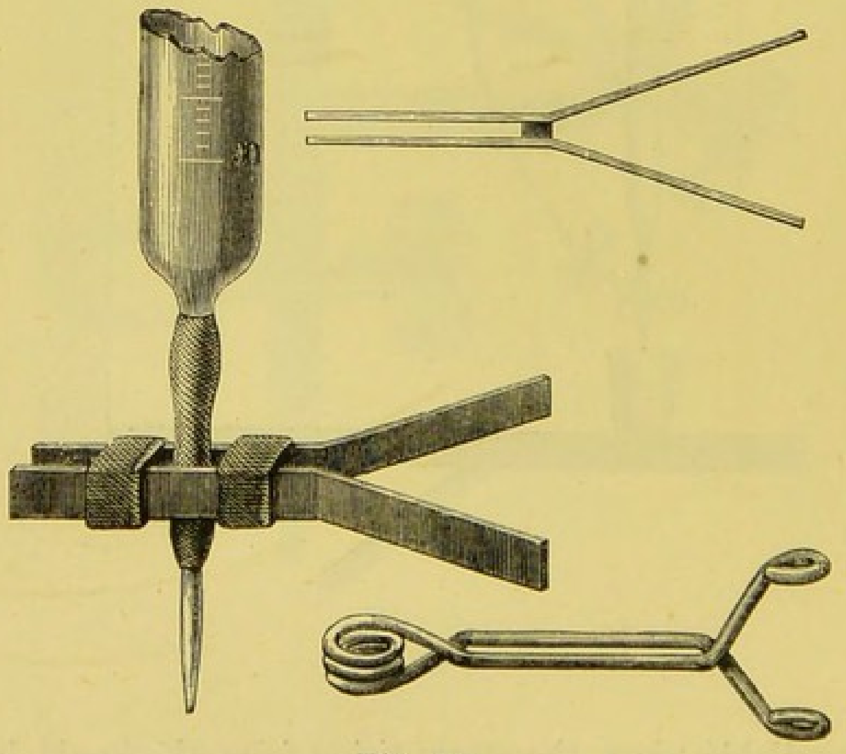

Fig. 10.

Binks', or, as it is sometimes called, the English burette, is well known, and need not be described; it is the least recommendable of all forms, except for very rough estimations.

It is most convenient to have burettes graduated to contain 25 or 30 c.c. in $\frac{1}{10}$ c.c., 50 or 60 c.c. in $\frac{1}{5}$ c.c., and 100 or 110 c.c. in $\frac{1}{2}$ or $\frac{1}{1}$ c.c.

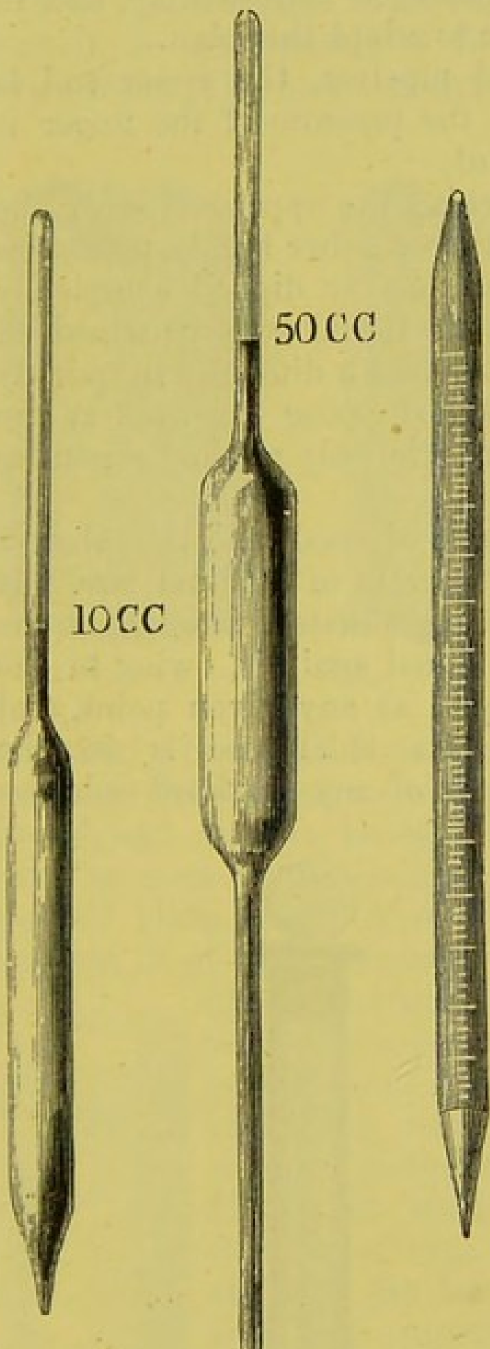

Fig. 11.

The kind of pinch-cock generally used in Mohr's burette is shown in fig. 1. These are made of brass and soldered, which is objectionable, as they frequently come to pieces under the action of the solutions. I have for some time used pinch-cocks made of one piece of steel wire, as devised by Hart; the wire is softened by heating and coiling round, as shown in fig. 10.

When the proper shape has been attained, the clip is hardened and tempered so as to convert it into a spring.

Another useful pinch-cock is shown in fig. 10. It may be made of hard wood, horn, or preferably, of flat glass rod. The levers should be long. A small piece of cork, of the same thickness as the elastic tube of the burette when pressed close, should be fastened at the angles of the levers as shown in the engraving.

The use of any kind of pinch-cock can be avoided, and a very delicate action obtained, by simply inserting a not too tightly fitting piece of solid glass rod into the elastic tube, between the end of the burette and the spit, a firm squeeze being given by the finger and thumb to the elastic tube surrounding the rod, a small canal is opened, and thus the liquid escapes, and of course can be controlled by the operator at his will.

## THE PIPETTE.

§ 6. The pipettes used in volumetric analysis are of two kinds, viz., those which deliver one certain quantity only, and those which are graduated on the stem, so as to deliver various quantities at the discretion of the analyst. In the former kind, or whole pipette, the graduation may be either that in which the fluid is suffered to run out by its own momentum, or in which it is blown out by the breath. The best form is that in which the liquid flows out by its own momentum, but in this case the last few drops empty themselves very slowly; but if the lower end of the pipette be touched against the moistened edge of the beaker or the surface of the fluid into which it is emptied, the flow is hastened considerably, and in graduating the pipette, it is preferable to adopt this plan.

In both the whole and graduated pipettes, the upper end is narrowed to about $\frac{1}{8}$ inch, so that the pressure of the finger is sufficient to arrest the flow at any point.

Pipettes are invariably filled by sucking the upper end with the mouth, unless the liquid contain volatile or other highly poisonous matter, in which case the instrument may be dipped completely into the fluid, but in this case the outside liquid must be wiped off before measuring. Beginners invariably find a difficulty in quickly filling the pipette above the mark, and stopping the fluid at the exact point. Practice with pure water is the only method of getting over this difficulty.

Fig. 11 shows two whole pipettes, one of small and the other of large capacity, and also a graduated pipette of medium size. It must be borne in mind that the pipette graduated throughout the stem is not a reliable instrument for actual analysis, owing to the difficulty of stopping the flow of liquid at any given point, and reading off the exact measurement. Its chief use is in the approximate estimation of the strength of any standard solution in the course of preparation.

### THE MEASURING FLASKS.

§ 7. THESE indispensable instruments are made of various capacities; they serve to mix up standard solutions to a given volume, and also for the subdivision of the substance to be tested by means of the pipettes, and are in many ways most convenient. They should be tolerably wide at the mouth, and have a well-ground glass stopper, and the graduation line should fall just below the middle of the neck, so as to allow room for shaking up the fluid. Convenient sizes are 100 c.c. (to deliver), 100, 200, 250, 300, 500, and 1000 c.c., the latter all graduated to *contain* the respective quantities. A liter flask is shown in fig. 12.

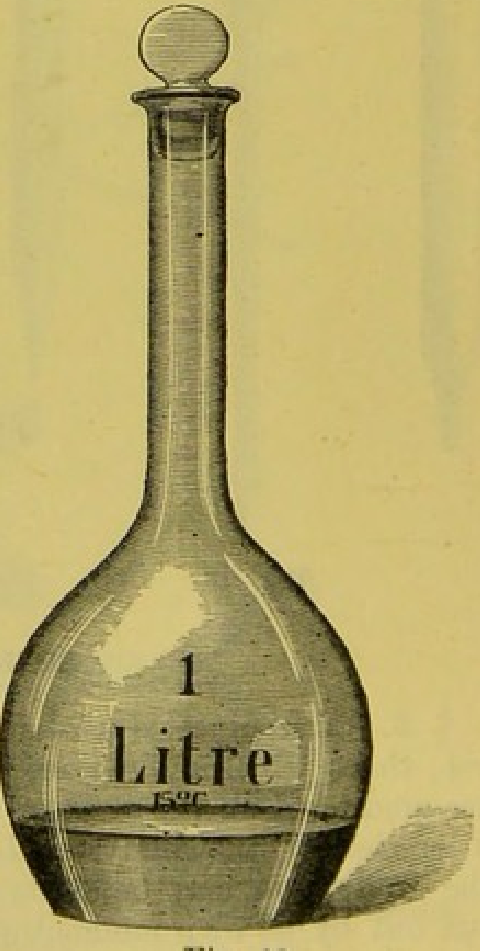

Fig. 12.

## ON THE CORRECT READING OF GRADUATED INSTRUMENTS.

§ 8. THE surface of liquids contained in narrow tubes is always curved, in consequence of the capillary attraction exerted by the sides of the tube, and consequently there is a difficulty in obtaining a distinct level in the fluid to be measured. If, however, the lowest point of the curve is made to coincide with the graduation mark, a correct proportional reading is always obtained, hence this method of reading is the most satisfactory (see fig. 13).

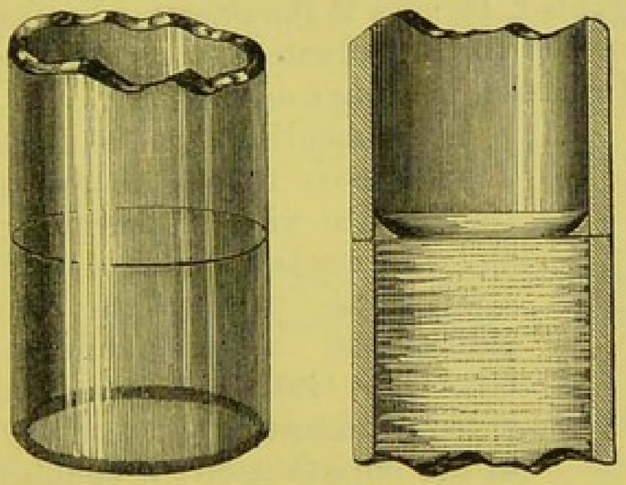

Fig. 13.

The eye may be assisted materially in reading the divisions on a graduated tube by using a small card, the lower half of which is blackened, the upper remaining white. If the line of division between the black and white be held about an eighth of an inch below the surface of the liquid, and the eye brought on a level with it, the meniscus then can be seen by transmitted light, bounded below by a sharply defined black line. A card of this kind, sliding up and down a support, is of great use in verifying the graduation of the burettes or pipettes with a cathetometer. Another good method is to use a piece of mirror, upon which are gummed two strips of black paper, half an inch apart; apply it in contact with the burette so that the eye can be reflected in the open space. The burette or pipette is filled with water at the proper temperature, and the contents of each division of 10 c.c. or so carefully read off with the telescope and weighed. In order to do this with pipettes they must be fixed in a burette support, and have over their upper end a tightly fitting elastic tube closed with a pinch-cock. The operator may here consult with advantage the details of graduating and verifying measuring instruments for the analysis of gases as described in Part 7. It is hardly necessary to say, that in taking the readings of burettes, pipettes, and flasks, the graduation mark should coincide as nearly as possible with the level of the operator's eye.

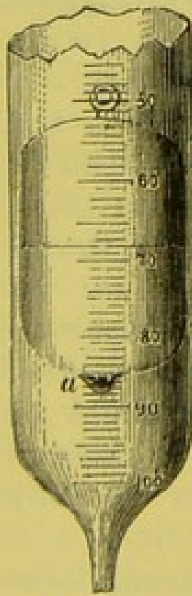

Fig. 14.

*Erdmann's Float.* This useful little instrument to accompany Mohr's burette, gives the most accurate reading that can be obtained; one of its forms is shown in fig. 14. It consists of an elongated glass bulb, rather smaller in diameter than the burette itself, and weighted at the lower end with a globule of mercury, like an hydrometer. It is drawn to a point at the upper end, and the point is bent round so as to form a small hook, by means of which it can be lifted in and out of the burette with a bent wire; a line is made with a diamond round its middle by means of a lathe, and the coincidence of this line with the graduation mark of the burette is accepted as the true reading. The actual height of the liquid in the burette is not regarded, because if the operator begins with the line on the float, opposite the 0 graduation mark on the burette, the same proportional division is always maintained.

It is essential that the float should move up and down in the burette without wavering, and the circle upon it should always be parallel to the graduations of the burette. One great value of this float is found in testing the accuracy of the burette itself; it enables a strict comparison to be made between say each 10 c.c., with very slight differences in weighing, supposing the instrument to be correct. It is always well, however, to bear in mind that absolute accuracy cannot be obtained in graduating instruments; 5 or 10 milligrams of water either way in 10 c.c. may safely be disregarded.

To prevent evaporation and the entrance of dust in Mohr's burette, while in use, a small beaker or wide test tube should be dropped over its orifice. In burettes containing caustic alkaline solutions, a cork with carbonic acid tube should be used if the solution is allowed to remain in them for any length of time.

Besides the measuring flasks it is necessary to have graduated vessels of cylindrical form, for the purpose of preparing standard solutions, etc.

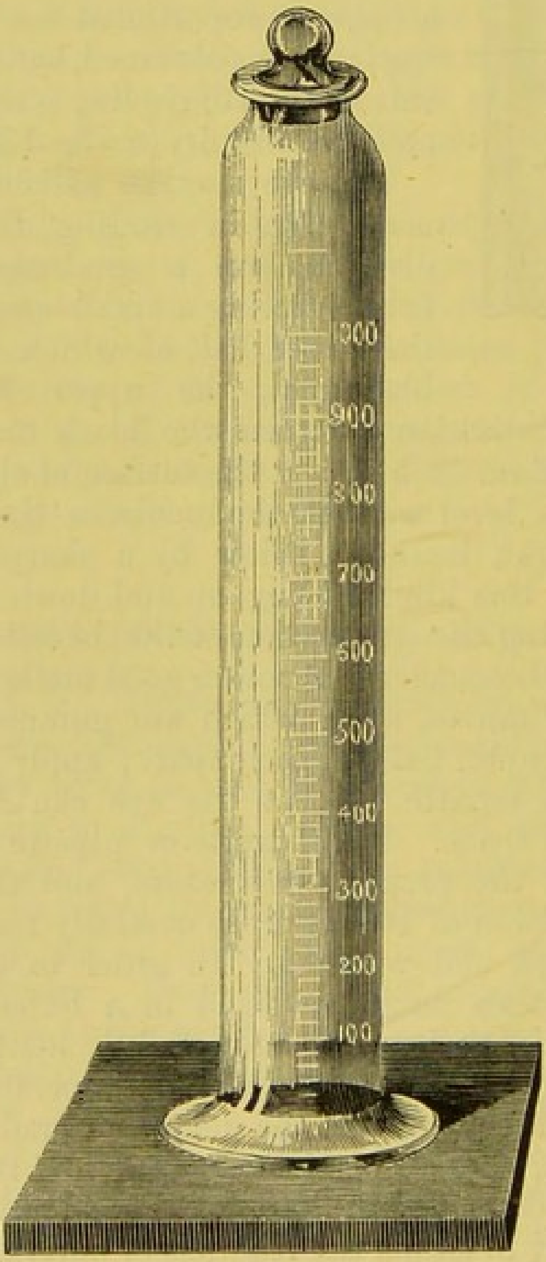

Fig. 15.

Fig. 15 shows a stoppered cylinder for this purpose, generally called a test mixer.

### FILTER FOR ASCERTAINING THE END-REACTION IN CERTAIN PROCESSES.

Fig. 16.

This is shown in fig. 16, and the instrument is known as Beale's filter. It serves well for taking a few drops of clear solution from any liquid in which a precipitate will not settle readily. To use it, a piece of filter paper is tied over the lower end, and over that a piece of fine muslin to keep the paper from being broken. When dipped into a muddy mixture, the clear fluid rises and may be poured out of the little spout for testing. If the process in hand is not completed, the contents are washed back to the bulk, and the operation repeated as often as may be required.

### ON THE SYSTEM OF WEIGHTS AND MEASURES TO BE ADOPTED IN VOLUMETRIC ANALYSIS.

§ 9. It is much to be regretted that the decimal system of weights and measures used on the Continent is not universally adopted, for scientific and medicinal purposes, in England. Its great advantage is its uniformity throughout. The unit of weight is the gram (= 15·43235 grains troy), and a gram of distilled water at 4° C., or 39° Fahr., measures exactly a cubic centimeter. The kilogram contains 1000 grams, the liter 1000 cubic centimeters.

It may not be out of place here to give a short description of the origin of the French decimal system, now used exclusively for scientific purposes in that country, and also in Prussia, Austria, Holland, Sweden, Denmark, Belgium, and Spain.

The commission appointed in France for the purpose of instituting a decimal system of weights and measures, founded their standard on the length of the meridian arc between the pole and equator, the ten-millionth part of which was called the *mètre* (= 39·3710 English inches), although the accuracy of this measurement has been disputed. It would have been preferable, as since proposed, that the length of a pendulum vibrating exactly 86,400 times in twenty-four hours, or one second for each vibration, equivalent to 39·1372 English inches, should have been taken as the standard *mètre*, in which case it would have been much easier to verify the standard in case it should be damaged or destroyed. However, the actual *mètre* in use is equal to 39·371 inches, and from this standard its multiples and subdivisions all proceed decimally; its one-tenth part being the *decimètre*, one-hundredth the *centimètre*, and one-thousandth the *millimètre*.

In accordance with this, a cube of distilled water at its greatest density, viz., 4° C., or 39° Fahr., whose side measures one decimeter, has exactly the weight of one kilogram, or 1000 grams, and occupies the volume of one liter, or 1000 cubic centimeters.

This simple relationship between liquids and solids is of great value in a system of volumetric analysis, and even for ordinary analysis by weight; for technical purposes it is equally as applicable as the grain system, the results being invariably tabulated in percentages.

With these brief explanations, therefore, I have only to state that the French decimal sytem will be mainly used throughout this treatise; but at the same time, those who may desire to adhere to the ordinary grain weights, can do so without interfering with the accuracy of the processes described.

As has been before stated, the true cubic centimeter contains one gram of distilled water at its greatest density, viz., 4° C., or 39° Fahr.; but as this is a degree of temperature at which it is impossible to work for more than a month or two in the year, it is better to take the temperature of 16° C., or about 60° Fahr., as the standard; because in winter most laboratories or rooms have furnaces or other means of warmth, and in summer the same localities ought not, under ordinary circumstances, to have a much higher degree of heat than 16° C. In order, therefore, that the graduation of instruments on the metrical system may be as uniform as possible with our own fluid measures, the cubic centimeter should contain one gram of distilled water at 16° C. The true c.c. (*i.e.* = 1 gm. at 4° C., or 39° Fahr.) contains only 0·999 gm. (strictly 0·998981) at that temperature; but for convenience of working, and for uniformity with our own standards of volume, it is better to make the c.c. contain one gram at 16° C. The real difference is one-thousandth part. The operator, therefore, supposing he desires to graduate his own measuring flasks, must weigh into them 250, 500, or 1000 grams of distilled water at 16° C., or 60° Fahr.

Fresenius and others have advocated the use of the strict liter by the graduation of instruments, so that they shall contain 999 gm. at 16° C. Mohr, on the contrary, uses a 1000 gm., at the temperature of 17·5°, the real difference being 1·2 c.c. in the liter, or about one eight-hundredth part.

It will be seen above that I have advocated a middle course on two grounds: (1) That in testing instruments it is much easier to verify them by means of round numbers, such as 5 or 10 gm. (2) That there are many thousands of instruments already in use varying between the two extremes; and as these cannot well be annihilated, the adoption of a mean will give a less probable amount of error between the respective instruments; and, moreover, the difference between the liter at 4° and 16° being one-thousandth part, it is easy to correct the measurement for the exact liter.

It matters not which plan is followed, if all the instruments in a particular set coincide with each other; but it would be manifestly wrong to use one of Mohr's burettes with one of Fresenius' measuring flasks. Operators can, however, without much difficulty, re-mark their measuring flasks to agree with their smaller graduated instruments, if they are found to differ to any material extent.

*Variations of Temperature.*—In the preparation of standard solutions, one thing must especially be borne in mind; namely, that saline substances on being dissolved in water have a considerable effect upon the volume of the resulting liquid. The same is also the case in mixing solutions of various salts or acids with each other (see Gerlach, "Specifische Gewichte der Salzlösungen;" also Gerlach, "Sp. Gewichte von wässerigen Lösungen," *Z. a. C.* viii. 245).

In the case of strong solutions, the condensation in volume is as a rule considerable: and, therefore, in preparing such solutions for volumetric analysis, or in diluting such solutions to a given volume for the purpose of removing aliquot portions subsequently for examination, sufficient time must be given for liquids to assume their constant volume at the standard temperature. If the strength of a standard solution is known for one temperature, the strength corresponding to another temperature can only be calculated if the rate of expansion by heat of the liquid is known. The variation cannot be estimated by the known rule of expansion in distilled water; for Gerlach has shown that even weak solutions of acids and salts expand far more than water for certain increments of temperature. The rate of expansion for pure water is known, and may be used for the purpose of verifying the graduation of instruments, where extreme accuracy is required. The following short table furnishes the data for correction (Watts' *Dict. of Chem.* i. 256).

The weight of 1000 c.c. of water of t° C., when determined by means of brass weights in air of t° C., and at 0·76 m.m. pressure, is equal to 1000 — x gm.

Slight variations of atmospheric pressure may be entirely disregarded.

| t° | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| x | 1·34 | 1·43 | 1·52 | 1·63 | 1·76 | 1·89 | 2·04 | 2·2 | 2·37 | 2·55 | |
| t° | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| x | 2·74 | 2·95 | 3·17 | 3·39 | 3·63 | 3·88 | 4·13 | 4·39 | 4·67 | 4·94 | 5·24 |

Bearing the foregoing remarks in mind, therefore, the safest plan in the operations of volumetric analysis, so far as measurement is concerned, is to use solutions as dilute as possible. Absolute accuracy in estimating the strength of standard solutions can only be secured by weight, the ratio of the weight of the solution to the weight of active substance in it being independent of temperature.

Casamajor (*C. N.* xxxv. 160) has made use of the data given by Matthiessen in his researches on the expansion of glass, water, and mercury, to construct a table of corrections to be used in case of using any weak standard solution at a different temperature to that at which it was originally standardized.

The expansion of water is different at different temperatures; the expansion of glass is known to be constant for all temperatures up to 100°. The correction of volume, therefore, in glass burettes, must be the known expansion of each c.c. of water for every 1° C., less the known expansion of glass for the same temperature.

It is not necessary here to reproduce the entire paper of Casamajor, but the results are shortly given in the following table.

The normal temperature is 15° C.; and the figures given are the relative contractions below, and expansions above, 15° C.

| Deg. C. | | |
|---|---|---|
| 7 | — | ·000612 |
| 8 | — | ·000590 |
| 9 | — | ·000550 |
| 10 | — | ·000492 |
| 11 | — | ·000420 |
| 12 | — | ·000334 |
| 13 | — | ·000236 |
| 14 | — | ·000124 |
| 15 | | Normal |
| 16 | + | ·000147 |
| 17 | + | ·000305 |
| 18 | + | ·000473 |
| 19 | + | ·000652 |
| 20 | + | ·000841 |
| 21 | + | ·001039 |
| 22 | + | ·001246 |
| 23 | + | ·001462 |
| 24 | + | ·001686 |
| 25 | + | ·001919 |
| 26 | + | ·002159 |
| 27 | + | ·002405 |
| 28 | + | ·002657 |
| 29 | + | ·002913 |
| 30 | + | ·003179 |
| 31 | + | ·003453 |
| 32 | + | ·003739 |
| 33 | + | ·004035 |
| 34 | + | ·004342 |
| 35 | + | ·004660 |
| 36 | + | ·004987 |
| 37 | + | ·005323 |
| 38 | + | ·005667 |
| 39 | + | ·006040 |
| 40 | + | ·006382 |

By means of these numbers it is easy to calculate the volume of liquid at 15° C. corresponding to any volume observed at any temperature. If 35 c.c. of solution has been used at 37° C., the table shows that 1 c.c. of water in passing from 15° to 37° is increased to 1·005323 c.c.; therefore, by dividing 35 c.c. by 1·005323 is obtained the quotient 34·819 c.c., which represents the volume at 15° corresponding to 35 c.c. at 37°; or the operation can be simplified by obtaining the factor, thus:

$$\frac{1}{1\cdot005323}=0\cdot994705$$

A table can thus be easily constructed which would show the factor for each degree of temperature.

These corrections are useless for concentrated solutions, such as normal alkalies or acids; with great variations of temperature these solutions should be used by weight.

The accurate graduation of burettes and pipettes can only be done by carefully constructed machines, and is, therefore, generally speaking, beyond the compass of the analyst himself; nevertheless, they should be carefully tested by him before being used, as, unfortunately, they do not always possess the accuracy to which they pretend. In the verification of both burettes and pipettes, it is only necessary to allow ten cubic centimeters of distilled water to flow from the instrument to be tested into a dry and accurately tared flask or beaker. If the weight at 16° C., or 60° Fahr., is 10 grams, it is sufficient; the next 10 c.c. may be tried in like manner, and so on until the entire capacity is proved; differences of 5 or 10 milligrams may be disregarded. Thorpe (*Quantit. Chem. Anal.* p. 119) attaches the burette or pipette with elastic tube and pinch-cock to a balance, and thus weighs the respective volumes of fluid delivered.

Beside the liter flask, it is advisable to have flasks graduated for 100, 200, 250, 300, and 500 c.c., as they are extremely serviceable in dividing small quantities of substance into still smaller proportional parts. Suppose, for instance, it is desired to take the tenth part of a solution for the purpose of separating any single constituent, let it be put into a 200 c.c. flask, which is then filled to the mark with water or other appropriate liquid, and well shaken; 20 c.c. taken out with a pipette will at once give the quantity required.

*Instruments graduated on the Grain System.*—Burettes, pipettes, and flasks may also be graduated in grains, in which case it is best to take 10,000 grains as the standard of measurement. In order to lessen the number of figures used in the grain system, so far as liquid measures are concerned, I propose that ten fluid grains be called a decem, or for shortness dm.; this term corresponds to the cubic centimeter bearing the same proportion to the 10,000 grain measure as the cubic centimeter does to the liter, namely, the one-thousandth part. The use of a term like this will serve to prevent the number of figures, which are unavoidably introduced by the use of a small unit like the grain.

Its utility is principally apparent in the analysis for percentages, particulars of which will be found hereafter.

The 1000 grain burette or pipette will therefore contain 100 decems, the 10,000 gr. measure 1000 dm., and so on.

The capacities of the various instruments graduated on the grain system may be as follows:—

Flasks: 10000, 5000, 2500, and 1000 grs. = 1000, 500, 250, and 100 dm. Burettes: 300 grs. in 1-gr. divisions, for very delicate purposes = 30 dm. in $\frac{1}{10}$; 600 grs. in 2-gr. divisions, or $\frac{1}{5}$ dm.; 1100 grs. in 5-gr. divisions, or $\frac{1}{2}$ dm.; 1100 grs. in 10-gr. divisions, or 1 dm. The burettes are graduated above the 500 or 1000 grs.

in order to allow of analysis for percentages by the residual method. Whole pipettes to deliver 10, 20, 50, 100, 200, 500, and 1000 grs., graduated ditto, 100 grs. in $\frac{1}{10}$ dm.; 500 grs. in $\frac{1}{2}$ dm.; 1000 grs. in 1 dm.

Those who may desire to use the decimal systems constructed on the gallon measure = 70,000 grains, will bear in mind that the "septem" of Griffin, or the "decimillen" of Acland, are each equal to 7 grs., and therefore bear the same relation to the pound = 7000 grs., as the cubic centimeter does to the liter, or the decem to the 10,000 grs. An entirely different set of tables for calculations, etc., is required for these systems; but the analyst may readily construct them when once the principles contained in this treatise are understood.

## VOLUMETRIC ANALYSIS BASED ON THE SYSTEM OF CHEMICAL EQUIVALENCE AND THE PREPARATION OF NORMAL TITRATED SOLUTIONS.

§ 10. When analysis by measure first came into use, the test solutions were generally prepared so that each substance to be tested had its own special re-agent; and the strength of the standard solution was so calculated as to give the result in percentages. Consequently, in alkalimetry, a distinct standard acid was used for soda, another for potash, a third for ammonia, and so on, necessitating a great variety of standard solutions.

Griffin and Ure appear to have been the first to suggest the use of standard test solutions based on the atomic system; and following in their steps, Mohr has worked out and verified many methods of analysis, which are of great value to all who concern themselves with scientific and especially technical chemistry. Not only has Mohr done this, but in addition to it, he has enriched his processes with so many original investigations, and improved the necessary apparatus to such an extent, that he may with justice be called the father of the volumetric system.

*Normal Solutions.*—It is of great importance that no misconception should exist as to what is meant by a normal solution; but it does unfortunately occur, as may be seen by reference to the chemical journals, also to Muir's translation of Fleischer's book (see Allen, *C. N.* xl. 239). Normal solutions as originally devised are prepared so that one liter at 16° C. shall contain the hydrogen equivalent of the active re-agent weighed in grams ($H=1$). Seminormal, quintinormal, decinormal, and centinormal solutions are also required, and may be shortly designated as $\frac{N}{2}$ $\frac{N}{5}$ $\frac{N}{10}$ and $\frac{N}{100}$ solutions.*

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* Winckler in his *Maasanalyse* (Freiberg, 1883) endeavours to establish the system of making solutions of double the strength here advocated, and calling them normal. The practice is followed here and there by others, leading to much confusion. The original system adopted by Mohr, followed by Fresenius and many other well-known chemists throughout the world, is certainly entitled to preference.

In the case of univalent substances, such as silver, iodine, hydrochloric acid, sodium, etc., the equivalent and the atomic (or in the case of salts, molecular) weights are identical; thus, a normal solution of hydrochloric acid must contain 36.37 grams of the acid in a liter of fluid, and sodic hydrate 40 grams. In the case of bivalent substances, such as lead, calcium, oxalic acid, sulphurous acid, carbonates, etc., the equivalent is one-half of the atomic (or in the case of salts, molecular) weight; thus, a normal solution of oxalic acid would be made by dissolving 63 grams of the crystallized acid in distilled water, and diluting the liquid to the measure of one liter.

Further, in the case of trivalent substances, such as phosphoric acid, a normal solution of sodic phosphate would be made by weighing $\frac{358}{3} = 119 \cdot 3$ grams of the salt, dissolving in distilled water, and diluting to the measure of one liter.

One important point, however, must not be forgotten, namely, that in preparing solutions for volumetric analysis the value of a reagent as expressed by its equivalent hydrogen-weight must not always be regarded, but rather its particular reaction in any given analysis; for instance, tin is a quadrivalent metal, but when using stannous chloride as a reducing agent in the analysis of iron, the half, and not the fourth, of its molecular weight is required, as is shown by the equation $Fe^2\,Cl^6 + Sn\,Cl^2 = 2\,Fe\,Cl^2 + Sn\,Cl^4$.

In the same manner with a solution of potassic permanganate $Mn\,KO^4$ when used as an oxidizing agent, it is the available oxygen which has to be taken into account, and hence in constructing a normal solution one-fifth of its molecular weight $\frac{158}{5} = 31 \cdot 6$ grams must be contained in the liter.

Other instances of a like kind occur, the details of which will be given in the proper place.

A further illustration may be given in order to show the method of calculating the results of this kind of analysis.

Each c.c. of $\frac{N}{10}$ silver solution will contain $\frac{1}{10000}$ of the atomic weight of silver = 0·010766 gm., and will exactly precipitate $\frac{1}{10000}$ of the atomic weight of chlorine = 0·003537 gm. from any solution of a chloride.

In the case of normal oxalic acid each c.c. will contain $\frac{1}{2000}$ of the molecular weight of the acid = 0·063 gm., and will neutralize $\frac{1}{2000}$ of the molecular weight of sodic monocarbonate = 0·053 gm., or will combine with $\frac{1}{2000}$ of the atomic weight of a dyad metal such as lead = 0·1032 gm., or will exactly saturate $\frac{1}{1000}$ of the molecular weight of sodic hydrate = 0·040 gm., and so on.

Where the 1000 grain measure is used as the standard in place of the liter, 63 grains of oxalic acid would be used for the normal solution; but as 1000 grains is too small a quantity to make, it is better to weigh 630 grains, and make up the solution to 10,000 grain measures = 1000 dm. The solution would then have exactly the same strength as if prepared on the liter system, as it is proportionally the same in chemical power; and either solution may be used indiscriminately for instruments graduated on either scale, bearing in mind that the substance to be tested with a c.c. burette must be weighed on the gram system, and *vice versâ*, unless it be desired to calculate one system of weights into the other.

The great convenience of this equivalent system is, that the numbers used as coefficients for calculation in any analysis are familiar, and the solutions agree with each other, volume for volume. We have hitherto, however, looked only at one side of its advantages. For technical purposes the plan allows the use of all solutions of systematic strength, and simply varies the amount of substance tested according to its equivalent weight.

Thus, the normal solutions say, are—

Crystallized oxalic acid = 63 gm. per liter.
Sulphuric acid = 49 gm. ,,
Hydrochloric acid = 36·37 gm. ,,
Nitric acid = 63 gm. ,,
Anhydrous sodic carbonate = 53 gm. ,,
Sodic hydrate = 40 gm. ,,
Ammonia = 17 gm. ,,

100 c.c. of any one of these normal acids should exactly neutralize 100 c.c. of any of the normal alkalies, or the corresponding amount of pure substance which the 100 c.c. contain. In commerce we continually meet with substances used in manufactures which are not pure, and it is necessary to know how much pure substance they contain.

Let us take, for instance, refined soda ash (sodic carbonate). If it were absolutely pure, 5·3 gm. of it should require exactly 100 c.c. of any normal acid to saturate it. If we therefore weigh that quantity, bring it into solution with water, add litmus, and deliver into the mixture the normal acid from a 100 c.c. burette, the number of c.c. required to saturate it will show the percentage of pure sodic carbonate in the sample. Suppose 90 c.c. are required $=90^{\circ}/_{\circ}$.

Again—a manufacturer buys common oil of vitriol, and requires to know the exact percentage of pure hydrated acid in it; 4·9 grams are weighed, diluted with water, litmus added, and normal alkali delivered in from a 100 c.c. burette till saturated; the number of c.c. used will be the percentage of real acid. Suppose 58·5 c.c. are required $=58{\cdot}5^{\circ}/_{\circ}$.

On the grain system, in the same way, 53 grains of the sample of soda ash would require 90 dm. of normal acid, also equal to $90^{\circ}/_{\circ}$.

Or, suppose the analyst desires to know the equivalent percentage of dry caustic soda, free and combined, contained in the above sample of soda ash, without calculating it from the carbonate found as above, 3·1 gm. is treated as before, and the number of c.c.

required is the percentage of sodic oxide. In the same sample 52·6 c.c. would be required = 52·6 per cent. of sodic oxide, or 90 per cent. of sodic carbonate.

*Method for percentage of Purity in Commercial Substances.*—The rules, therefore, for obtaining the percentage of pure substance in any commercial article, such as alkalies, acids, and various salts, by means of systematic normal solutions such as have been described are these—

1. With normal solutions $\frac{1}{10}$ or $\frac{1}{20}$ (according to its atomicity) of the molecular weight in grams of the substance to be analyzed is to be weighed for titration, and the number of c.c. required to produce the desired reaction is the percentage of the substance whose atomic weight has been used.

With decinormal solutions $\frac{1}{100}$ or $\frac{1}{200}$ of the molecular weight in grams is taken, and the number of c.c. required will, in like manner, give the percentage.

Where the grain system is used it will be necessary, in the case of titrating with a normal solution, to weigh the whole or half the molecular weight of the substance in grains, and the number of decems required will be the percentage.

With decinormal solutions, $\frac{1}{10}$ or $\frac{1}{20}$ of the molecular weight in grains is taken, and the number of decems will be the percentage.

It now only remains to say, with respect to the system of weights and measures to be used, that the analyst is at liberty to choose his own plan. Both systems are susceptible of equal accuracy, and he must study his own convenience as to which he will adopt. The normal solutions prepared on the gram system are equally applicable for that of the grain, and *vice versâ*, so that there is no necessity for having distinct solutions for each system.

*Factors, or Coefficients, for the Calculation of Analyses.*—It frequently occurs that from the nature of the substance, or from its being in solution, this percentage method cannot be conveniently followed. For instance, suppose the operator has a solution containing an unknown quantity of caustic potash, the strength of which he desires to know; a weighed or measured quantity of it is brought under the acid burette and saturated exactly by the aid of litmus, 32 c.c. being required. The calculation is as follows:—

The molecular weight of potassic hydrate being 56 : 100 c.c. of normal acid will saturate 5·6 gm.; therefore, as 100 c.c. are to 5·6 gm., so are 32 c.c. to $x, \frac{5\cdot60 \times 32}{100} = 1\cdot792$ gm. KHO.

The simplest way, therefore, to proceed, is to multiply the number of c.c. of test solution required in any analysis, by the $\frac{1}{1000}$ (or $\frac{2}{1000}$ if bivalent) of the molecular weight of the substance sought, which gives at once the amount of substance present.

An example may be given—1 gm. of marble or limestone is taken for the estimation of pure calcic carbonate, and exactly saturated with standard nitric or hydrochloric acid—(sulphuric or oxalic acid are, of course, not admissible) 17·5 c.c. are required, therefore 17·5 × 0·050 (the $\frac{1}{2000}$ of the molecular weight of $CaCO^3$) gives 0·875 gm., and as 1 gm. of substance only was taken=87·5°/$_{\circ}$ calcic carbonate.

*Preservation of Solutions.*—There are test solutions which, in consequence of their proneness to decomposition, cannot be kept at any particular strength for a length of time; consequently they must be titrated on every occasion before being used. Stannous chloride and sulphurous acids are examples of such solutions. Special vessels have been devised for keeping solutions liable to alter in strength by access of air, as shown in figs. 17 and 18.

Fig. 17 is especially applicable to caustic alkaline solutions, the tube passing through the caoutchouc stopper being filled with dry soda-lime, resting on cotton wool.

Fig. 18, designed by Mohr, is a considerable improvement upon this, since it allows of the burette being filled with the

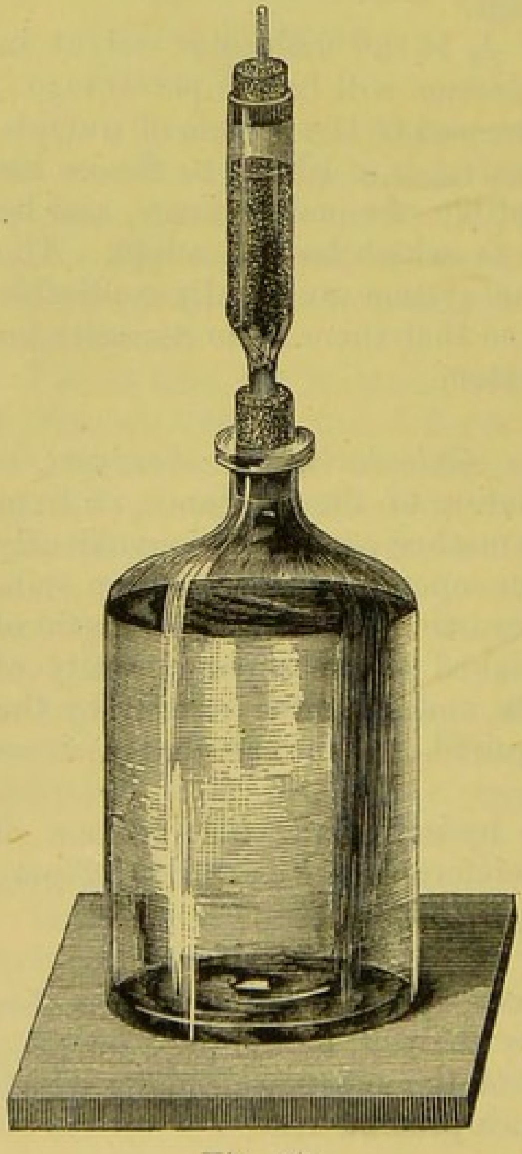

Fig. 17.

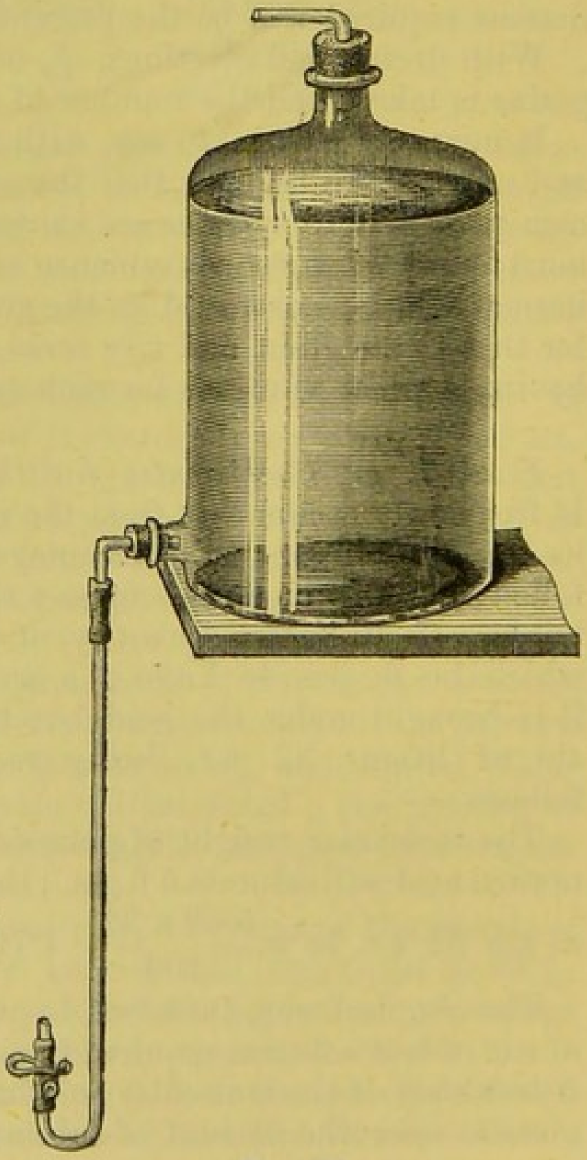

Fig. 18.

solution from the store bottle quietly, and without any access of air whatever. The vessel can be used for caustic alkalies, baryta, stannous chloride, permanganate, and sulphurous acids, or any other liquid liable to undergo change by absorbing oxygen. The corks are dried and soaked in melted paraffine; or, still better, may be substituted by caoutchouc stoppers; and a thin layer of petroleum oil, such as is used for burning, is poured on the top of the solution, where, of course, owing to its low specific gravity, it always floats, placing an impermeable division between the air and the solution; and as this body (which should always be as pure as possible) is not affected by these reagents in their diluted state, this form offers great advantages. Solutions not affected chemically by contact with air should nevertheless be kept in bottles, the corks or stoppers of which are perfectly closed, and tied over with india-rubber or bladder to prevent evaporation, and should further be always shaken before use, in case they are not quite full. The influence of bright light upon some solutions is very detrimental to their chemical stability; hence it is advisable to preserve some solutions not in immediate use in the dark, and at a temperature not exceeding 15 or 16° C.

## ON THE DIRECT AND INDIRECT PROCESSES OF ANALYSIS AND THEIR TERMINATION.

§ 11. The direct method includes all those analyses where the substance under examination is decomposed by simple contact with a known quantity or equivalent proportion of some other body capable of combining with it, and where the end of the decomposition is manifested in the solution itself.

It also properly includes those analyses in which the substance reacts upon another body to the expulsion of a representative equivalent of the latter, which is then estimated as a substitute for the thing required.

Examples of this method are readily found in the process for the determination of iron by potassic permanganate, where the beautiful rose colour of the permanganate asserts itself as the end of the reaction.

The testing of acids and alkalies comes, also, under this class, the great sensitiveness of litmus, or other indicators, allowing the most trifling excess of acid or alkali to alter their colour.

The indirect method is exemplified in the analysis of manganese ores, and also other peroxides and oxygen acids, by boiling with hydrochloric acid. The chlorine evolved is estimated as the equivalent of the quantity of oxygen which has displaced it. We are indebted to Bunsen for a most accurate and valuable series of processes based on this principle.

The residual method is such that the substance to be analyzed is not estimated itself, but the excess of some other body added for the purpose of combining with it or of decomposing it; and the quantity or strength of the body added being known, and the conditions under which it enters into combination being also known, by deducting the remainder or excess (which exists free) from the original quantity, it gives at once the proportional quantity of the substance sought.

An example will make the principle obvious :—Suppose that a sample of native calcic or baric carbonate is to be tested. It is not possible to estimate it with standard nitric or hydrochloric acid in the exact quantity it requires for decomposition. There must be an excess of acid and heat applied also to get it into solution; if, therefore, a known excessive quantity of standard acid be first added, and solution obtained, and the liquid then titrated backward with an indicator and standard alkali, the quantity of free acid can be exactly determined, and consequently that which is combined also.

In some analyses it is necessary to add a substance which shall be an indicator of the end of the process; such, for instance, is litmus or the azo colours in alkalimetry, potassic chromate in silver and chlorine, and starch in iodine estimations.

There are other processes, the end of which can only be determined by an indicator separate from the solution; such is the case in the estimation of iron by potassic bichromate, where a drop of the liquid is brought into contact with another drop of solution of red potassic prussiate on a white slab or plate; when a blue colour ceases to form by contact of the two liquids, the end of the process is reached..

# PART II.

## ANALYSIS BY SATURATION.

### ALKALIMETRY.

§ 12. Gay Lussac based his system of alkalimetry upon a titrated solution of sodic carbonate, with a corresponding solution of sulphuric acid. It possesses the recommendation, that a pure standard solution of sodic carbonate can be more readily obtained than any other form of alkali. Mohr introduced the use of caustic alkali instead of a carbonate, the strength of which is established by a standard solution of oxalic or sulphuric acid. The advantage in the latter system is, that in titrating acids with a caustic alkali, the well-known interference produced in litmus by carbonic acid is avoided: this difficulty is now overcome with carbonates by the new indicators to be described.

### INDICATORS USED IN ALKALIMETRY.

§ 13. 1. **Litmus Solution.**—This well-known indicator is best prepared as follows:—Extract all soluble matters from the solid litmus by repeated quantities of hot water; evaporate the mixed extracts to a moderate bulk, and add acetic acid in slight excess to decompose carbonates; evaporate to a thick extract, transfer this to a beaker, and add a large proportion of 90-per-cent. alcohol or methylated spirit: by this treatment the blue colour is precipitated, and the alkaline acetates, together with some red colouring matter, remain dissolved; the fluid with precipitate is thrown on a filter, washed with spirit, and the pure colouring matter finally dissolved in warm distilled water, through the filter, for use.

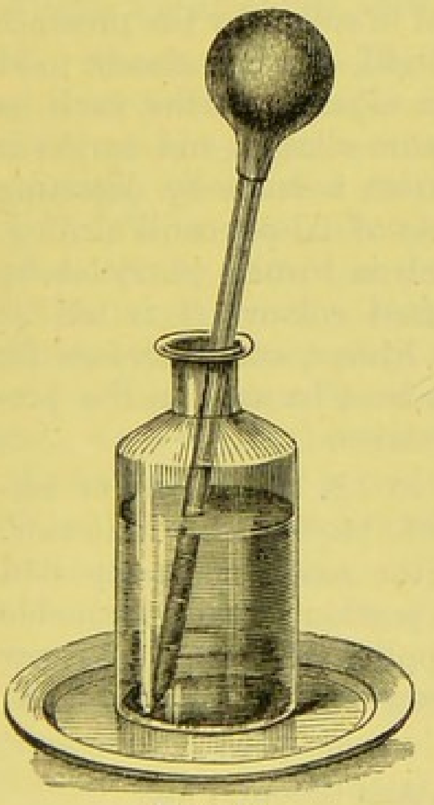
Fig. 19.

Free carbonic acid interferes considerably with the production of the blue colour, and its interference in titrating acid solutions with alkaline carbonates can only be got rid of by boiling the liquid during the operation, in order to displace the gas from the solution. If this is not done, it is easy to overstep the exact point of neutrality in endeavouring to produce the blue colour. The same difficulty is also found in obtaining the pink-red when acids are used for titrating alkaline carbonates, hence the great value of the caustic alkaline solutions free from carbonic acid when this indicator is used.*

It sometimes occurs that titration by litmus is required at night. Ordinary gas or lamp light is not adapted for showing the reaction in a satisfactory manner; but a very sharp line of demarcation between red and blue may be found by using a monochromatic light. With the yellow sodium flame the red colour appears perfectly colourless, while the blue or violet appears like a mixture of black ink and water. The transition is very sudden, and even sharper than the change by daylight.

The operation should be conducted in a perfectly dark room; and the flame may be best obtained by heating a piece of platinum coil sprinkled with salt, or a piece of pumice saturated with a concentrated solution of salt, in the Bunsen flame.

2. **Litmus Paper.**—Is simply made by dipping strips of filtering paper in the solution and drying them; if required red, the liquid is slightly acidified.

3. **Cochineal Solution.**—This indicator possesses the advantage over litmus, that it is not so much modified in colour by the presence of carbonic acid, and can be used by gas-light. It can also be used with the best effect with solutions of the alkaline earths, such as lime and baryta water; the colour with pure alkalies and earths is especially sharp and brilliant. The solution is made by digesting 1 part of powdered cochineal with 10 parts of 25-per-cent. alcohol. Its natural colour is yellowish red, which is turned to violet by alkalies; mineral acids restore the original colour; it is not so easily affected by weak organic acids as litmus, and therefore for these acids the latter is preferable. It cannot be used in the presence of iron or alumina compounds or acetates.

4. **Turmeric Paper.**—Pettenkofer, in his estimation of carbonic acid by baryta water, prefers turmeric paper as an indicator. It is best prepared by digesting pieces of the root, first in repeated small quantities of water to remove a portion of objectionable colouring matter, then in alcohol, and dipping strips of filter paper into the alcoholic solution, drying and preserving them in the dark.

### New Indicators derived from the Azo Colours, etc.

An immense stride has been taken in the application of these modern indicators since the last edition of this book, and the best thanks of all chemists are due to R. T. Thompson for his valuable researches on these indicators, laid before the Chemical Section of the Philosophical Society of Glasgow, and published in their

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* Litmus solution must always be kept exposed to the air or it loses its colour (restorable by exposure). The bottle shown in Fig. 19 is a convenient vessel for its storage and use.

Transactions; also reprinted (*C. N.* xlvii. 123, 185; xlix. 32, 119). The experiments recorded in these papers are most carefully carried out, and the truthfulness of their results has been verified by Lunge and other practical men as well as by myself.

Space will only permit here of a record of the results, fuller details being given in the publications to which reference has been made.

5. **Methyl Orange.**—The chemical name of this substance is sulphobenzene-azo-dimethylaniline, occurring as a bright orange red powder, soluble in water. A convenient strength for the solution is 1 gm. per liter. One or two drops of such a liquid produce a faint yellow colour, and suffice for the titration of ordinary volumes of colourless liquids. For larger volumes, and more or less coloured solutions, more may be necessary; but as the change in colour is very delicate, highly tinted liquids are inadmissible.

Mineral acids alone can be safely titrated with this indicator, the colour being pink with the slightest excess, and faint yellow with alkali. Its superiority to litmus is shown by its indifference to carbonic and sulphydric acids in the cold.

Hot liquids are, as a rule, inadmissible. It is an admirable indicator for ammonia and its salts.

6. **Phenacetolin.**—This substance is soluble only in alcohol, and a convenient strength is 2 gm. per liter. The solution is dark brown, which gives a scarcely perceptible yellow with caustic soda or potash, when a few drops are used with the ordinary volumes of liquid. With ammonia and the normal alkaline carbonates it gives a dark pink, with bicarbonate a much more intense pink, and with mineral acids a golden yellow. This indicator may be used to estimate the amount of caustic potash or soda in the presence of their normal carbonates if the proportion of the former is not very small, or of caustic lime in the presence of carbonate.

Practice however is required with solutions of known composition, so as to acquire knowledge of the exact shades of colour.

7. **Phenolphthalein.**—This substance is of a resinous nature, but quite soluble in 50-per-cent. alcohol. A convenient strength is 1 gm. per liter.

A few drops of the indicator show no colour in the ordinary volumes of neutral or acid liquids: the faintest excess of caustic alkalies, on the other hand, gives a sudden change to purple red.

This indicator is absolutely useless for the titration of free ammonia or its compounds, or for the fixed alkalies when salts of ammonia are present.

It may however be used like phenacetolin for estimating the proportions of hydrate and carbonate of soda or potash in the same sample where the proportion of hydrate is not too small. Unlike methyl orange, this indicator is especially useful in titrating all varieties of organic acids; viz., oxalic, acetic, citric, tartaric, etc.

8. **Rosolic Acid.**—This indicator is soluble in 50-per-cent alcohol, and a convenient strength is 2 gm. per liter. Its colour is pale yellow, unaffected by acids, but turning to violet red with alkalies. It possesses very little advantage over litmus (except its permanency in a closed vessel), its delicacy being sensibly affected by salts of ammonia and by carbonic acid. It is excellent for all the mineral acids, but not reliable for the organic acids.

9. **Lacmoid.**—This indicator is prepared from resorcin, and is therefore somewhat allied to litmus, nevertheless, it differs from it in many respects, and has a pronounced and valuable character of its own, especially when used in the form of paper.

10. **Lacmoid Paper.**—This is prepared by dipping slips of fine filtering paper into the solution, either in its natural state, or reddened by slight excess of acid, and drying them.

There are a host of other indicators belonging to the same category as those mentioned above; but as they have no special advantages over them, and indeed are practically inferior in delicacy, no mention of them will occur here.

Special indicators for certain purposes, such as potassic chromate for silver, ferric sulphate for sulphocyanides, etc., will be described in their proper place.

## SHORT SUMMARY OF THOMPSON'S RESULTS WITH PURE SALTS OF THE ALKALIES AND ALKALINE EARTHS.

The whole of the base or acid in the following list of substances may be estimated with delicacy and precision unless otherwise mentioned.

**Litmus Cold.**—Hydrates of soda, potash, ammonia, lime, baryta, etc.; arsenites of soda and potash, and silicates of the same bases; nitric, sulphuric, hydrochloric, and oxalic acids.

**Litmus Boiling.**—The neutral and acid carbonates of potash, soda, lime, baryta, and magnesia, the sulphides of sodium and potassium, and the silicates of the same bases.

**Methyl Orange Cold.**—The hydrates, carbonates, bicarbonates, sulphides, arsenites, silicates, and borates of soda, potash, ammonia, lime, magnesia, baryta, etc., and all the mineral acids, sulphites, half the base in the alkaline and earthy alkaline phosphates and arseniates.

**Rosolic Acid Cold.**—The whole of the base or acid may be estimated in the hydrates of potash, soda, ammonia, and arsenites of the same; the mineral and oxalic acids.

**Rosolic Acid Boiling.**—The alkaline and earthy hydrates and carbonates, bicarbonates, sulphides, arsenites, and silicates.

**Phenacetolin Cold.**—The hydrates, arsenites, and silicates of the alkalies; the mineral acids.

**Phenacetolin Boiling.**—The alkaline and earthy hydrates, carbonates, bicarbonates, sulphides, arsenites, and silicates.

**Phenolphthalein Cold.**—The alkaline hydrates, except ammonia; the mineral acids, oxalic, citric, tartaric, acetic, and other organic acids.

**Phenolphthalein Boiling.**—The alkaline and earthy hydrates, carbonates, bicarbonates, and sulphides, always excepting ammonia.

**Lacmoid Cold.**—The alkaline and earthy hydrates, arsenites and borates, and the mineral acids. Many salts of the metals which are more or less acid to litmus are neutral to lacmoid, such as the sulphates and chlorides of iron, copper, and zinc; therefore this indicator serves for estimating free acids in such solutions.

**Lacmoid Boiling.**—The hydrates, carbonates, and bicarbonates of potash, soda, and alkaline earths.

**Lacmoid Paper.**—The alkaline and earthy hydrates, carbonates, bicarbonates, sulphides, arsenites, silicates, and borates; the mineral acids; half of the base in sulphites, phosphates, and arseniates.

This indicator re-acts alkaline with the chromates of potash or soda, but neutral with the bichromates, so that a mixture of the two, or of bichromates with free chromic acid, can be titrated by its aid.

The following substances can be determined by standard alcoholic potash, phenolphthalein as indicator. One c.c. normal caustic potash (1 c.c. = ·056 gm. KHO) is equal to—(Hehner and Allen).

| | | | | | |
|---|---|---|---|---|---|
| ·088 | gm. | butyric acid. | ·1007 | gm. | tributyrin. |
| ·282 | ,, | oleic. | ·2947 | ,, | triolein. |
| ·256 | ,, | palmitic. | ·2687 | ,, | tripalmitin. |
| ·284 | ,, | stearic | ·2967 | ,, | tristearin. |
| ·410 | ,, | cerotic. | ·6760 | ,, | myricin. |
| ·329 | ,, | resin acids (ordinary colophony, chiefly sylvic acid). | | | |

### General Characteristics of the Foregoing Indicators.

It is interesting to notice the different degrees of sensitiveness shown by indicators used in testing acids and alkalies. This is well illustrated by Thompson's experiments, where he used solutions of the indicator, containing a known weight of the solid material, and so adjusted as to give, as near as could be judged, the same intensity of colour in the reaction.

It was found that lacmoid, rosolic acid, phenacetolin, and phenolphthalein were capable of showing the change of colour with one-fifth of the quantity of acid or alkali which was required in the case of methyl orange or litmus; that is to say, in 100 c.c. of liquid, where the latter took 0·5 c.c., the same effect with the former was gained by 0·1 c.c.

Another important distinction is shown in their respective behaviour with mineral and organic acids.

It is true the whole of them are alike serviceable for the mineral acids and fixed alkalies; but they differ considerably in the case of the organic acids and ammonia. Methyl orange and lacmoid appear to be most sensitive to alkalies, while phenolphthalein is most sensitive to acids: the others appear to occupy a position between these extremes, each showing, however, special peculiarities. The distinction, however, is so marked, that, as Thompson says, it is possible to have a liquid which may be acid to phenolphthalein and alkaline to lacmoid.

The presence of certain neutral salts has, too, a definite effect on the sensitiveness of certain indicators. Sulphates, nitrates, chlorides, etc., retard the action of methyl orange slightly, while in the case of phenacetolin and phenolphthalein they have no effect. On the other hand, neutral salts of ammonia have such a disturbing influence on the latter as to render it useless.

Nitrous acid alters the composition of methyl orange; so also do nitrites when existing in any quantity. Forbes Carpenter has noted this effect in testing the exit gases of vitriol chambers (*J. S. C. I.* v. 287).

Sulphites of the fixed alkalies and alkaline earths are practically neutral to phenolphthalein, but alkaline to litmus, methyl orange, and phenacetolin.

Sulphides, again, can be accurately titrated with methyl orange in the cold, and on boiling off the $H^2S$ a tolerably accurate result can be obtained with litmus and phenacetolin, but with phenolphthalein, the neutral point occurs when half the alkali is saturated. The phosphates of the alkalies, arseniates, and arsenites, also vary in their effects on the various indicators.

Again, boric acid and the borates can be very accurately titrated by help of methyl orange or lacmoid, but the other indicators are practically useless.

## PREPARATION OF THE NORMAL ACID AND ALKALINE SOLUTIONS.

§ 14. It is quite possible to carry out the titration of acids and alkalies with only one standard liquid of each kind; but it frequently happens that standard acids or alkalies are required in other processes of titration beside mere saturation, and it is therefore advisable to have a variety.

Above all things it is absolutely necessary to have, at least, one standard acid and alkali prepared with the most scrupulous accuracy, to use as foundations for all others.

I prefer sulphuric acid for the normal acid solution, inasmuch as there is no difficulty in getting the purest acid in commerce. The normal acid made with it is totally unaffected by boiling, even when of full strength, which cannot be said of either nitric or hydrochloric acid. Hydrochloric acid is however generally preferred by alkali makers, owing to its giving soluble compounds with lime and similar bases. Nitric and oxalic acids are also sometimes convenient.

Sodic carbonate, on the other hand, is to be preferred for the standard alkali, because it can readily be obtained in a perfectly pure state, or can be easily made by igniting pure bicarbonate.

The chief difficulty hitherto with sodic carbonate has been, that with litmus as indicator, the titration must be carried on at a boiling heat in order to get rid of carbonic acid, which hinders the pure blue colour of the indicator, notwithstanding the alkali may be in great excess. This difficulty is now set aside by the use of methyl orange. In case the operator has not these indicators at hand, litmus gives perfectly accurate results, if the saturation is conducted by rapidly boiling the liquid in a thin flask for a minute after each addition of acid until the point is reached, when one drop of acid in excess gives a pink-red colour, which is not altered by further boiling.

As has been previously said, these two standards must be prepared with the utmost care, since upon their correct preparation and preservation depends the verification of other standard solutions.

It may, however, be remarked, that in place of a standard solution of sodic carbonate, which is of limited use for general purposes, the pure salt may be used for the rigid adjustment of normal acid. In this case about 2 or 3 grams of the pure salt are freshly heated to dull redness for a few minutes in a weighed platinum crucible, cooled under an exsiccator, the exact weight taken, then transferred to a flask by means of a funnel, through which it is washed and dissolved with distilled water, methyl orange added, and the operation completed by running the acid of unknown strength from a burette divided into $\frac{1}{5}$ c.c. into the soda solution in small quantities until exact saturation occurs.

A second portion of sodic carbonate should now be weighed as before, but not of necessity exactly the same quantity. Its exact weight must be noted; the saturation is carried out precisely as at first. The data for ascertaining the exact strength of the acid solution by calculation are now in hand.

A strictly normal acid should at 16° C. exactly saturate sodic carbonate in the proportion of 100 c.c. to 5·3 gm.

Suppose that 2·46 gm. sodic carbonate required 41·5 c.c. of the acid in the first experiment, then

$$2{\cdot}46 : 5{\cdot}3 :: 41{\cdot}5 : x = 89{\cdot}4 \text{ c.c.}$$

Again: 2·153 gm. sodic carbonate required 36·32 c.c. of acid, then

$$2{\cdot}153 : 5{\cdot}3 :: 36{\cdot}32 : x = 89{\cdot}4 \text{ c.c.}$$

The acid may now be adjusted by measuring 890 c.c. into the graduated liter cylinder, adding 4 c.c. from the burette, or with a small pipette, and filling to the liter mark with distilled water.

Finally, the strength of the acid so prepared must be proved by taking a fresh quantity of sodic carbonate, or by titration with a normal sodic carbonate solution previously made by direct weighing of 53 gm. to the liter, and using not less than 50 c.c. for the titration, so as to avoid as much as possible the personal errors of measurement in small quantities. If the measuring instruments all agree, and the operations are all conducted with due care, a drop or two in excess of either acid or alkali in 50 c.c. should suffice to reverse the colour of the indicator.

### 1. Normal Sodic Carbonate.

53 gm. $Na^2CO^3$ per liter.

This solution is made by dissolving 53 gm. of pure freshly ignited sodic monocarbonate in distilled water, and diluting to 1 liter at 16° C. If the pure salt is not at hand, the solution may be made as follows :—

About 85 gm. of pure sodic bicarbonate are heated to dull redness (not to fusion) in a platinum crucible, for fully ten minutes, to expel one-half of the carbonic acid, then placed under an exsiccator to cool; when placed upon the balance it will be found that very little more than 53 gm. remain. The excess is removed as quickly as possible, and the contents of the crucible washed into a beaker, and as soon as the salt is dissolved the solution is decanted into a liter flask and filled up to the mark with distilled water at 16°C.

### 2. Normal Potassic Carbonate.

69 gm. $K^2CO^3$ per liter.

This solution is sometimes, though rarely, preferable to the soda salt, and is of service for the estimation of combined acids in certain cases, where, by boiling the compound with this agent, an interchange of acid and base occurs.

It cannot be prepared by direct weighing of the potassic carbonate, and is therefore best established by titrating a solution of unknown strength with strictly normal acid.

### 3. Normal Sulphuric Acid.

49 gm. $H^2SO^4$ per liter.

About 30 c.c. of pure sulphuric acid of sp. gr. 1·840, or thereabouts, are mixed with three or four times the volume of distilled water and allowed to cool, then put into the graduated cylinder and diluted up to the liter. The solution may now be roughly tested by normal alkali, which is best done by putting 20 c.c. into a small beaker or flask with methyl orange, and allowing the acid to flow from a burette, divided into $\frac{1}{10}$ c.c., until the point of neutrality is reached. If more than 10 c.c. are required, the acid is too weak; if less, too strong. If the acid from which the solution was made was of the sp. gr. mentioned, it will generally be too strong, which is preferable. The final adjustment with sodic carbonate may now be made as before described.

The solution may also be controlled by precipitation with baric chloride, in which case 10 c.c. should produce as much baric sulphate as is equal to 0·49 gm. of sulphuric acid, or 49 gm. per liter.

### 4. Normal Oxalic Acid.

63 gm. $C^2O^4H^2,2H^2O$, or 45 gm. $C^2O^4H^2$ per liter.

This solution cannot very well be established by direct weighing, owing to uncertain hydration; hence it must be titrated by normal alkali of known accuracy.

The solution is apt to deposit some of the acid at low temperatures, but keeps well if preserved from direct sunlight, and will bear heating without volatilizing the acid. Very dilute solutions of oxalic acid are very unstable; therefore, if a decinormal or centinormal solution is at any time required, it should be made when wanted.

### 5. Normal Hydrochloric Acid.

36·37 gm. HCl per liter.

It has been shown by Roscoe and Dittmar (*J. C. S.* xii. 128, 1860) that a solution of hydrochloric acid containing 20·2 per cent. of the gas when boiled at about 760 m.m. pressure, loses acid and water in the same proportion, and the residue will therefore have the constant composition of 20·2 per cent., or a specific gravity of 1·10. About 181 gm. of acid of this gravity, diluted to one liter, serves very well to form an approximate normal acid.

The actual strength may be determined by precipitation with silver nitrate, or by titration with an exactly weighed quantity of pure sodic monocarbonate. Hydrochloric acid is useful on account of its forming soluble compounds with the alkaline earths, but it has the disadvantage of volatilizing at a boiling heat. Dittmar says that this may be prevented by adding a few grams of sodic sulphate. In many cases this would be inadmissible, for the same reason that sulphuric acid cannot be used. The hydrochloric acid from which standard solutions are made must be free from chlorine gas or metallic chlorides, and should leave no residue when evaporated in a platinum vessel.

### 6. Normal Nitric Acid.

63 gm. $HNO^3$ per liter.

A rigidly exact normal acid should be established by sodic carbonate, as in the case of normal sulphuric and hydrochloric acids.

The nitric acid used should be colourless, free from chlorine and nitrous acid, sp. gr. from 1·35 to 1·4. If coloured from the presence of nitrous or hyponitrous acids, it should be mixed with two volumes of water, and boiled until white. When cold it may be diluted and titrated as above.

### 7. Normal Caustic Soda or Potash.

40 gm. NaHO or 56 gm. KHO per liter.

Pure caustic soda made from metallic sodium may now be readily obtained in commerce, and hence it is easy to prepare a standard solution of exceeding purity, by simply dissolving the substance in distilled water till of about 1·05 sp. gr., or about 50 gm. to the liter, roughly estimating its strength by normal acid and methyl orange; then finally adjusting the exact strength by titrating 50 c.c. with normal acid.

However pure caustic soda or potash may otherwise be, they are both in danger of absorbing carbonic acid, and hence in using litmus the titration must be conducted with boiling. Methyl orange permits the use of these solutions at ordinary temperature notwithstanding the presence of $CO^2$.

Soda and potash may both be obtained in commerce sufficiently pure for all ordinary titration purposes, but in case they are not at hand the requisite solutions may be prepared as follows:—

Two parts of pure sodic or potassic carbonate are to be dissolved in twenty parts of distilled water, and boiled in a clean iron pot; during the boiling, one part of fresh quick-lime, made into a cream with water, is to be added little by little, and the whole boiled until all the carbonic acid is removed, which may be known by the clear solution producing no effervescence on the addition of dilute acid; the vessel is covered closely, and set aside to cool and settle; when cold, the clear supernatant liquid should be poured or drawn off and titrated by normal acid, and made of the proper strength as directed for sulphuric acid.

Soda solutions may be freed from traces of chlorine, sulphuric, silicic, and carbonic acids, by shaking with Millon's base trimercur-ammonium (*C. N.* xlii. 8).

In preparing these alkaline solutions, they should be exposed as little as possible to the air, and when the strength is finally settled, should be preserved in one of the bottles shown in fig. 16 or 17.

### 8. Semi-normal Ammonia.

8·5 gm. $NH^3$ per liter.

For some years past I have used this strength of standard ammonia for saturation analyses, and have been fully satisfied with its behaviour; it is cleanly, does not readily absorb carbonic acid, hold its strength well for two or three months when kept in a cool place and well stoppered; and can at any time be prepared in a few minutes, by simply diluting strong solution of ammonia with fresh distilled water.

A normal solution cannot be used with safety, owing to evaporation of the gas at ordinary temperatures.

It is necessary to add that, even in the case of $\frac{N}{2}$ strength, the solution should be titrated from time to time against correct normal acid. $\frac{N}{10}$ ammonia keeps its strength for a long time in well-closed bottles.

### 9. Standard Caustic Baryta (Pettenkofer).

**Especially serviceable for free carbonic acid and coloured acid liquids, such as commercial vinegars, etc.**

The solution of caustic baryta is best made from the crystallized hydrate. It is not advisable to have the solution too concentrated, since, when it is near complete saturation it is apt to deposit the hydrate at low temperature. The corresponding acid may be either $\frac{N}{10}$ oxalic, nitric, or hydrochloric. Oxalic acid is recommended by Pettenkofer for carbonic acid estimation, because it has no effect upon the baric carbonate suspended in weak solutions; but there is the serious drawback in oxalic acid, that in dilute solution it is liable to rapid decomposition; and as in my experience $\frac{N}{10}$ hydrochloric acid in dilute mixtures has no effect upon the suspended baric carbonate, it is preferable to use this acid.

The baryta solution is subject to constant change by absorption of carbonic acid, but this may be prevented to a great extent by preserving it in the bottle shown in fig. 17. A thin layer of petroleum oil on the surface of the liquid preserves the baryta at one strength for a long period.

The reaction between baryta and turmeric is very delicate, so that the merest trace of baryta in excess gives a decided brown tinge to the edge of the spot made by a glass rod on the turmeric paper. If the substance to be titrated is not too highly coloured, litmus may be used as an approximate indicator in the mixture; this enables the operator to find the exact point of saturation more conveniently.

### 10. Normal Ammonio-Cupric Solution for Acetic Acid and free Acids and Bases in Earthy and Metallic Solutions.

This acidimetric solution is prepared by dissolving pure cupric sulphate in warm water, and adding to the clear solution liquid ammonia, until the bluish-green precipitate which first appears is nearly dissolved; the solution is then filtered into the graduated cylinder, and titrated by allowing it to flow from a pipette graduated in $\frac{1}{5}$ or $\frac{1}{10}$ c.c. into 10 or 20 c.c. of normal sulphuric or nitric acid (not oxalic). While the acid remains in excess, the bluish-green precipitate which occurs as the drop falls into the acid rapidly disappears; but so soon as the exact point of saturation occurs, the previously clear solution is rendered turbid by the precipitate remaining insoluble in the neutral liquid.

The process is especially serviceable for the estimation of the free acid existing in certain metallic solutions, *i.e.* mother-liquors, etc., where the neutral compounds of such metals have an acid reaction on litmus—such as the oxides of zinc, copper, and magnesia, and the protoxides of iron, manganese, cobalt, and nickel; it is also applicable to acetic and the mineral acids.

If cupric nitrate be used for preparing the solution instead of sulphate, the presence of barium, or strontium, or metals precipitable by sulphuric acid, is of no consequence. The solution is standardized by normal nitric or sulphuric acid; and as it slightly alters by keeping, a coefficient must be found from time to time by titrating with normal acid, by which to calculate the results systematically. Oxides or carbonates of magnesia, zinc, or other admissible metals, are dissolved in excess of normal nitric acid, and titrated residually with the copper solution.

*Example:* 1 gm. pure zinc oxide was dissolved in 27 c.c. normal acid, and 2·3 c.c. normal copper solution required to produce the precipitate =24·7 c.c. acid; this multiplied by 0·0405, the coefficient for zinc oxide, =1·000 gm.

For the vinegars of commerce this process seems peculiarly applicable, as a large amount of dilution is of no consequence.

## ESTIMATION OF THE CORRECT STRENGTH OF STANDARD SOLUTIONS NOT STRICTLY NORMAL OR SYSTEMATIC.

§ 15. In discussing the preparation of the foregoing standard solutions, it has been assumed that they shall be strictly and absolutely correct,—that is to say, if the same measure be filled first with any alkaline solution, then with an acid solution, and the two mixed together, a perfectly neutral solution shall result, so that a drop or two either way will upset the equilibrium.

Where it is possible to weigh directly a pure dry substance, this approximation may be very closely reached. Sodic monocarbonate, for instance, admits of being thus accurately weighed. On the other hand, the caustic alkalies cannot be so weighed, nor can the liquid acids. An approximate quantity, therefore, of these substances must be taken, and the exact power of the solution found by experiment.

In titrating such solutions it is exceedingly difficult to make them so exact in strength, that the precise quantity, to a drop or two, shall neutralize each other. In technical matters a near approximation may be sufficient, but in scientific investigations it is of the greatest importance that the utmost accuracy should be obtained; it is therefore advisable to ascertain the actual difference, and to mark it upon the vessels in which the solutions are kept, so that a slight calculation will give the exact result.

Suppose, for instance, that a standard sulphuric acid is prepared, which does not rigidly agree with the normal sodic carbonate (not at all an uncommon occurrence, as it is exceedingly difficult to hit the precise point); in order to find out the exact difference it must be carefully titrated as in § 14. Suppose the weight of sodic carbonate to be 1·9 gm., it is then dissolved and titrated with the standard acid, of which 36·1 c.c. are required to reach the exact neutral point.

If the acid were rigidly exact it should require 35·85 c.c.; in order, therefore, to find the factor necessary to bring the quantity of acid used in the analysis to an equivalent quantity of normal strength, the number of c.c. actually used must be taken as the denominator, and the number which should have been used, had the acid been strictly normal, as the numerator, thus:—

$$\frac{35{\cdot}85}{36{\cdot}1} = 0{\cdot}993\,;$$

0·993 is therefore the factor by which it is necessary to multiply the number of c.c. of that particular acid used in any analysis in order to reduce it to normal strength, and should be marked upon the bottle in which it is kept.

On the other hand, suppose that the acid is too strong, and that 35·2 c.c. were required instead of 35·85,

$$\frac{35{\cdot}85}{35{\cdot}2} = 1{\cdot}0184\,;$$

1·0184 is therefore the factor by which it is necessary to multiply the number of c.c. of that particular acid in order to bring it to the normal strength. This plan is much better than dodging about with additions of water or acid.

Under all circumstances, it is safer to prove the strength of any standard solution by experiment, even though its constituent has been accurately weighed in the dry and pure state.

Further, let us suppose that a solution of caustic soda is to be made by means of lime as described previously. After pouring off the clear liquid, water is added to the sediment to extract more alkaline solution; by this means we may obtain two solutions, one of which is stronger than necessary, and the other weaker. Instead of mixing them in various proportions and repeatedly trying the strength, we may find, by two experiments and a calculation, the proportions of each necessary to give a normal solution, thus:—

The exact actual strength of each solution is first found, by separately running into 10 c.c. of normal acid as much of each alkaline solution as will exactly neutralize it. We have, then, in the case of the stronger solution, a number of c.c. required less than 10. Let us call this number V.

In the weaker solution the number of c.c. is greater than 10, represented by $v$. A volume of the stronger solution $= x$ will saturate 10 c.c. of normal acid as often as V is contained in $x$.

A volume of the weaker solution $= y$ will, in like manner, saturate $\frac{10\,y}{v}$ c.c. of normal acid; both together saturate $\frac{10\,x}{V} + \frac{10\,y}{v}$, and the volume of the saturated acid is precisely that of the two liquids, thus—

$$\frac{10x}{V} + \frac{10y}{v} = x + y.$$

Whence

$$10\,v\,x + 10\,V\,y = V\,v\,x + V\,v\,y$$
$$v\,x\,(10-V) = V\,y\,(v-10).$$

And lastly,

$$\frac{x}{y} = \frac{V\,(v-10)}{v\,(10-V)}$$

An example will render this clear. A solution of caustic soda was taken, of which 5·8 c.c. were required to saturate 10 c.c. normal acid; of another solution, 12·7 c.c. were required. The volumes of each necessary to form a normal solution were found as follows:—

$$5{\cdot}8\ (12{\cdot}7-10) = 15{\cdot}66$$
$$12{\cdot}7\ (10-5{\cdot}8) = 53{\cdot}34$$

Therefore, if the solutions are mixed in the proportion of 15·66 c.c. of the stronger with 53·34 c.c. of the weaker, a correct solution ought to result. The same principle of adjustment is, of course, applicable to standard solutions of every class.

Again: suppose that a standard solution of sulphuric acid has been made, approximating as nearly as possible to the normal strength, and its exact value found by precipitation with baric chloride, or a standard hydrochloric acid with silver nitrate, and such a solution has been calculated to require the coefficient 0·995 to convert it to normal strength,—by the help of this solution, though not strictly normal, we may titrate an approximately normal alkaline solution thus:—Two trials of the acid and alkaline solutions show that 50 c.c. alkali$=$48·5 c.c. acid, having a coefficient of 0·995$=$48·25 c.c. normal; then, according to the equation, $x\ 50 = 48{\cdot}25$ is the required coefficient for the alkali.

$$\frac{48{\cdot}25}{50} = 0{\cdot}965.$$

And here, in the case of the alkaline solution being sodic carbonate, we can bring it to exact normal strength by a calculation based on the equivalent weight of the salt, thus—

$$1 : 0{\cdot}965 :: 53 : 51{\cdot}145.$$

The difference between the two latter numbers is 1·855 gm., and this weight of pure sodic carbonate, added to one liter of the solution, will bring it to normal strength.

## TABLE FOR THE SYSTEMATIC ANALYSIS OF ALKALIES, ALKALINE EARTHS AND ACIDS.

| Substance. | Formula. | Atomic Weight. | Quantity to be weighed so that 1 c.c. Normal Solution=1 per cent. of substance. | Normal Factor.* |
|---|---|---|---|---|
| Soda . . . . . . | $Na^2O$ | 62 | 3·1 gm. | 0·031 |
| Sodic Hydrate . . | $NaHO$ | 40 | 4·0 gm. | 0·040 |
| Sodic Carbonate . . | $Na^2CO^3$ | 106 | 5·3 gm. | 0·053 |
| Sodic Bicarbonate . | $NaHCO^3$ | 84 | 8·4 gm. | 0·084 |
| Potash . . . . . | $K^2O$ | 94 | 4·7 gm. | 0·047 |
| Potassic Hydrate . . | $KHO$ | 56 | 5·6 gm. | 0·056 |
| Potassic Carbonate . | $K^2CO^3$ | 138 | 6·9 gm. | 0·069 |
| Potassic Bicarbonate | $KHCO^3$ | 100 | 10·0 gm. | 0·100 |
| Ammonia . . . . | $NH^3$ | 17 | 1·7 gm. | 0·017 |
| Ammonic Carbonate | $(NH^4)^2CO^3$ | 96 | 4·8 gm. | 0·048 |
| Lime (Calcic Oxide) | $CaO$ | 56 | 2·8 gm. | 0·028 |
| Calcic Hydrate . . | $CaH^2O^2$ | 74 | 3·7 gm. | 0·037 |
| Calcic Carbonate . . | $CaCO^3$ | 100 | 5·0 gm. | 0·050 |
| Baric Hydrate . . | $BaH^2O^2$ | 171 | 8·55 gm. | 0·0855 |
| Do. (Crystals) . | $BaO^2H^2(H^2O)^8$ | 315 | 15·75 gm. | 0·1575 |
| Baric Carbonate . . | $BaCO^3$ | 197 | 9·85 gm. | 0·0985 |
| Strontia . . . . . | $SrO$ | 103·5 | 5·175 gm. | 0·05175 |
| Strontic Carbonate . | $SrCO^3$ | 147·5 | 7·375 gm. | 0·07375 |
| Magnesia . . . . | $MgO$ | 40 | 2·00 gm. | 0·020 |
| Magnesic Carbonate. | $MgCO^3$ | 84 | 4·20 gm. | 0·012 |
| Nitric Acid . . . | $HNO^3$ | 63 | 6·3 gm. | 0·063 |
| Hydrochloric Acid . | $HCl$ | 36·37 | 3·637 gm. | 0·03637 |
| Sulphuric Acid . . | $H^2SO^4$ | 98 | 4·9 gm. | 0·049 |
| Oxalic Acid . . . | $C^2O^4H^2(H^2O)^2$ | 126 | 6·3 gm. | 0·063 |
| Acetic Acid . . . | $C^2O^2H^4$ | 60 | 6·0 gm. | 0·060 |
| Tartaric Acid . . . | $C^4O^6H^6$ | 150 | 7·5 gm. | 0·075 |
| Citric Acid . . . . | $C^6O^7H^8 + H^2O$ | 210 | 7·0 gm. | 0·070 |
| Carbonic Acid . . . | $CO^2$ | 44 |  | 0·022 |

* This is the coefficient by which the number of c.c. of normal solution used in any analysis is to be multiplied, in order to obtain the amount of pure substance present in the material examined.

If grain weights are used instead of grams, the decimal point must be moved one place to the right to give the necessary weight for examination; thus sodic carbonate, instead of 5·3 gm., would be 53 grains; the normal factor in this case would also be altered to 0·53.

## THE TITRATION OF ALKALINE SALTS.

### 1. Caustic Soda or Potash, and their Neutral or Acid Carbonates.

§ 16. The necessary quantity of substance being weighed or measured, as the case may be, and mixed with distilled water to a proper state of dilution (say about one per cent. of solid material), an appropriate indicator is added, and the solution is ready for the burette. Normal acid is then cautiously added from a burette till the change of colour occur. In the case of caustic alkalies free from $CO^2$, the end reaction is very sharp with any of the indicators; but if $CO^2$ is present, the only available indicators in the cold are methyl orange or lacmoid paper. If the other indicators are used, the $CO^2$ must be boiled off after each addition of acid.

In examining carbonates of potash or soda, or mixtures of caustic and carbonate, where it is only necessary to ascertain the total alkalinity, the same method applies.

In the examinations of samples of commercial refined soda or potash salts, it is advisable to proceed as follows:—

Powder and mix the sample thoroughly, weigh 10 gm. in a platinum or porcelain crucible, and ignite gently over a spirit or gas lamp, and allow the crucible to cool under the exsiccator. Weigh again, the loss of weight gives the moisture; wash the contents of the crucible into a beaker, dissolve and filter if necessary, and dilute to the exact measure of 500 c.c. with distilled water in a half-liter flask; after mixing it thoroughly take out 50 c.c. = 1 gm. of alkali with a pipette, and empty it into a small flask, bring the flask under a burette containing normal acid and graduated to $\frac{1}{5}$ or $\frac{1}{10}$ c.c., allow the acid to flow cautiously as before directed, until the neutral point is reached: the process may then be repeated several times if necessary, in order to be certain of the correctness of the analysis.

*Residual Titration:* As the presence of carbonic acid with litmus and the other indicators, except methyl orange, always tends to confuse the exact end of the process, the difficulty is best overcome by allowing an excess of acid to flow into the alkali, boiling to expel the $CO^2$, and then cautiously adding normal caustic alkali, drop by drop, until the liquid suddenly changes colour; by deducting the quantity of caustic alkali from the quantity of acid originally used, the exact volume of acid necessary to saturate the 1 gm. of alkali is ascertained.

This method of re-titration gives a very sharp end-reaction, as there is no carbonic acid present to interfere with the delicacy of the indicator. It is a procedure sometimes necessary in other cases, owing to the interference of impurities dissipated by boiling, *e.g.* sulphuretted hydrogen, which would otherwise bleach the indicator, except in the case of methyl orange and lacmoid paper, either of which are indifferent to $H^2S$ in the cold. An example will make the plan clear:—

*Example:* 50 c.c. of the solution of alkali prepared as directed, equal to 1 gm. of the sample, is put into a flask, and 20 c.c. of normal acid allowed to flow into it; it is then boiled and shaken till all $CO^2$ is expelled, and normal caustic alkali added till the neutral point is reached; the quantity required is 3·4 c.c., which deducted from 20 c.c. of acid leaves 16·6 c.c. The following calculation, therefore, gives the percentage of real alkali, supposing it to be soda:—31 is the half molecular weight of dry soda, $Na^2O$* and 1 c.c. of the acid is equal to 0·031 gm., therefore 16·6 c.c. is multiplied by 0·031, which gives 0·5146; and as 1 gm. was taken, the decimal point is moved two places to the right, which gives 51·46 per cent. of real alkali; if calculated as carbonate, the 16·6 would be multiplied by 0·053, which gives 0·8798 gm. = ·98 per cent.

### 2. Mixed Caustic and Carbonated Alkaline Salts.

The alkaline salts of commerce, and also alkaline lyes used in soap, paper, starch, and other manufactories, consist often of a mixture of caustic and carbonated alkali. If it be desired to ascertain the proportion in which these mixtures occur, the total alkaline power of a weighed or measured quantity of substance (not exceeding 1 or 2 gm.) is ascertained by normal acid and noted; a like quantity is then dissolved in about 150 c.c. of water in a 200 c.c. flask, and enough solution of baric chloride added to remove all carbonic acid from the soda or potash.

Watson Smith has shown (*J. S. C. I.* i. 85) that whenever an excess of baric chloride is used in this precipitation so as to form baric hydrate, there is an invariable loss of soda: exact precipitation is the only way to secure accuracy.

The flask is now filled up to the 200 c.c. mark with distilled water, securely stoppered, and put aside to settle. When the supernatant liquid is clear, take out 50 c.c. with a pipette, and titrate with normal hydrochloric acid to the neutral point. The number of c.c. multiplied by 4 will be the quantity of acid required for the caustic alkali in the original weight of substance, because only ¼ was taken for analysis. The difference is calculated as carbonate, or the precipitated baric carbonate may be thrown upon a dry filter, washed well and quickly with boiling water, and titrated with normal acid, instead of the original analysis for the total alkalinity; or both plans may be adopted as a check upon each other.

The principle of this method is, that when baric chloride is added to a mixture of caustic and carbonated alkali, the carbonic acid of the latter is precipitated as an equivalent of baric carbonate, while the equivalent proportion of caustic alkali remains in solution as baric hydrate. By multiplying the number of c.c. of acid required to saturate this free alkali with the $\frac{1}{1000}$ atomic weight of caustic potash or soda, according to the alkali present, the quantity of substance originally present in this state will be ascertained.

As caustic baryta absorbs $CO^2$ very readily when exposed to the atmosphere, it is preferable to allow the precipitate of baric carbonate to settle in the flask as here described, rather than to filter the solution as recommended by some operators, especially also that the filter obstinately retains some baric hydrate.

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* The commercial standard (so called English test) often used is 32 (being based on the old erroneous equivalent of Na=24).

A very slight error, however, always occurs in all such cases, in consequence of the volume of the precipitate being included in the measured liquid.

### 3. Estimation of Hydrates of Soda or Potash with small proportions of Carbonate.

This may be accomplished by means of phenacetolin (Lunge, *J. S. C. I.* i. 56). The alkaline solution is coloured of a scarcely perceptible yellow with a few drops of the indicator. The standard acid is then run in until the yellow gives place to a pale rose tint: at this point all the caustic alkali is saturated, and the volume of acid used is noted. Further addition of acid now intensifies this red colour until the carbonate is decomposed, when a clear golden yellow results. The neutralization of the NaHO or the KHO is indicated by a rose tint permanent on standing; that of $Na^2CO^3$ or $K^2CO^3$, by the sudden passage from red to yellow.

Practice is required with solutions of known composition to accustom the eye to the changes of colour. Phenolphthalein may also be employed for the same purpose as follows:—

Add normal acid to the cold alkaline solution till the red colour is discharged, taking care to use a very dilute solution, and keeping the spit of the burette in the liquid so that no $CO^2$ escapes. The point at which the colour is discharged occurs when all the hydrate is neutralized and the carbonate converted into bicarbonate; the volume of acid is noted, and the solution heated to boiling, with small additions of acid, till the red colour produced by the decomposition of the bicarbonate is finally destroyed.

In both these methods it is preferable, after the first stage, to add excess of acid, boil off the $CO^2$, and titrate back with normal alkali. The results are quite as accurate as the method of precipitation with barium.

### 4. Estimation of Alkaline Bicarbonates in presence of Normal Carbonates (Lunge, J. S. C. I. i. 57).

To a weighed quantity of the solid bicarbonate, or a measured quantity of a solution, there is added an excess of $\frac{N}{2}$ ammonia, followed by an excess of solution of baric chloride. The mixture is made in a measuring flask, and the whole diluted with hot distilled water to the mark.

A portion of the clear settled liquid, or filtered through a dry filter, is then titrated with normal acid: the alkaline strength due to the excess of ammonia, above that required to convert the bicarbonate into normal carbonate, deducted from the total ammonia added, gives the equivalent of the bicarbonate present.

*Example* (Lunge): 20 gm. sodic bicarbonate in the course of manufacture were dissolved to a liter. 50 c.c. of this solution required 12·1 c.c. normal acid = 0·3751 gm. $Na^2O$; 50 c.c. were then mixed with 50 c.c. of standard ammonia (50 c.c. = 24·3 normal acid) and the whole treated with excess of baric chloride. One half of the clear liquid required 6·25 c.c. normal acid = 11·8 c.c. corrected for strength and double quantity: this is, therefore, the equivalent of the $CO^2$ as bicarbonate.

$$NaHCO^3 : 11{\cdot}8 \times {\cdot}084 = {\cdot}9912 \text{ gm.}$$
$$Na^2CO^3 : (12{\cdot}1 - 11{\cdot}8) \times {\cdot}053 = {\cdot}0159$$

A simpler plan than the above has been devised by Thompson, which gives good results when carefully carried out.

To the cold solution of the sample, an excess of normal caustic soda, free from $CO^2$, is added, the $CO^2$ is then precipitated with neutral solution of baric chloride, and the excess of sodic hydrate found by standard acid, using phenolphthalein as indicator. The precipitate of baric carbonate has no effect on the indicator in the cold. The calculation is the same as before.

### 5. Estimation of small quantities of Sodic or Potassic Hydrates in presence of Carbonates.

This method, by Thompson, has just been alluded to, and consists in precipitating the carbonates by neutral solution of baric chloride in the cold: the baric carbonate being neutral to phenolphthalein, this indicator can be used for the process. When the barium solution is added, a double decomposition occurs, resulting in an equivalent quantity of sodic or potassic chloride, while the baric carbonate is precipitated, and the alkaline hydrate remains in solution.

*Example* (Thompson): 2 gm. of pure sodic carbonate were mixed in solution with ·02 gm. of sodic hydrate; excess of baric chloride was then added, together with the indicator, and the solution titrated with $\frac{N}{10}$ acid, of which in three trials an average of 5 c.c. were required; therefore, 5 × ·004 = ·02 gm. exactly the quantity used.

In this process the presence of chlorides, sulphates, and sulphites do not interfere; neither do phosphates, as baric phosphate is neutral to the indicator. With sulphides, half of the base will be estimated; but if hydrogen peroxide be added, and the mixture allowed to rest for a time, the sulphides are oxidized to sulphates, which have no effect. If silicates or aluminates of alkali are present, the base will of course be recorded as hydrate.

Thompson further says :—

"The foregoing method can also be applied to the determination of hydrate of sodium or potassium in various other compounds, which give precipitates with baric chloride neutral to phenolphthalein, such as the normal sulphites and phosphates of the alkali metals. An illustration of the use to which the facts I have stated in this and former papers may be put will be found in the analysis of sulphite of sodium. Of course sulphate, thiosulphate, and chloride are determined as usual, but to estimate sulphite, carbonate and hydrate, or bicarbonate of sodium by methods in ordinary use is rather a tedious operation. To find the proportion of hydrate, all that is necessary is to precipitate with baric chloride and titrate with standard acid, as above described. Then, by simple titration of another portion of the sample in the cold, using phenolphthalein as indicator, the hydrate and half of the carbonate can be found, and finally, by employment of methyl orange as indicator, and further addition of acid, the other half of the carbonate and half of the sulphite can be estimated. By simple calculations, the respective proportions of these three compounds can be obtained, a result which can be accomplished in a few minutes. It must be borne in mind that if a large quantity of sodic carbonate is in the sample the proportion of that compound found will only be an approximation to the truth, as the end-reaction is only delicate with small proportions of sodic carbonate. If there is no hydrate found, bicarbonate of sodium can be tested for, and determined by the method described in § 16. 4."

### 6. Estimation of Caustic Soda or Potash by standard Bichromate of Potash.

This process was devised by Richter, or rather the inverse of it, for estimating bichromate with caustic alkali by the aid of phenolphthalein. Exact results may be obtained by it in titrating soda or potash as hydrates, but not ammonia as recommended by Richter.

For the process there are required a decinormal solution of bichromate containing 14·74 gm. per liter, and $\frac{N}{10}$ soda or potash solution titrated against sulphuric acid. A comparison liquid containing about 1 gm. of monochromate of potash in 150—200 c.c. water is advisable for ascertaining the exact end of the reaction; 50 c.c. of the alkali being diluted with the same volume of water, is coloured with phenolphthalein, and the bichromate run in from a burette; the fine red tint changes to reddish yellow, which remains till the neutral point is nearly reached, when the yellow colour of the monochromate is produced; the change is not instantaneous as with mineral acids, so that a little time must be allowed for the true colour to declare itself.

### 7. Estimation of Potash in Neutral Salts free from Soda.

Stolba precipitates the potash from a tolerably concentrated solution of the substances with hydrofluosilicic acid and strong alcohol. The method is also applicable to the estimation of potash in potassic platinum chloride. To ensure complete decomposition, it is well to warm the mixture for a little time before adding the alcohol, which must be of about the same volume as the liquid itself. After some hours, when the precipitate has settled, the solution is filtered off, the beaker and precipitate well washed with equal mixtures of alcohol and water, the whole transferred to a white porcelain basin, water rather freely added, and heated to boiling, a few drops of litmus added, and normal or semi-normal alkali run in until exact saturation occurs; or a known excess of alkali may be added, and the amount found by residual titration with normal acid. The results are generally about 1°/₀ too low, owing to the difficulty of fully decomposing the precipitate.

2 eq. alkali = 1 eq. potash.

The process is very limited in its use, and is not applicable when sulphates are present, nor in the presence of any great amount of free acid. Sulphuric acid may be previously removed by calcic acetate and alcohol; other acids by moderate ignition previous to precipitation. Large proportions of ammonia salts must also be removed; and, of course, all other matters precipitable by hydrofluosilicic acid, especially soda.

### 8. Direct estimation of Potash in the presence of Soda.

Fleischer recommends the following method; and my own experiments confirm his statements, so far at least as the pure salts are concerned.

The solution must contain no other bases except the alkalies, nor any acids except nitric, hydrochloric, or acetic. This can almost invariably be easily accomplished. Earthy alkalies are removed by ammonic carbonate or phosphate; sulphuric, chromic, phosphoric, and arsenic acids by baric chloride, followed by ammonic carbonate.

The solution should be tolerably concentrated, and the volume about 25 or 30 c.c.; 10—15 c.c. of neutral solution of ammonic acetate of sp. gr. 1·035 are added; followed by finely powdered pure tartaric acid in sufficient quantity to convert the potash into acid tartrate, with an excess to form some ammonic tartrate, but not enough to decompose the whole. This is the weak part of the method; however, as a guide, it is not advisable to add more than 5 gm. tartaric acid for 10 c.c. of ammonic acetate. If the quantity of potash is approximately known, it is best to add about one-third more than is sufficient to convert the whole into acid tartrate.

After adding the tartaric acid the mixture must be well stirred for five or ten minutes, without rubbing the sides of the beaker; a like volume of 95-per-cent. alcohol is added, and again well stirred. The precipitate contains the whole of the potash as tartrate, and a portion of ammonium tartrate. After standing half an hour with occasional stirring, the precipitate is collected on a porous filter, and repeatedly washed with alcohol and water in equal parts until clean.

When the washing is finished the precipitate will be entirely free from soda; filter and precipitate are transferred to a porcelain basin, treated with sufficient hot water to dissolve the tartrates, then exactly neutralized with normal alkali and litmus, and the volume so used noted. A like volume, or preferably, a larger known volume of normal alkali is now added, and the mixture boiled to expel all ammonia; the end may be known by holding litmus paper in the steam. The excess of normal alkali is now found by titration with normal acid; the amount so found must be deducted from that which was added in excess after the exact titration of the tartrate; the difference equals the ammonia volatilized. By deducting this difference from the volume of normal alkali originally required, the volume corresponding to potash is found.

*Example:* 29·4 c.c. of normal alkali were required in the first instance to neutralize a given precipitate; 40 c.c. of the same alkali were then added, the boiling accomplished, and 22·5 c.c. normal acid used for the excess; then 40—22·5 = 17·5 c.c., and again 29·4 − 17·5 = 11·9, which multiplied by the factor for KHO = 0·056 gives 0·6664 gm.

The soda in filtrate may be obtained by evaporation with hydrochloric acid as sodic chloride, and estimated as in § 38.

### 9. Mixed Caustic Soda and Potash.

This process depends upon the fact, that potassic bitartrate is almost insoluble in a solution of sodic bitartrate.

Add to the solution containing the mixed salts, a standard solution of tartaric acid till neutral or faintly acid—this produces neutral tartrates of the alkalies—now add the same volume of standard tartaric acid as before—they are now acid tartrates, and the potassic bitartrate separates almost completely, filter off the sodic bitartrate and titrate the filtrate with normal caustic soda; the quantity required equals the soda, originally in the mixture—the quantity of tartaric acid required to form bitartrate with the soda subtracted from the total quantity added to the mixture of the two alkalies, gives the quantity required to form potassic bitartrate, and thus the quantity of potash is found.

This process is only applicable for technical purposes.

### 10. Potash as Platino-chloride.

In cases where potash exists in combination as a neutral salt, such as kainit or kieserit, etc., or as a constituent of minerals, it has to be first separated as double chloride of potassium and platinum. The method usually adopted is that of collecting the double salt upon a tared filter, when the weight of the dry double salt is obtained, the weight of potash is ascertained by calculation.

It may, however, be arrived at by volumetric means as follows:—

The potash having been converted into double chloride in the usual way is dried, collected, and mixed with about double its weight of pure sodic oxalate, and gently smelted in a platinum crucible; this operation results in the production of metallic platinum, chlorides of sodium and potassium, with some carbonate of soda. The quantity of potash present is, however, solely measured by the chlorine; in order to arrive at this, the fused mass is lixiviated with water, filtered, nearly neutralized with acetic acid, and the chlorine estimated with $\frac{N}{10}$ silver and chromate, the number of c.c. of silver required is multiplied by the factor 0·00157, which gives at once the weight of potash. This factor is used because 1 molecule of double chloride contains 3 atoms chlorine, hence the quantity of $\frac{N}{10}$ silver used is three times as much as in the case of sodic or potassic chloride.

### 11. Separation of the Potash as Bitartrate.

The mixed salts being rendered as nearly neutral as possible, a saturated solution of sodic bitartrate is added in excess, and the whole evaporated to dryness in the water bath. The dry mass is then deprived of the excess of sodic bitartrate by washing it on a filter with a saturated solution of potassic bitartrate; when all the soda salt has been removed, the potash salt is dissolved in hot water, and titrated with normal alkali, of which 1 c.c. represents 0·039 gm. K. In cases where potash is to be separated as bitartrate, the operator should consult § 25. 2 and 3.

### 12. Indirect Estimation of Potash (Dubenard).

This process is ingenious, but, like all attempts at estimating this base volumetrically, is not very exact, except with extreme precautions.

*The Analysis:* The potassic salt, acidified with nitric acid, is precipitated by a standard solution of sodic chloroplatinate, the excess of which is reduced by zinc, and then determined by means of standard silver nitrate. The process is applicable to sulphates, chlorides, nitrates, etc. 12 to 15 parts of sodic chloroplatinate are dissolved in 100 of alcohol, and 12 to 15 parts of silver nitrate in 1000 of water. The solutions are standardized as follows:—10 c.c. of the platinum solution are reduced by boiling for a minute with a small quantity of zinc powder, the whole of the platinum being precipitated, and all the chlorine remains in solution as chlorides of zinc and of sodium; the solution is made up to 100 c.c. and filtered. In 50 c.c. of the filtrate the chlorine is determined by titrating with the silver solution, of which, say, 40 c.c. are required. Then $40 \times 4 = 160$ = the number of c.c. which corresponds to 20 c.c. of the platinum solution. 0·5 gm. of potassic nitrate or sulphate is then dissolved in a few c.c. of water, acidified with nitric acid, the potassium precipitated with 20 c.c. of the platinum solution, and the volume made up to 100 c.c. with alcohol (95 per cent.); the solution is filtered, and 50 c.c. of it reduced by boiling with a little zinc, again made up to 100 c.c., and filtered; 50 c.c. of this filtrate is titrated with the silver solution, of which, say, 12 c.c. are required; then 12 c.c. × 4 = 48 c.c., subtracted from 160 c.c., represents the amount of chlorine precipitated as potassic chloroplatinate by the potassic nitrate; thus (160—48) c.c. = 112 c.c. corresponds to 0·5 gm. of potassic nitrate, *i.e.*, to 0·232 $K^2O$. To determine now the amount of potassium in any salt the process just described is followed, taking 10 c.c. of a solution containing 50 gm. of the salt per liter. The amount of chlorine present in the salt, as a chloride, must be determined by titration, and allowed for before calculating the amount of potassium. Thus, if the 10 c.c. of the solution (*i.e.*, 0·5 gm. of the sample) required 8 c.c. of the silver solution and 27 c.c. were required of it after the reduction with zinc, the calculation would be (27 × 4—8) c.c. = 100 c.c. and $\frac{100 \times 0{\cdot}232}{112} = 0{\cdot}207$ gm. of potash in 0·5 gm., *i.e.*, the sample contained 41·52 per cent. of $K^2O$.

This process has been critically examined under the direction of Dr. Wiley (*C. N.* liii. 176), who states, that owing to uncertainty in estimating the chlorine, the conclusions are not satisfactory. This has given me no difficulty when using potassic chromate as indicator, taking the precaution to add a little pure calcic carbonate to insure neutrality. It has given me good approximate results with tolerably pure and concentrated potassium salts, viz., nitrate, sulphate, and chloride. I doubt its value however for estimation of small percentages of potash in manures, etc. The process is rapid and easy, but care should be taken in filtering the alcoholic mixture of the double chloride to avoid loss by evaporation before measuring. The solutions precipitated by zinc need no filtering, as they settle rapidly. $\frac{N}{10}$ silver solution is available for the chlorine estimation; the weak point in the process is probably due to the strong saline liquids affecting the delicacy of the chromate indicator.

## TECHNICAL EXAMINATION OF SOME ALKALINE COMPOUNDS FOUND IN COMMERCE OR OCCURRING IN COURSE OF MANUFACTURE.

There is now considerable unanimity among English and foreign manufacturers of alkaline compounds, as to methods of analysis to be adopted either for guidance in manufacture or commercial valuation. Lunge has contributed important papers on the subject (*J. S. C. I.* i. 12, 16, 55, 92), also in conjunction with Hurter in the *Alkali Makers' Pocket Book*,[*] which contains valuable tables and processes bearing on the subject. So far as volumetric methods are concerned, the same processes will be given here with others.

### 13. Soda Ash, Black Ash, Mother-liquors, etc.

*Soda Ash or Refined Alkali.*—5 or 10 gm. are dissolved in about 150 c.c. of warm distilled water, and any insoluble matter filtered off (German chemists do not filter), and the volume diluted to ½ or 1 liter.

The total quantity of alkali is determined in 50 c.c. by normal sulphuric, nitric, or hydrochloric acid, as in § 16. 1.[†]

The quantity of caustic alkali present in any sample is determined as in § 16. 2 or 5.

The presence of sulphides is ascertained by the smell of sulphuretted hydrogen when the alkali is saturated with an acid, or by dipping paper steeped in sodic nitro-prusside into the solution: if the paper turns blue or violet, sulphide is present.

The quantity of sulphide and sulphite may be determined by saturating a dilute solution of the alkali with a slight excess of acetic acid, adding starch liquor, and titrating with $\frac{N}{10}$ iodine solution till the blue colour appears. The quantity of iodine required is the measure of the sulphuretted hydrogen and sulphurous acid present.

The proportion of sulphide is estimated as follows:—13·820 gm. of pure silver are dissolved in dilute nitric acid, and the solution, together with an excess of liquid ammonia, made up to a liter. Each c.c. = 0·005 gm. $Na^2S$.

*The Analysis:* 100 c.c. of the alkali liquor is heated to boiling, some ammonia added, and the silver solution dropped in from a burette until no further precipitate of $Ag^2S$ is produced. Towards the end filtration will be necessary, in order to ascertain the exact point, to which end the Beales filter is serviceable (fig. 16). The amount of $Na^2S$ so found is deducted from the total sulphide and sulphite found by iodine.

Sodic chloride (common salt) may be determined by carefully neutralizing 1 gm. of the alkali with nitric acid, and titrating with decinormal silver solution and potassic chromate. Each c.c. represents 0·005837 gm. of common salt. Since the quantity of acid necessary to neutralize the alkali has already been found, the proper measure of $\frac{N}{10}$ nitric acid may at once be added.

Sodic sulphate is determined, either directly or indirectly, as in § 73. Each c.c. or dm. of normal baric chloride is equal to 0·071 gm. or 0·71 grn. of dry sodic sulphate.

Black ash and raw mother-liquors and lyes can be examined as follows:—

Black Ash.—Digest 50 gm. with warm water in a ½ liter flask, fill up to mark, and allow to settle clear.

---

[*] Bell & Sons, York Street, Covent Garden.

[†] This gives a slight error, owing to traces of aluminate of soda and lime, which consume acid.

(1) *Total Alkali* existing as carbonate, hydrate, and sulphide, is found by titrating 10 c.c. = 1 gm. of ash with standard acid and methyl orange in the cold.

(2) *Caustic Soda.*—20 c.c. of the liquid is put into a 100 c.c. flask with 10 c.c. of solution of chloride of barium of 10 per cent. strength, filled up with hot water, well shaken, and corked after settling a few minutes. The clarified liquid is filtered, and 50 c.c. = 1 gm. ash, titrated with standard acid and methyl orange; or it may be titrated without filtration if standard oxalic acid and phenolphthalein are used, this acid having no effect on the baric carbonate. Each c.c. normal acid = 0·031 $Na^2O$. This includes sulphides.

(3) *Sodic Sulphide.*—Put 10 c.c. of liquor into a flask, acidulate with acetic acid, dilute to about 200 c.c., and titrate with $\frac{N}{10}$ iodine and starch liquor. Each c.c. = 0·0039 $Na^2S$, or 0·0031 $Na^2O$.

(4) *Sodic Chloride.*—10 c.c. are neutralized exactly with normal nitric acid, and boiled till all $H^2S$ is evaporated. Any sulphur which may have been precipitated is filtered off, and the filtrate titrated with $\frac{N}{10}$ silver and chromate. Each c.c. = 0·005837 gm. NaCl.

(5) *Sodic Sulphate.*—This is best estimated by precipitation as baric sulphate, and weighing, the quantity being small. If, however, volumetric estimation is desired, it may be done, as in § 73, taking 50 c.c. of liquor.

For the detailed examination of the various solid and liquid alkali wastes used for soda and sulphur recovery, etc., the reader is referred to the *Alkali Makers' Pocket Book* already mentioned.

### 14. Salt Cake

Is the impure sodic sulphate used in alkali manufacture or left in the retorts in preparing hydrochloric acid from sulphuric acid and salt, or nitric acid from sodic nitrate. It generally contains free sulphuric acid existing as sodic bisulphate, the quantity of which may be ascertained by direct titration with normal alkali.

The common salt present is estimated by decinormal silver solution and chromate; having first saturated the free acid with pure sodic carbonate, 1 c.c. or 1 dm. silver solution is equal to 0·005837 gm. or 0·05837 grn. of salt.

Sulphuric acid, combined with soda, is estimated either directly or indirectly as in § 73; 1 c.c. or 1 dm. of normal baryta solution is equal to 0·071 gm. or 0·71 grn. of dry sodic sulphate.

Iron is precipitated from a filtered solution of the salt cake with ammonia in excess, the precipitate of ferric oxide re-dissolved in sulphuric acid, reduced to the ferrous state with zinc and titrated with permanganate.

Grossmann adopts a method suggested by Bohlig (see § 28), and has worked out the process in the case of salt cake in careful detail (*C. N.* xli. 114) as follows:—

The neutral solution of salt cake (3·55 gm.) is put into a 500 c.c. flask, a measured quantity of baric hydrate in solution (250 c.c. of a cold saturated solution) is added in excess, the flask filled up with water, and shaken up. Of the filtered clear liquid 250 c.c. are put in an ordinary flask, carbonic acid passed through for about ten minutes, and then the contents of the flask boiled so as to decompose any baric bicarbonate which may be in solution. After cooling, the contents of the flask are again transferred to the 500 c.c. flask, the latter filled up with water to the mark, shaken up, and filtered. 250 c.c. of the filtrate—*i.e.*, one-fourth of the original quantity used—are then titrated with one-fourth normal sulphuric acid. The number of c.c. of one-fourth normal acid used multiplied by two will give the percentage of sodic sulphate.

There are, however, sources of error in the experimental working of this method which make certain corrections necessary. They arise—

(1) From the impurities of the caustic baryta.
(2) From the precipitate formed in the measured liquid.
(3) From certain constant losses.

The commercial caustic baryta always contains baric nitrate, and sometimes baric chloride. It is evident that on adding a solution of baric hydrate which contains baric nitrate to a solution of sodic sulphate, a quantity of the latter, equivalent to the quantity of the baric nitrate present, will be converted into sodic nitrate, and thus escape the alkalimetric test, as will be seen by the following equations :—

$$Ba(NO^3)^2 + Na^2SO^4 = BaSO^4 + 2NaNO^3.$$
$$Ba(NO^3)^2 + 2NaOH + CO^2 = BaCO^3 + 2NaNO^3 + H^2O.$$

It is therefore necessary to measure approximately the quantity of baryta solution used, so as to know the amount of baric nitrate introduced into the process. The latter can be easily ascertained by passing carbonic acid in excess through the cold saturated solution of baric hydrate, boiling, filtering, and precipitating the baryta left in solution by sulphuric acid as usual. 250 c.c. of a baryta solution used for experiment yielded 0·0280 gm. $BaSO^4$, which corresponds to 0·0171 gm. $Na^2SO^4$, or 0·96 c.c. of one-fourth normal acid; and it follows that for every 250 c.c. of this baryta solution was found 0·0171 gm. $Na^2SO^4$ too little; or, that there must be added 0·24 c.c. of one-fourth normal acid to the result of the final titration (of one-fourth of the original quantity). If the baryta contain caustic alkali, a corresponding quantity of baric nitrate will be found less by the test; but it is easily understood, that the calculations will not be influenced as long as the baric nitrate is in excess of the caustic alkali, which is always the case in good commercial baryta.

The second error arises from the precipitates of baric sulphate and carbonate taking up some space in the 500 c.c. flask, the final results thus being found too high. If it is assumed that a cold saturated solution of baryta contains about 23 gm. BaO per liter, it will be near enough for all practical purposes if in the experiment, working with 3·55 gm. of $Na^2SO^4$ and 250 c.c. of baryta solution, 0·4 per cent. is subtracted from the final results for this error.

Three experiments made with 3·55 gm. of pure ignited sodic sulphate gave the following results :—

I.

| | |
|---|---|
| Used one-fourth normal acid ... | 49·37 c.c. |
| Add for $Ba(NO^3)^2$ ... ... ... | 0·24 c.c. |
| | 49·61 c.c. |

= 99·22 per cent. $Na^2SO^4$.

II.

| | |
|---|---|
| Used one-fourth normal acid ... | 49·21 c.c. |
| Add for $Ba(NO^3)^2$ ... ... ... | 0·24 c.c. |
| | 49·45 c.c. |

= 98·90 per cent. $Na^2SO^4$.

III.

| | |
|---|---|
| Used one-fourth normal acid ... | 49·37 c.c. |
| Add for $Ba(NO^3)^2$ ... ... ... | 0·24 c.c. |
| | 49·61 c.c. |

= 99·22 per cent. $Na^2SO^4$.

The average of these three experiments gives 99·1 per cent.; and if 0·4 per cent. be subtracted for the precipitate, the result is 98·7 per cent. instead of 100.

Grossmann states that this loss of 1·3 per cent. in working with 3·55 gm. of sulphate in the given dilution is a constant, and by dividing all results by 0·987 correct results are obtained.

It now remains to show the applicability of this method to the assay of salt cake and like substances. The following is a complete analysis of a sample of salt cake made in the usual way:—

| | |
|---|---|
| Moisture ... ... ... ... ... ... | 0·49 |
| Insoluble ... ... ... ... ... ... | 0·29 |
| Free sulphuric hydrate ... ... ... | 0·38 |
| Aluminium sulphate ... ... ... | 0·23 |
| Ferric sulphate ... ... ... ... ... | 0·42 |
| Calcic sulphate ... ... ... ... ... | 1·17 |
| Sodic chloride ... ... ... ... ... | 2·00 |
| Sodic sulphate (by difference) ... ... | 95·02 |
| | 100·00 |

In order to make a good test of salt cake it is now necessary to estimate seven constituents, to find by difference the quantity of actual sodic sulphate, which is the only constituent wanted.

When baric hydrate is added to a solution of salt cake the free acid is precipitated, so are alumina and iron, and the sulphuric acid combined with them and with lime. The lime is partly thrown down as such, and what is left as lime in solution is precipitated as carbonate in the second operation. Thus, whatever other sulphates be present, only the sodic sulphate is given; and by one simple test we are thus able to get a result which formerly could only be attained by a tedious complete analysis.

The salt cake, of which a complete analysis is given above, was tested by the alkalimetric method. 3·55 gm. required—

| | |
|---|---|
| One-fourth normal acid ... ... | 48·20 c.c. |
| Add for $Ba(NO^3)^2$ ... ... ... | 0·24 c.c. |
| | 48·44 c.c. |

$=96{\cdot}88$ per cent. $Na^2SO^4$.

$(96{\cdot}88-0{\cdot}40)=96{\cdot}48.$
$96{\cdot}48 : 0{\cdot}987=95{\cdot}2$ per cent. $Na^2SO^4$

Thus, by the alkalimetric test, 95·2 per cent. $Na^2SO^4$ occurs whereas the analysis gives 95·02 per cent. If it be considered how difficult it is to wash soda salts completely from precipitates, it is not surprising to find the result too low in the complete analysis, as in five precipitates a very minute quantity will make up 0·2 per cent.

It is hardly necessary to point out that none of the figures for the correction of the errors enumerated above can be used by any one else working by this method, but that they must be ascertained in every individual case. It is absolutely necessary to ascertain after the first operation that there is no sulphate, and after the second (before titrating) that there is no baryta in solution.

### 15. Raw Salt, Brine, etc.

Lime may be estimated by precipitation with ammonic oxalate, and the precipitate titrated with permanganate, as in § 48.

Sulphuric acid as in § 73.

Magnesia is precipitated as ammoniacal phosphate, by a solution of sodic phosphate containing ammonia, first removing the lime by ammonic oxalate, the precipitate of double phosphate of magnesia and ammonia is brought on a filter, washed with cold water containing ammonia, then dissolved in acetic acid, and titrated with standard uranium solution, or by the process for $P^2O^5$ (§ 23.2).

The quantity of real salt in the sample may be ascertained by treating a weighed quantity in solution with caustic baryta, boiling, setting aside that the excess of baryta may precipitate itself as carbonate, or more quickly by adding ammonic carbonate, filtering, evaporating the solution to dryness, and gently igniting—the residue is pure salt. The loss of weight between this and the original specimen taken for analysis, will show the percentage of impurities.

### 16. Soap.

The methods here given are a combination of those published by A. R. Leeds (*C. N.* xlviii. 166) and C. A. Wright (*Journ. Soc. Arts*, 1885, 1117)

(1) *Moisture and Volatile Matters.*—15 gm. are dried to a constant weight, first at 100°, then at 120° C.

(2) *Free Fats.*—Residue of 1 is exhausted with light petroleum ether, and the extract, after evaporation of the ether, weighed.

(3) *Fatty Acids, Chlorides, Sulphates, Glycerine, etc.*—The residue from (2), which has been treated with ether, represents 15 gm. soap; it is weighed, and two-thirds of it are dissolved in water, and normal nitric acid added in excess to separate the fatty acids. These are collected on a tared filter, dried, and weighed. The acid filtrate is now titrated with normal soda or potash (free from chlorides or sulphates), with phenolphthalein as indicator: the difference between the volumes of acid and alkali used gives roughly the total alkali. The residual neutral liquid is divided into two equal parts, in one of which chlorine is estimated with $\frac{N}{10}$ silver and chromate, and in the other sulphuric acid by normal baric chloride. If glycerine is present, it may be estimated by Muter's copper test in the absence of sugar. Sugar is, however, often largely used in transparent soaps in place of glycerine: when both are present, the separate estimation is difficult, but Wright suggests the method of Fehling for the sugar, first inverting with acid, and the copper retained in solution by the glycerine estimated colorimetrically, using for comparison a liquid containing both sugar and glycerine to known extents, treated side by side with the sample tested.

(4) *Free and Total Alkali.*—These are obtained by Wright's alcohol test. One-third of the residue obtained in (1) is boiled with 95 per cent. alcohol, the extract filtered off and residue washed with alcohol. The solution so obtained may be either positively alkaline with caustic alkali, or negatively alkaline from the presence of fatty acids or a diacid soap, according to the kind of soap used. Phenolphthalein is added, which shows at once whether free alkali is present, and in accordance with this either standard alcoholic acid or alkali is used for titration. The residue on the filter is then dissolved in water, and titrated with normal or decinormal acid. The sum of the two titrations will be the total alkalinity in case both showed an alkaline re-action; if otherwise, the alkali used to produce a colour in the alcoholic extract is deducted from the volume of acid used in the water extract. This method of taking the alkalinity of a soap is very fairly exact; the error ought never to exceed ± 0·5 per cent.

## TITRATION OF ALKALINE EARTHS.

§ 17. Standard hydrochloric or nitric acid must in all cases be used for the titration of the caustic or carbonated alkaline earths, as these are the only acids yielding soluble compounds, except in the case of magnesia. The hydrates, such as caustic lime, baryta, strontia, or magnesia, may all be estimated by any of the indicators, using the residual method, *i.e.*, adding a known excess of standard acid, boiling to expel any trace of $CO^2$, and re-titrating with standard alkali.

The carbonates of the same bases may of course also be estimated in the same way, bearing in mind, that when methyl orange is used, the liquid is best cooled before re-titration. All heating may be avoided when using methyl orange in titrating mixtures of hydrates and carbonates, or the latter only, unless it is impossible to dissolve the substance in the cold. A good excess of acid is generally sufficient.

The total amount of base in mixtures of caustic and carbonated alkaline earths is also estimated in the same way.

(1) *Estimation of Mixed Hydrates and Carbonates.*—This may be done either by phenacetolin or phenolphthalein as indicator. The former has been recommended by Degener and Lunge: the method, however, requires practice in order to mark the exact change of colour.

The liquid containing the compound in a fine state of division is tinted with the indicator so as to be of a faint yellow; standard acid is then cautiously added until a permanent pink occurs (at this stage all the hydrate is saturated), more acid is now cautiously added until the colour becomes deep yellow, the volume of acid so used represents the carbonate.

The method is especially adapted to mixtures of hydrate and carbonate of lime. It is also applicable to barium, but not to magnesium, owing to the great insolubility of magnesic hydrate in dilute acid. If phenolphthalein is used as indicator, the method is as follows:—

Heat the liquid to boiling, and cautiously add standard acid until the red colour is just discharged. The carbonates of lime and baryta, rendered dense by boiling, are both quite neutral to the indicator. To obtain the whole of the base, excess of standard acid is used, and the mixture re-titrated with standard alkali.

Magnesia in solution as bicarbonate may be accurately estimated in the cold with methyl orange as indicator.

(2) *Estimation of Calcium, Barium, and Strontium in Neutral Soluble Salts.*—The amount of base in the chlorides and nitrates of these alkaline earths may be readily estimated as follows:—

The weighed salt is dissolved in water, cautiously neutralized if acid or alkaline, phenolphthalein added, heated to boiling, and standard sodic carbonate delivered in from time to time with boiling until the red colour is permanent.

Magnesium salts cannot however be estimated in this way, or even mixtures of lime and magnesia, as magnesic carbonate affects the indicator in a different manner to the other carbonates.

(3) *Precipitation of the Alkaline Earths from their Neutral Salts as Carbonates.*—Soluble salts of lime, baryta, and strontia, such as chlorides, nitrates, etc., are dissolved in water, and the base precipitated as carbonate, with excess of ammonic carbonate and some free ammonia. The mixture is heated to about 60° C. for a few minutes. The precipitated carbonate is then to be filtered, well washed with hot water till all soluble matters, especially ammonia, are removed, and the precipitate with filter titrated with normal acid, as already described.

Magnesia salts require caustic soda or potash instead of ammonic carbonate; but the process gives results slightly too low, owing to the slight solubility of magnesic hydrate in the alkaline liquid.

(4) *Lime and Magnesia Carbonates in Waters.*—The amount of calcic, or calcic and magnesic carbonates, dissolved in ordinary non-alkaline waters may be very readily, and with accuracy, found by taking 200 or 300 c.c. of the water, heating to near boiling, adding phenacetolin or lacmoid, and titrating cautiously with $\frac{N}{10}$ nitric or sulphuric acid. Cochineal has been frequently used for this method of estimation, but the indicators mentioned are much more delicate.

(5) *Hardness of Water estimated without Soap Solution.*—As is generally known, the soap-destroying power of a water is ascertained in Clark's process by a standard solution of soap in weak alcohol, titrated against a standard solution of calcic chloride. The valuation is in so-called degrees, each degree being equal to 1 grain of calcic carbonate, or its equivalent, in the imperial gallon. The process is an old and familiar one, but open to many objections from a scientific point of view. The scale of degrees is arbitrary, and is seriously interfered with by the presence of varying proportions of magnesia.

We are indebted, primarily to Mohr, and subsequently to Hehner, for an ingenious method of determining both the temporary and permanent hardness of a water without the use of soap solution.

The standard solutions required are $\frac{N}{50}$ sodic carbonate and $\frac{N}{50}$ sulphuric acid. Each c.c. of standard acid exactly neutralizes 1 m.gm. of $CaCO^3$, and each c.c. of the alkali precipitates the like amount of $CaCO^3$, or its equivalent in magnesia, in any given water.

*The Analysis:* 100 c.c. of the water is tinted with an indicator of suitable character, heated to near boiling, and standard acid cautiously added until the proper change of colour occurs. Hehner recommends phenacetolin; but my own experiments give the preference to lacmoid, which is also commended by Thompson. Draper (*C. N.* li. 206) points out the value of lacmoid and carminic acid for such a process, and I fully endorse his opinion with respect to both indicators. Practice is desirable in order to recognize the precise end-reaction. The number of c.c. of acid used represents the number of degrees of temporary hardness per 100,000. To obtain degrees per gallon, multiply the number of c.c. by 0·7. The permanent hardness is ascertained by taking 100 c.c. of the water and adding to it a rather large known excess of the standard sodic carbonate. The quantity must of course be regulated by the amount of sulphates, chlorides, or nitrates of lime and magnesia present in the water; as a rule, a volume equal to the water will more than suffice. Evaporate in a platinum dish to dryness (glass or porcelain will not do, as they affect the hardness), then extract the soluble portion, with small quantities of distilled water, through a very small filter, and titrate the filtrate with the standard acid for the excess of sodic carbonate: the difference represents the permanent hardness.

Some waters contain alkaline carbonates, in which case there is of course no permanent hardness, because the salts to which this is due are decomposed by the alkaline carbonate.

In examining a water of this kind, the temporary hardness will be shown to be greater than it really is, owing to the alkaline carbonate; and the estimation for permanent hardness will show more sodic carbonate than was actually added. If the difference so found is deducted from the temporary hardness, as first noted, the remainder will be the true temporary hardness.

## AMMONIA.

$NH^3=17$.

§ 18. IN estimating the strength of solutions of ammonia by the alkalimetric method, it is better to avoid the tedious process of weighing any exact quantity, and to substitute for it the following plan, which is applicable to most liquids for the purpose of ascertaining both their absolute and specific weights.

Let a small and accurately tared flask, beaker, or other convenient vessel be placed upon the balance, and into it 10 c.c. of the ammoniacal solution delivered from a very accurately graduated 10 c.c. pipette. The weight found is, of course, the absolute weight of the liquid in grams; suppose it to be 9·65 gm., move the decimal point one place to the left, and the specific weight or gravity is at once given (water being 1), which in this case is 0·965.

It must be borne in mind that this system can only be used properly with tolerably delicate balances and very accurate pipettes. The latter should invariably be tested by weighing distilled water at 16° C.

The 10 c.c., weighing 9·65 gm., is now titrated with normal acid, of which 49 c.c. are required, therefore $49 \times 0{\cdot}017 = 0{\cdot}833$ gm. $NH^3 = 8{\cdot}64$ per cent. of real ammonia; according to Otto's table, 0·965 sp. gr. is equal to 8·50 per cent. Ammonic carbonate, and a mixture of the same with bicarbonate, as it most commonly occurs in commerce, may be titrated direct with normal acid for the percentage of real ammonia, using methyl orange as indicator. The carbonic acid can be determined by precipitating the solution while hot with baric chloride, and when the precipitate is well washed, dissolving it with an excess of normal acid and titrating backward with normal alkali; the number of c.c. of acid used multiplied by 0·022 (the ½ mol. wt. of $CO^2$) will give the weight of carbonic acid present in the sample.

### 1. Estimation of Combined Ammonia by distillation with Alkalies or Alkaline Earths.

This method allows of the expulsion of ammonia from all its salts. Caustic soda, potash, or lime, may any of them be used where no organic nitrogenous compound exists in the substance;

but should such be the case, it is preferable to use freshly ignited magnesia.

The distilling apparatus may conveniently be arranged by connecting an ordinary well-stoppered small retort to a small Liebig condenser, and leading the distilled gas into a vessel containing an excess of normal acid. After the operation is ended, the excess of acid is ascertained by residual titration with normal alkali or $\frac{N}{2}$ ammonia, and thus the amount of displaced ammonia is found.

The retort must be so supported that its neck inclines well upwards, in order that any alkali mechanically carried into it by the spray which occurs during ebullition shall not reach the condenser. An angle of about 30° suffices; and in order that a convenient connection may be made with the condenser, the end of the retort is bent downward, and the connection securely made with india-rubber tubing. In like manner, the end of the condenser is elongated by a glass tube and india-rubber joint, so that the tube dips into a two-necked bottle or bulb, containing the measured normal acid; the end of this tube should be cut obliquely, and reach nearly, but not quite, to the surface of the acid. The outlet of the receiver is fitted with a tube containing glass wool, broken glass, or fibrous asbestos, wetted with a portion of the normal acid, so that any traces of ammonia which may possibly escape condensation in the bulk of the acid may be retained.

The retort containing the ammoniacal compound in solution being securely fixed, and all the apparatus tightly connected, the stopper of the retort is removed, and a strong solution of caustic alkali, or, in case of compounds in which ammonia is quickly released, pieces of solid alkali are rapidly introduced, the stopper inserted, and the distillation forthwith commenced. Lime or magnesia, suspended in water, must be added through a small funnel; the distillation is continued until the steam has washed all traces of ammonia out of the condenser tube into the normal acid. Cold water is of course run continuously through the condenser as usual. Finally, the tubes connected with the receiver are well washed out into the bulk of normal acid, methyl orange added, and the titration completed with normal alkali or $\frac{N}{2}$ ammonia.

Each c.c. of normal acid neutralized by the displaced ammonia represents 0·017 gm. $NH^3$.

The apparatus shown in fig. 20 is of great value in determining accurately all the forms of ammonia which can be displaced by soda, potash, or lime, and the gas so evolved collected in a known volume in excess of normal acid, the excess of acid being afterwards found by residual titration with normal alkali or $\frac{N}{2}$ ammonia.

Many modifications of this apparatus have been suggested, such as the introduction of a condenser between the two flasks to cool the distillate; another is the use of a U tube containing some standard acid in place of *c*. I do not find that any of these modifications are required to secure accuracy, if the apparatus is tightly fitted. It is, however, necessary that a bulb should exist in the distilling tube, just above the cork of the distilling flask, otherwise I have found that the spray from the boiling liquid is occasionally projected into the tube, and is blown over with the condensed steam. Another precaution is advisable where dilute liquids are boiled, and much steam generated, that is, to immerse the condenser flask in cold water.

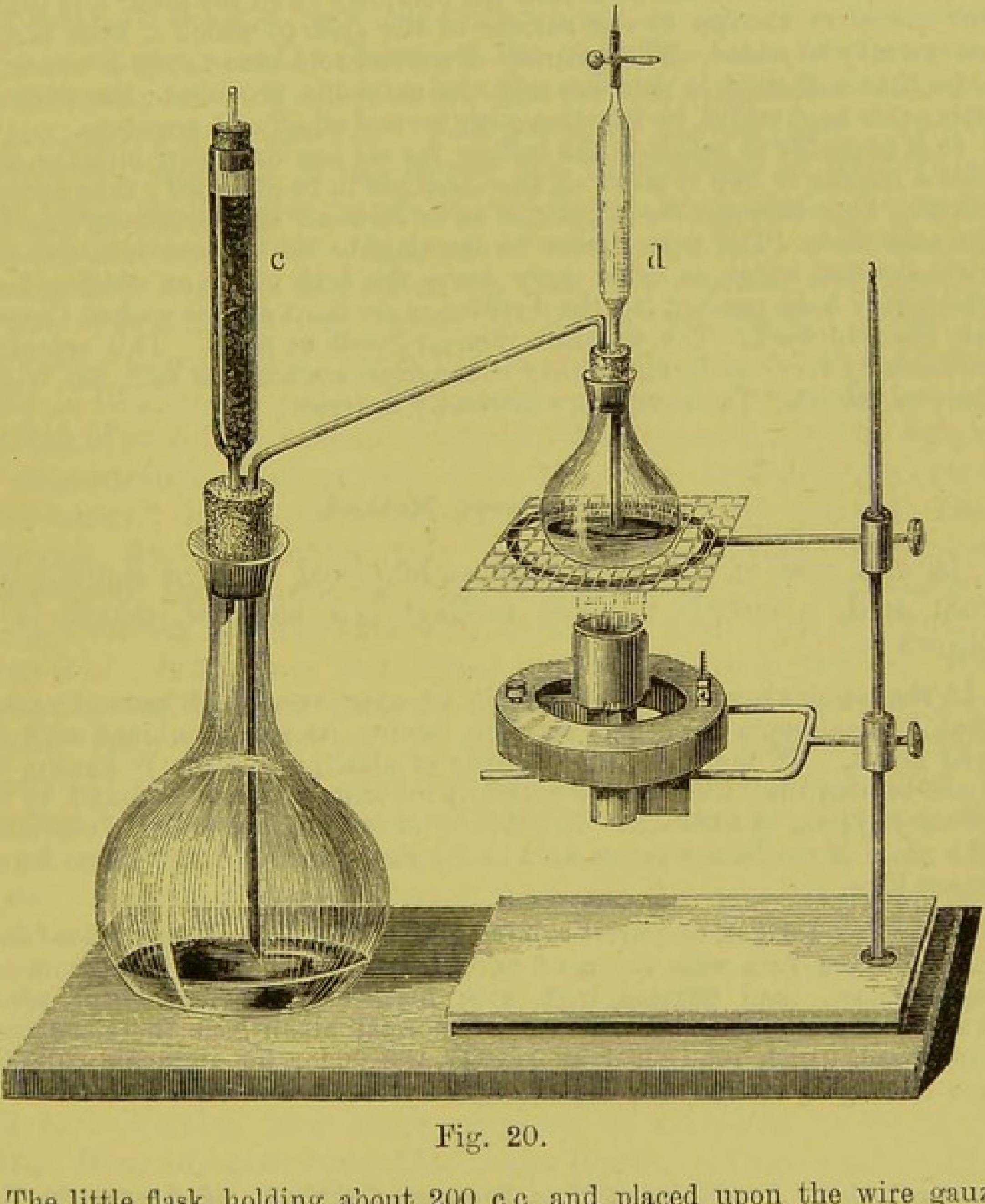

Fig. 20.

The little flask, holding about 200 c.c. and placed upon the wire gauze, contains the ammoniacal substance. The tube *d* is filled with strong solution of caustic potash or soda. The large flask holds about half a liter, and contains a measured quantity of normal acid, part being contained in the tube *c*, which is filled with glass wool or broken glass, and through which the normal acid has been poured. The stoppers of the flasks should be caoutchouc, failing which, good corks soaked in melted paraffine may be used.

The substance to be examined is weighed or measured, and put into the distilling flask with a little water, the apparatus then being made tight at every part; some of the caustic alkali is allowed to flow in by opening the clip, and the spirit lamp is lighted under it.

The contents are brought to gentle boiling, taking care that the froth, if any, does not enter the distilling tube. It is well to use a movable gas burner or common spirit lamp held under the flask in the hand; in case there is any tendency to boil over, the heat can be removed immediately, and the flask blown upon by the breath, which reduces the pressure in a moment. In examining guano and other substances containing ammoniacal salts and organic matter by this means, the tendency to frothing is considerable; and unless the above precautions are taken, the accuracy of the results will be interfered with.*

The distilling tube has both ends cut obliquely; and the lower end nearly, but not quite, reaches to the surface of the acid, to which a little methyl orange may be added. The quantity of normal acid used must, of course, be more than sufficient to combine with the ammonia produced; the excess is afterwards ascertained by titration with normal alkali or $\frac{N}{2}$ ammonia.

It is advisable to continue the boiling for say ten or fifteen minutes, then wait a minute or two to allow all the ammonia to be absorbed; then opening the clip, blow through the pipette so as to force all the remaining gas into the acid flask. The tube *c* must be thoroughly washed out into the flask with distilled water, so as to carry down the acid with any combined gas which may have reached it; the distilling tube must also be washed through into the acid flask. The titration then proceeds as usual. This process is particularly serviceable for testing commercial ammoniacal salts, gas liquor, etc. (see below). The results are extremely accurate.

### 2. Indirect Method.

In the case of tolerably pure ammoniacal salts or liquids, free from acid, a simple indirect method can be used, which is as follows:—

If the ammoniacal salt be boiled in an open vessel with normal caustic alkali, the ammonia is entirely set free, leaving its acid combined with the fixed alkali. If, therefore, the quantity of alkaline solution is known, the excess beyond that, necessary to supplant the ammonia, can be found by the ordinary system of titration. The boiling of the mixture must be continued till a piece of red litmus paper, held in the steam from the flask, is no longer turned blue.

*Example:* 1·5 gm. of purest sublimed ammonic chloride was placed in a wide-mouthed flask with 40 c.c. of normal soda, and boiled till all ammonia was expelled, then titrated back with normal sulphuric acid, of which 11·9 c.c. were required; 28·1 c.c. of normal alkali had therefore been neutralized, which multiplied by 0·05337, the factor for ammonic chloride, gave 1·499 gm., instead of 1·5 gm. originally taken.

### 3. Technical Analysis of Gas Liquor, Sulphate of Ammonia, Sal Ammoniac, etc., arranged for the use of Manufacturers.

This process depends upon the fact, that when ammoniacal salts are heated with caustic soda, potash, or lime, the whole of the ammonia is expelled in a free state, and can by a suitable apparatus (fig. 21) be estimated with extreme accuracy (see § 18.1).

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* In the figure the distilling tube is not shown correctly. There should be a bulb just above the cork of the distilling flask, to arrest any spray from the alkaline liquid which might find its way into the tube and be forced over.

The set of apparatus here described consists of a distilling flask B, and condensing flask F, fitted together in such a manner, that no loss of free ammonia can occur; the whole of the ammonia being liberated from the distilling flask into a measured quantity of free acid contained in the condensing flask, where its amount is afterwards found by the method hereinafter described.

*Analysis of Gas Liquor.*—This liquid consists of a solution of carbonates, sulphates, hyposulphites, sulphides, cyanides, and other salts of ammonia. The object of the ammonia manufacturer is to get all these out of his liquor into the form of sulphate or chloride as economically as possible. The whole of the ammonia existing as free or carbonate in the liquor, can be distilled off at a steam heat; the fixed salts, however, require to be heated with soda, potash, or lime (the latter is generally used on a large scale as most economical), in order to liberate the ammonia contained in them.

The valuation of gas liquor is almost universally made by Twaddle's hydrometer, every degree of which is taken to represent what is technically called "two-ounce strength;" that is to say, a gallon of such liquor should neutralize exactly two ounces by weight of concentrated oil of vitriol—thus 5 degrees, Twaddle, is called "ten-ounce" liquor—but experiment has clearly proved, that although the hydrometer may be generally a very convenient indicator of the commercial value of gas liquor, it is not accurate enough for the manufacturer who desires to work with the utmost economy. Sometimes the liquor contains a good deal of free ammonia, and in such case the hydrometer would show it to be weaker than it really is; on the other hand, sometimes, from accidental causes, other solid matters than ammonia salts occur in the liquor, and the hydrometer shows it to be stronger than it really is. The method of saturation, by mixing standard acid with the liquor, is perhaps more correct than the hydrometer; but this system is entirely at fault in the presence of much fixed ammonia, and is, moreover, a very offensive and poisonous operation.

The apparatus here described is exactly the same on a small scale as is necessary in the actual manufacture of sulphate of ammonia in quantities; and its use enables any manufacturer to tell to a fraction how much sulphate of ammonia he ought to obtain from any given quantity of gas liquor. It also enables him to tell exactly how much ammonia can be distilled off with heat alone, and how much exists in a fixed condition requiring lime.

The measures used in this process are on the metrical system; the use of these may, perhaps, at first sight appear strange to English manufacturers; but as the only object of the process is to obtain the percentage of ammonia in any given substance, it is a matter of no importance which system of measures or weights are used, as when once the percentage is obtained, the tables will at once show the result in English terms of weight or measure.

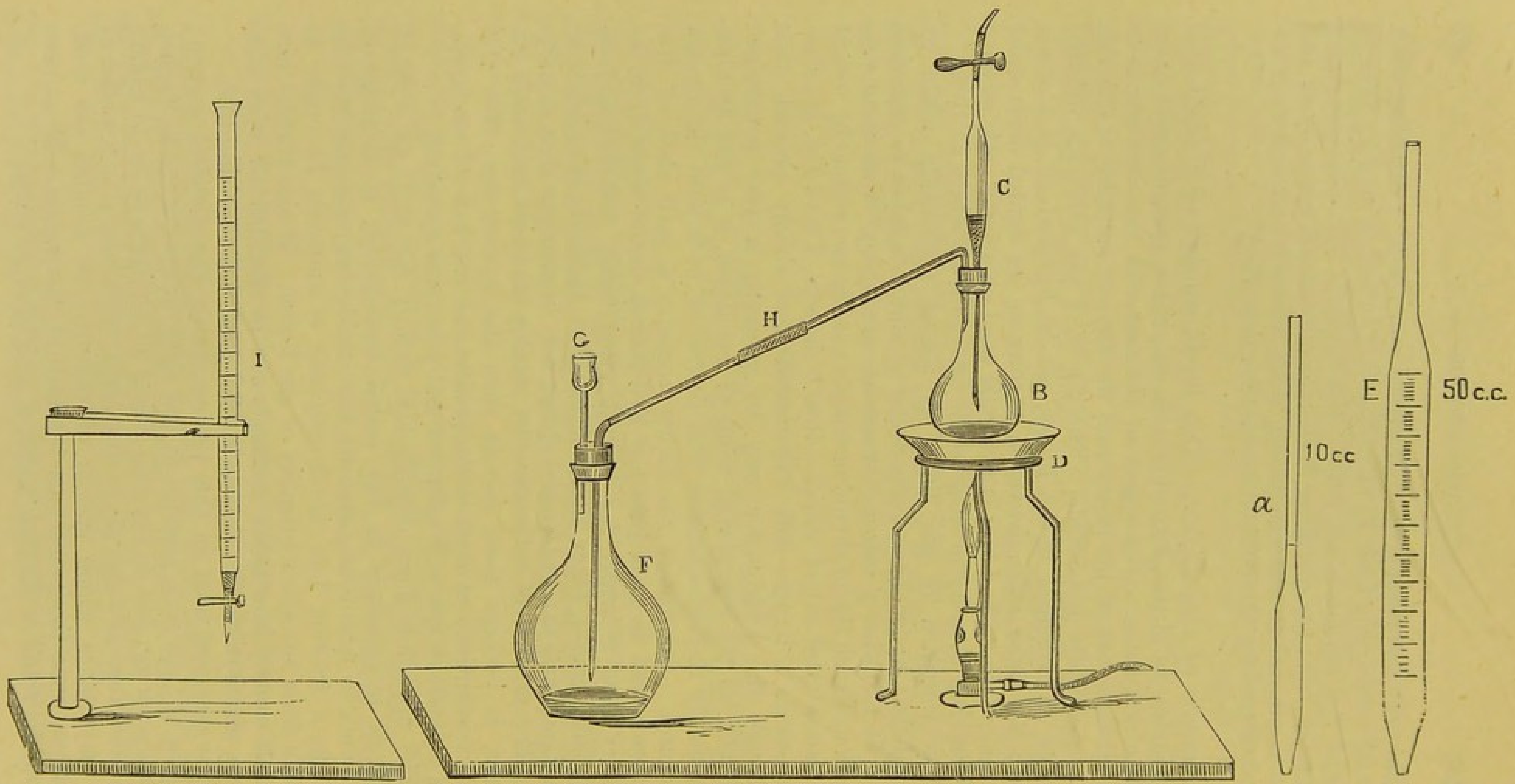

Fig. 21. Experience has shown, that it is preferable to have a small bulb blown in the tube H above the cork in flask B, to prevent carrying over into F any traces of fixed alkali sprayed into the tube.

*a* is a small pipette, holding 10 cubic centimeters to the mark in neck: this is the invariable quantity of liquor used for the analysis, whatever the strength may be. This measure is filled to the mark by suction and transferred, without spilling a drop, to flask B—the fittings being previously removed—the tube C is then filled in the same manner, with strong caustic soda solution from a clean cup or other vessel, in order to do which, the clip at the top must be opened; the cork is then replaced, and the flask B is then securely imbedded in perfectly dry sand, in the sand-bath D. The graduated pipette E is then filled in the same manner to the O mark, with standard acid, and 20, 30, 40, or 50 c.c. (according to the estimated strength of the liquor) allowed to flow into the flask F, through the cup G, which is filled with glass wool, or fibrous asbestos. The wool should be completely wetted with the acid, so that any vapours of ammonia which may escape the acid in the flask shall become absorbed by the acid. The quantity of standard acid to be used is regulated by the approximately known strength of the liquor, which of course can be told by Twaddle's hydrometer: thus, for a liquor of 3° Twaddle=6-oz. liquor, 20 c.c.—8-oz., 25 c.c.—10-oz, 30 c.c. of acid will be sufficient—but there must always be an excess. The required quantity can always be approximately known, since every 10 c.c. of acid represents 1 per cent. of ammonia. The standard acid having been carefully measured through the glass wool, the apparatus is fitted together at H by the elastic tube, and the india-rubber stoppers securely inserted in both flasks; this being done, the lamp is lighted under the sand-bath, and at the same time the spring clip on C is pressed, so as to allow about two-thirds of the caustic soda to flow into B; the rest will gradually empty itself during the boiling. The heat is continued to boiling, and allowed to go on till the greater bulk of the liquid in B is boiled away into F. A quarter of an hour is generally sufficient for this purpose, but if the boiling is continued till the liquid in B just covers the bottom of the flask, all the ammonia will have gone over to F; during the whole operation the distilling tube must never dip into the acid in F. In order to get rid of the last traces of ammonia vapour out of B, the lamp is removed, and the mouth being applied to the tube over the spring clip, the latter is opened, and a good blast of air immediately blown through. The apparatus may then be detached at H; distilled or good boiled drinking water is then poured repeatedly through G in small quantities, till all traces of acid are removed; and some water is also poured down the distilling tube, so as to wash all traces of ammonia which may be hanging about into flask F. This latter now contains all the ammonia out of the sample of liquor, with an excess of acid, and it is necessary now to find out the quantity of acid in excess. This is done by means of the burette I, and the standard solution of ammonia. The standard solution of ammonia is of exactly the same strength as the standard acid. In order to find out how much of the standard acid has been neutralized by the ammonia in the liquor distilled, the burette I is filled to O with standard ammonia, and two or three drops of methyl orange being added to the contents of flask F, the ammonia is slowly dropped into it from the burette, with constant shaking, until the indicator changes colour (litmus or any other indicator, except phenolphthalein, may be used). The number of c.c. of ammonia so used, deducted from the number of c.c. of standard acid used, will show the number neutralized by the ammonia in the liquor distilled; therefore, if the number of c.c. of ammonia used to destroy the pink colour be deducted from the number of c.c. of standard acid originally used, it will show the number of c.c. of standard acid neutralized by the ammonia, which has been distilled out of the liquor, and the strength of the solutions is so arranged that this is shown without any calculation. The following examples will suffice to show this:—Suppose that a liquor is to be examined which marks 5° Twaddle, equal to 10-ounce liquor; 10 c.c. of it is distilled into 30 c.c.

of the standard acid, and it has afterwards required 6 c.c. of standard ammonia to neutralize it; this leaves 24 c.c. as the volume of acid saturated by the distilled ammonia, and this represents 2·4 per cent.; and on referring to the table it is found that this number corresponds to a trifle more than 11 ounces, the actual figures being 2·384 per cent. for 11-ounce strength.

The strength of the standard ammonia and acid solutions is so arranged, that when 10 c.c. of liquor is distilled, every 10 c.c. of acid solution represents 1 per cent. of ammonia in the liquor. In like manner 13 c.c. of acid will represent 1·3 per cent. of ammonia corresponding to 6-ounce liquor.

The burette is divided into tenths of a cubic centimeter, and those who are familiar with decimal calculations can work out the results to the utmost point of accuracy; the calculation being, that every 1 per cent. of ammonia requires 4·61 ounces of concentrated oil of vitriol (sp. gr. 1·845) per gallon, to convert it into sulphate: thus, suppose that 10 c.c. of any given liquor have been distilled, and the quantity of acid required amounts to 18·6 c.c., this is 1·86 per cent., and the ounce strength is shown in ounces and decimal parts as follows:—

$$\begin{array}{rl} 4{\cdot}61 & \\ 1{\cdot}86 & \\ \hline 2766 & \\ 3688\phantom{0} & \\ 461\phantom{00} & \\ \hline 8{\cdot}5746 & \text{ounces of oil of vitriol.} \\ \hline \end{array}$$

The liquor is therefore a trifle over 8½-ounce strength.

*Spent Liquors.*—It is frequently necessary to ascertain the percentage of ammonia in spent liquors, to see if the workmen have extracted all the available ammonia. In this case the same measure, 10 c.c. of the spent liquor, is taken, and the operation conducted precisely as in the case of a gas liquor.

*Example:* 10 c.c. of a spent liquor were distilled, and found to neutralize 3 c.c. of acid; this represents three-tenths of a per-cent. equal to 1 oz., and four-tenths of an ounce, or nearly 1¼ oz. Such a liquor is too valuable to throw away, and should be worked longer to extract more ammonia.

*Analysis of Sulphate of Ammonia or Sal Ammoniac:* An average sample of the salt being drawn, ten grams are weighed, transferred without loss to a beaker or flask having a 100 c.c. mark upon it, distilled or boiled drinking water poured on it, and well stirred till dissolved, and finally water added exactly to the mark. The 10 c.c. measure is then filled with the solution, and emptied into the distilling flask B; 30 c.c. of standard acid are put into flask F and the distillation carried on precisely as in the case of a gas liquor. The number of c.c. of standard acid required shows directly the percentage of ammonia; thus, if 24·6 c.c. are used in the case of sulphate, it contains 24·6 per cent. of ammonia.

The liquors when tested must be measured at ordinary temperatures, say as near to 60° F. as possible. The standard solutions must be kept closely stoppered and in a cool place.

The following table is given to avoid calculations: of course, it will be understood that the figures given are on the assumption that the whole of the ammonia contained in the liquor is extracted in the manufacture as closely as it is in the experiment. With the most perfect arrangement of plant, however, this does not as a rule take place; but it ought to be very near the mark with proper apparatus, and care on the part of workmen.

| Approximate measure of Standard Acid in c.c. and tenths. | Percentage of Ammonia $NH^3$ | Ounce strength per gallon. | Weight of Sulphuric Acid in pounds and decimal parts required for each gallon of Liquor. | | | Yield of Sulphate per gallon in lbs. and decimal parts. |
|---|---|---|---|---|---|---|
| | | | C. O. V. 169° Tw. | B. O. V. 144° Tw. | Chamber Acid 120° Tw. | |
| 2·2 | ·2168 | 1 | ·0625 | ·0781 | ·0893 | ·0841 |
| 4·3 | ·4336 | 2 | ·1250 | ·1562 | ·1786 | ·1682 |
| 6·5 | ·6504 | 3 | ·1875 | ·2343 | ·2679 | ·2523 |
| 8·7 | ·8672 | 4 | ·2500 | ·3124 | ·3572 | ·3364 |
| 10·1 | 1·0840 | 5 | ·3125 | ·3905 | ·4465 | ·4205 |
| 13·0 | 1·3000 | 6 | ·3750 | ·4686 | ·5358 | ·5046 |
| 15·2 | 1·5176 | 7 | ·4375 | ·5467 | ·6251 | ·5887 |
| 17·3 | 1·7344 | 8 | ·5000 | ·6248 | ·7144 | ·6728 |
| 19·5 | 1·9512 | 9 | ·5625 | ·7029 | ·8037 | ·7569 |
| 21·7 | 2·1680 | 10 | ·6250 | ·7810 | ·8930 | ·8410 |
| 23·8 | 2·3840 | 11 | ·6875 | ·8591 | ·9823 | ·9251 |
| 26·0 | 2·6016 | 12 | ·7500 | ·9372 | 1·0716 | 1·0092 |
| 28·2 | 2·8184 | 13 | ·8125 | 1·0153 | 1·1609 | 1·0933 |
| 30·4 | 3·0350 | 14 | ·8750 | 1·0934 | 1·2502 | 1·1774 |
| 32·5 | 3·2520 | 15 | ·9375 | 1·1715 | 1·3395 | 1·2615 |
| 34·7 | 3·4688 | 16 | 1·0000 | 1·2496 | 1·4288 | 1·3456 |
| 36·9 | 3·6856 | 17 | 1·0625 | 1·3277 | 1·5181 | 1·4297 |
| 39·0 | 3·9024 | 18 | 1·1250 | 1·4058 | 1·6074 | 1·5138 |
| 41·2 | 4·1192 | 19 | 1·1875 | 1·4839 | 1·6967 | 1·5979 |
| 43·3 | 4·3360 | 20 | 1·2500 | 1·5620 | 1·7860 | 1·6820 |

The weight of sulphuric acid being given in decimals renders it very easy to arrive at the weight necessary for every thousand gallons of liquor, by simply moving the decimal point; thus, 8-oz. liquor would require 500 lbs. of concentrated oil of vitriol, 625 lbs. of brown oil of vitriol, or 714½ lbs. chamber acid for every 1000 gallons, and should yield in all cases 672·8 (say 673) lbs. of sulphate.

### 4. Combined Nitrogen in Organic Substances.

This process consists in heating the dried substance in a combustion tube with soda lime, by which the nitrogen is converted into ammonia; and this latter being led into a measured volume of normal acid contained in a suitable bulb apparatus, combines with its equivalent quantity; the solution is then titrated residually with standard alkali for the excess of acid, and thus the quantity of ammonia found.

As the combustion tube with its arrangements for organic analysis is well known, and described in any of the standard books on general analysis, it is not necessary to give a description here.

Instead of leading the ammonia through normal acid, hydrochloric acid of unknown strength may be used, the liquid brought into the distilling apparatus, and the ammonic chloride estimated by the process described in § 18.1.

When it is necessary to estimate very minute portions of ammonia, it may be brought into the form of chloride, and estimated by decinormal silver solution (§ 38); or in many cases preferably by Nessler's test, described in the section on Water Analysis.

### 5. Kjeldahl's Method.

This has met with considerable acceptance in lieu of the combustion method, on account of its easy management and accurate results. Moreover, the ammonia is obtained free from organic matters or colour. It was first described by the author (*Z. a. C.* xxii. 366), and has since been commented upon by many operators, among whom are Warington (*C. N.* lii. 162), Pfeiffer and Lehmann (*Z. a. C.* xxiv. 388), and Märcker (*Z. a. C.* xxiii. 553).

The process consists in heating the organic substance in a small flask, with concentrated sulphuric acid, at a temperature somewhat near its boiling point, and when the oxidation is nearly completed, adding finely powdered permanganate of potash in small quantities till a green colour remains constant: the whole of the nitrogen is thus converted into ammonia. The flask is then cooled, diluted with water somewhat, excess of caustic soda added, the ammonia distilled off into standard acid, and the amount found by titration in the usual way.

Some practical difficulties occur in the process: for instance, the final distillation with concentrated alkali gives rise to bumping, with a tendency to spray the liquid into the tube which leads into the acid. To overcome this, it is recommended to put some pieces of metallic zinc into the flask, which, by the generation of hydrogen gas, facilitate the operation. Experience has however shown that though this is the case, there is a greater chance of the distillate being contaminated with traces of alkali. This is especially so if a large excess of alkali with much zinc is used. Therefore it is proper to use only a moderate excess of alkali, and not much zinc.

Another difficulty is, that if nitrates are present in the compound analyzed, their reduction to ammonia is not certain nor regular, and unless this difficulty be overcome the value of the process is limited.

Warington has investigated this contingency, and finds that in order to get rid of them before the treatment with sulphuric acid, the material is best digested with ferrous sulphate and strong hydrochloric acid with heat, finally carried to dryness; the sulphuric acid is then added, and the process carried out as recommended by Kjeldahl. The nitrates are separately estimated by some other method.

*The Analysis:* From 0·1 to 1 gm. of the dry powdered substance, more or less according to its nature, is put into a long-necked boiling flask holding about 100—120 c.c., placed on wire gauze over a small naked Bunsen burner or spirit lamp, or a sand-bath may be used. The acid to be used for the destruction of the organic material is best made by mixing together about 200 c c. of strongest oil of vitriol, 50 c c. of Nordhausen vitriol, and 2 gm. of solid phosphoric acid in sticks: all these must of course be free from ammonia. 10 or 20 c.c. of this mixture of acids is to be poured over the substance, according to its nature and quantity, and the heat applied at once to such a degree as to be just below actual boiling. With prolonged heating the organic matter is gradually destroyed (this end being much aided by the addition of the sulphuric and phosphoric anhydrides), and the liquid becomes clear and quiet.* The complete oxidation and conversion into ammonia is now to be obtained by adding to the hot liquid small portions of powdered potassic permanganate. A good method of doing it is to sift it in from a glass tube, over the end of which a piece of wire gauze is fastened; a jerk of the tube thus projects a pinch into the liquid. A violent commotion takes place with every addition, but no fear of $NH^3$ being lost. When the mixture becomes permanently greenish the operation is ended, but a moderate heat is continued for a few minutes. The flask is now cooled, some water added, and the contents washed out into the distilling flask with as little water as possible. The distilling flask should hold about 700 c.c., with a caoutchouc stopper, through which passes a tube having two good-sized bulbs blown in it above the stopper: these will arrest and carry back any spray of soda from the liquid. Some operators use a wide piece of tube fitted by caoutchouc stoppers to the upright part of the delivery tube, filling it with glass beads, or with a platinum cone, to arrest spray. My experience, however, shows that two good bulbs suffice, and give far less trouble or chance of loss from leakage. Connection with a condenser is made in the usual way,† the delivery end of the condenser tube is either drawn out to a small bore, or a piece of glass tube connected therewith by rubber led into a flask containing a measured excess of standard acid there is no necessity for dipping it into the acid, and the flask may remain uncorked. The caustic solution may be either soda or potash, sp. gr. about 1·3, and should not be too much diluted by the wash water used for

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* Wilfarth (*Chem. Centrbl.* 1885, 17—113) has made numerous experiments on this process, and finds that the period of digestion may be much curtailed by the use of some metallic oxide, and recommends the substance to be heated with 20 c.c. of acid mixture and 0·7 gm. of mercuric oxide until decomposition is complete. After cooling it is diluted with water and boiled with a solution of caustic potash, to which some solution of potassic sulphide is added, together with a small portion of metallic zinc. Caustic potash is said to be less liable to bumping than soda. Some operators use no zinc, trusting to careful regulation of the heat; others obviate the violent action of the permanganate by using a mixture previously made of powdered permanganate and concentrated sulphuric acid.

† Since the above was written, I have had experiments made in my laboratory to ascertain whether the condenser might be dispensed with, and I find that by using an enlarged form of the apparatus Fig. 20, and placing the receiving flask in cold water, perfectly accurate results may be obtained. It is essential that two large bulbs (about one inch diameter) be blown on the distilling tube before it is bent into the receiving flask, and the tube containing the broken glass wetted with standard acid should be of good size.

the material analyzed. The alkali must not contain nitrates or nitrites, otherwise, when boiled with zinc, ammonia will be produced. As this is a common impurity in commercial caustic alkalies, it is safer in all cases to boil the solution openly with zinc, and allow to cool before use.

The titration of the distillate is made in the usual way with methyl orange or some other indicator other than phenolphthalein. Kjeldahl prefers to titrate a measured small portion of the distillate for excess of acid by the iodine and starch reaction described in § 19.

This method of analysis and titration has given me excellent results as compared with the combustion method. It is largely used at various State Agricultural Laboratories in Germany. By special arrangement of apparatus, several analyses may be kept going at the same time, needing no attention either during the digestion with acid or the subsequent distillation.

## ACIDIMETRY OR THE TITRATION OF ACIDS.

§ 19. This operation is simply the reverse of all that has been said of alkalies, and depends upon the same principles as have been explained in alkalimetry.

With free liquid acids, such as hydrochloric, sulphuric, or nitric, the strength is generally taken by means of the hydrometer or specific-gravity bottle, and the amount of real acid in the sample ascertained by reference to the tables constructed by Otto, Bineau, or Ure. The specific gravity may very easily be taken with the pipette, as recommended with ammonia, and of course the real acid may be quickly estimated by normal caustic alkali and an appropriate indicator.

In the case of titrating concentrated acids of any kind it is preferable in all cases to weigh accurately a small quantity, dilute to a definite volume, and take an aliquot portion for the analysis.

### Delicate End-reaction in Acidimetry.

If an alkaline iodate or bromate be added to a solution of an alkaline iodide in the presence of a mineral acid, iodine is set free and remains dissolved in the excess of alkaline iodide, giving the solution the well-known colour of iodine. This reaction has been long observed, and is capable of being used with excellent effect as an indicator for the delicate titration of acids, and therefore of alkalies, by the residual method. Kjeldahl, for instance, uses it in his ammonia process, where the distillate contains necessarily an excess of standard acid. The reaction is definite in character, and may be used in various ways in volumetric processes. For instance, potassic bromate liberates iodine in exact proportion to its contained oxygen in the presence of excess of dilute mineral acid, and the iodine so liberated may be accurately titrated with sodic thiosulphate.

In acidimetry, however, the method is simply used for its exceeding delicacy as an end-reaction, one drop of $\frac{N}{100}$ sulphuric, nitric, or hydrochloric acid being quite sufficient to cause a deep blue colour in the presence of starch liquor.

The adjustment of the standard liquids is made as follows :—2 or 3 c.c. of $\frac{N}{10}$ acid is run into a flask, diluted somewhat with water, and a crystal or two of potassic iodide thrown in ; 1 or 2 c.c. of a 5 per cent. solution of potassic iodate are then added, which at once produces a brown colour, due to free iodine. A solution of sodic thiosulphate is added from a burette, with constant shaking, until the colour is nearly discharged ; a few drops of freshly prepared starch liquor are now poured in, and the blue colour removed by the very cautious addition of thiosulphate. The quantity of thiosulphate used represents the comparative strengths of it and the standard acid, and is used as the basis of calculation in other titrations. The first discharge of the blue colour must be taken in all cases as the correct ending, because on standing a few minutes the blue colour re-occurs, due to some obscure reaction from the thiosulphate. This has been probably regarded as one of the drawbacks of the process, and another is the instability of the thiosulphate solution ; but these by no means invalidate its accuracy, and it moreover possesses the advantage of being applicable to excessively dilute solutions, and may be used by artificial light. The organic acids cannot be estimated by this method, the action not being regular. Neutral alkaline and alkaline earthy salts have no interference, but salts of the organic acids and borates must be absent.

## ACETIC ACID.

$C^2H^4O^2=60$.

§ 20. In consequence of the anomaly existing between the sp. gr. of strong acetic acid and its actual strength, the hydrometer is not reliable, but the volumetric estimation is now rendered extremely accurate by using phenolphthalein as indicator, acetates of the alkalies and alkaline earths having a perfectly neutral behaviour to this indicator. Even coloured vinegars may be titrated when highly diluted. Where, however, the colour is too much for this method to succeed, recourse must be had to litmus paper, upon which streaks of the liquid should be made from time to time during the titration with a glass rod.

Several processes have at various times been suggested for the accurate and ready estimation of acetic acid, among which is that of Greville Williams, by means of a standard solution of lime syrup. The results obtained were very satisfactory.

C. Mohr's process consists in adding to a known quantity of the acid a known excessive quantity of baric or calcic carbonate in fine powder. Pure calcic carbonate is preferable, as it dissolves more readily than baric salt. When the decomposition is as nearly as possible complete in the cold, the mixture must be heated to expel the $CO^2$, and to complete the saturation; the residual carbonate is then brought upon a filter, washed with boiling water, and titrated with excess of normal acid and back with alkali.

This process is applicable in all cases, and however dark the colour may be. In testing the impure brown pyroligneous acid it is especially serviceable.

Pettenkofer titrates acetic acid or vinegar with a known excess of baryta water; and estimates the excess of the latter with $\frac{N}{10}$ nitric or oxalic acid by the help of turmeric paper.

The titration of acetic acid or vinegar may also be performed by the ammonio-cupric solution described in § 14.10.

**1. Free Mineral Acids in Vinegar.**—Hehner has devised an excellent method for this purpose (*Analyst* i. 105).

Acetates of the alkalies are always present in commercial vinegar; and when such vinegar is evaporated to dryness, and the ash ignited, the alkalies are converted into carbonates having a distinct alkaline reaction on litmus; if, however, the ash has a neutral or acid reaction, some free mineral acid must have been present. The alkalinity of the ash is diminished in exact proportion to the amount of mineral acid added to the vinegar as an adulteration. Hence the following process :—

50 c.c. of the vinegar are mixed with 25 c.c. of $\frac{N}{10}$ soda or potash, evaporated to dryness, and ignited at a low red heat to convert the acetates into carbonates; when cooled, 25 c.c. of $\frac{N}{10}$ acid are added; the mixture heated to expel $CO^2$, and filtered; after washing the residue, the filtrate and washings are exactly titrated with $\frac{N}{10}$ alkali; the volume so used equals the amount of mineral acid present in the 50 c.c. of vinegar.

1 c.c. $\frac{N}{10}$ alkali = 0·0049 gm. $H^2SO^4$ or 0·003637 gm. HCl.

If the vinegar contains more than 0·2 per cent. of mineral acid, more than 25 c.c. of $\frac{N}{10}$ alkali must be used to the 50 c.c. vinegar before evaporating and igniting.

**2. Acetates of the Alkalies and Earths.**—These salts are converted by ignition into carbonates, and can be then residually titrated with normal acid; no other organic acids must be present, nor must nitrates, or similar compounds decomposable by heat. 1 c.c. normal acid = 0·06 gm. acetic acid.

**3. Metallic Acetates.**—Neutral solutions of lead and iron acetates may be precipitated by an excess of normal sodic or potassic carbonate, the precipitate well boiled, filtered, and washed with hot water, the filtrate and washings made up to a definite volume, and an aliquot portion titrated with N or $\frac{N}{10}$ acid; the difference between the quantity so used and calculated for the original volume of alkali will represent the acetic acid.

If such solutions contain free acetic or mineral acids, they must be exactly neutralized previous to treatment.

If other salts than acetates are present, the process must be modified as follows :—

Precipitate with alkaline carbonate in excess, exactly neutralize with hydrochloric acid, evaporate the whole or part to dryness, ignite to convert the acetates into carbonates, then titrate residually with normal acid. Any other organic acid than acetic will, of course, record itself in terms of acetic acid.

4. **Commercial Acetate of Lime.**—The methods just described are often valueless in the case of this substance, owing to tarry matters, which readily produce an excess of carbonates.

Fresenius (*Z. a. C.* xiii. 153) adopts the following process for tolerably pure samples:—5 gm. are weighed and transferred to a 250 c.c. flask, dissolved in about 150 c.c. of water, and 70 c.c. of normal oxalic acid added; the flask is then well shaken, and filled to the mark, 2 c.c. of water are added to allow for the volume occupied by the precipitate, the whole is again well shaken, and left to settle. The solution is then filtered through a dry filter into a dry flask : the volume so filtered must exceed 200 c.c.

100 c.c. are first titrated with normal alkali and litmus; or, if highly coloured, by help of litmus or turmeric paper; the volume used multiplied by 2·5 will give the volume for 5 gm.

Another 100 c.c. are precipitated with solution of pure calcic acetate in slight excess, warmed gently, the precipitate allowed to settle somewhat, then filtered, well washed, dried, and strongly ignited, in order to convert the oxalate into calcic carbonate or oxide, or a mixture of both. The residue so obtained is then decomposed with excess of normal acid, and titrated residually with normal alkali. By deducting the volume of acid used to neutralize the precipitate from that of the alkali used in the first 100 c.c., and multiplying by 2·5, is obtained the volume of alkali expressing the weight of acetic acid in the 5 gm. of acetate.

In the case of very impure and highly coloured samples of acetate, it is only possible to estimate the acetic acid by repeated distillations with phosphoric acid and water to incipient dryness, and then titrating the acid direct with $\frac{N}{10}$ alkali, each c.c. of which represents 0·006 gm. acetic acid.

The distillation is best arranged as suggested by Stillwell and Gladding, or later by Harcourt Phillips (*C. N.* liii. 181).

A 100 to 120 c.c. retort, the tubulure of which carries a small funnel fitted in with a caoutchouc stopper, and the neck of the funnel stopped tightly with a glass rod shod with elastic tube, is supported upon a stand in such a way that its neck inclines upwards at about forty-five degrees: the end of the neck is drawn out, and bent so as to fit into the condenser by help of an elastic tube. The greater part of the retort neck is coated with flannel, so as to prevent too much condensation.

1 gm. of the sample being placed in the retort, 10 c.c. of a 40 per cent. solution of $P^2O^5$ is added, together with as much water as will make about 50 c.c. A small naked flame is used, and if carefully manipulated, the distillation may be carried on to near dryness without endangering the retort. After the first operation the retort is allowed to cool somewhat, then 50 c.c. of hot water added through the funnel, another distillation made as before, and the same repeated a third time, which will suffice to carry over all the acetic acid. The distillate is then titrated with alkali and phenolphthalein.

By this arrangement the frothing and spirting is of no consequence, and the whole process can be completed in less than an hour. The results are excellent for technical purposes.

Weber (*Z. a. C.* xxiv. 614) has devised a ready and fairly accurate method of estimating the real acetic acid in samples of acetate of lime, based on the fact that acetate of silver is insoluble in alcohol.

*The Analysis:* 10 gm. of the sample in powder is placed in a 250 c.c. flask, a little water added, and heated till all soluble matters are extracted, cooled, and made up to the measure: 25 c.c. are then filtered through a dry filter, put into a beaker, 50 c.c. of absolute alcohol added, and the acetic acid at once precipitated with an alcoholic solution of silver nitrate. The silver acetate, together with any chloride, sulphate, etc., separates free from colour. The precipitate is brought on a filter, well washed with 60 per cent. alcohol till the free silver is removed; precipitate is then dissolved in weak nitric acid, and titrated with $\frac{N}{10}$ salt solution. Each c.c. represents 0·006 gm. acetic acid.

Several trials made in comparison with the distillation method with phosphoric acid gave practically the same results.

## CITRIC ACID.

$C^6O^7H^8 + H^2O = 210.$

§ 21. This acid in the free state may readily be titrated with pure normal soda and phenolphthalein. 1 c.c. normal alkali =0·07 gm. crystallized citric acid.

**1. Citrates of the Alkalies and Earths.**—These citrates may be treated with neutral solution of lead nitrate or acetate, in the absence of other acids precipitable by lead. The lead citrate is washed with a mixture of equal parts alcohol and water, the precipitate suspended in water, and $H^2S$ passed into it till all the lead is converted into sulphide; the clear liquid is then boiled to remove $H^2S$, and titrated with normal alkali.

**2. Fruit Juices, etc.**—If tartaric is present, together with free citric acid, the former is first separated as potassic bitartrate, which can very well be done in the presence of citric acid, as follows:—

A cold saturated proof spirit solution of potassic acetate is added to a somewhat strong solution of the mixed acids in proof spirit, in sufficient quantity to separate all the tartaric acid as bitartrate, which after stirring well is allowed to stand some hours; the precipitate is then transferred to a filter, and first washed with proof spirit, then rinsed off the filter with a cold saturated solution of potassic bitartrate, and allowed to stand some hours, with occasional stirring; this treatment removes any adhering citrate. The bitartrate is again brought on to a filter, washed once with proof spirit, then dissolved in hot water, and titrated with normal acid, 1 c.c. of which= 0·075 gm. tartaric acid.

The first filtrate may be titrated for the free citric acid present after evaporating the bulk of the alcohol.

3. **Lime and Lemon Juices.**—The citric acid contained in lemon, lime, and similar juices, may be very fairly estimated by Warington's method (*J. C. S.* 1875, 934).

15 or 20 c.c. of ordinary juice, or 3—4 c.c. of concentrated juice, are first exactly neutralized with pure normal soda, made up, if necessary, to about 50 c.c., heated to boiling on a salt bath, and so much solution of calcic chloride added as to be slightly in excess of the organic acids present. The mixture is kept at the boiling point for about half-an-hour, the precipitate collected on a filter and washed with hot water, filtrate and washings concentrated to about 15 c.c. and a drop of ammonia added; this will produce a further precipitate, which is collected separately on a very small filter by help of the previous filtrate, then washed with a small quantity of hot water. Both filters, with their precipitates, are then dried, ignited at a low red heat, and the ash titrated with normal or $\frac{N}{10}$ alkali, each c.c. of which represents respectively 0·07 or 0·007 gm. $H^3 \overline{Ci} + H^2O$.

## OXALIC ACID.

$C^2H^2O^4 2H^2O = 126.$

§ 22. The free acid can be accurately titrated with normal alkali and phenolphthalein.

In combination with alkalies, the acid can be precipitated with calcic chloride as calcic oxalate, where no other matters occur precipitable by calcium; if acetic acid is present in slight excess it is of no consequence, as it prevents the precipitation of small quantities of sulphates. The precipitate is well washed, dried, ignited, and titrated with normal acid, 1 c.c. of which $= 0·063$ gm. $\overline{O}$.

Acid oxalates are titrated direct for the amount of free acid. The reaction continues to be acid until alkali is added in such proportion that 1 molecule acid = 2 atoms alkali metal.

The combined acid may be found by igniting the salt, and titrating the residual alkaline carbonate as above.

The estimation of oxalic acid in various combinations by permanganate is fully explained in §§ 30.2 (*c*) and 48.

## PHOSPHORIC ACID.

$P^2O^5 = 142.$

§ 23. Free tribasic phosphoric acid cannot be titrated directly with normal alkali in the same manner as most free acids, owing to the fact, that when an alkaline base (soda, for instance) is added to the acid, a combination occurs in which at one and the same time red litmus paper is turned blue and blue red. This fact has been repeatedly noticed in the case of some specimens of urine, also in milk. In order, therefore, to estimate phosphoric acid, or alkaline phosphates, alkalimetrically, it is necessary to prevent the formation of soluble phosphate of alkali, and to bring the acid into a definite compound with an alkaline earth. Such a method gives tolerably good results when carried out as follows:—

The solution of free acid, or its acid or neutral combination with alkali in a somewhat dilute state, is placed in a flask, and a known volume of normal alkali in excess added, in order to convert the whole of the acid into a basic salt; a drop or two of rosolic acid is added, then sufficient neutral baric chloride poured in to combine with all the phosphoric acid, the mixture is heated nearly to boiling; and, while hot, the excess of alkali is titrated with normal acid. The suspended baric phosphate, together with the liquid, possesses a rose red colour until the last drop or two of acid, after continuous heating and agitation, gives a permanent white or slightly yellowish, milky appearance, when the process is ended.

The volume of normal alkali, less the volume of acid, represents the amount of alkali required to convert the phosphoric acid into a chemically neutral salt, *e.g.* trisodic phosphate. 1 c.c. alkali = 0·02366 gm. $P^2O^5$. In dealing with small quantities of material, it is better to use $\frac{N}{5}$ or $\frac{N}{10}$ standard solutions.

Thompson has shown in his researches on the indicators, that phosphoric acid, either in the free state, or in combination with soda or potash, may with very fair accuracy be estimated by the help of methyl orange and phenolphthalein. If, for instance, normal potash be added to a solution of phosphoric acid until the pink colour of methyl orange is discharged, $KH^2PO^4$ is formed ($112\ KHO = 142\ P^2O^5$). If now phenolphthalein is added, and the addition of potash continued until a red colour occurs, $K^2HPO^4$ is formed. (Again $112\ KHO = 142\ P^2O^5$.) On adding standard hydrochloric or sulphuric acid, until the pink colour of methyl orange reappears, the titration with standard potash may be repeated.

Many attempts have been made to utilize these reactions for the accurate estimation of $P^2O^5$ in manures, etc., but, so far as my own experience goes, without adequate success.

**Titration as Ammonio-magnesian Phosphate.**—Stolba (*Chem. Cent.* 1866, 727, 728) adopts an alkalimetric method, which depends upon the fact, that one molecule of the double salt requires two molecules of a mineral acid for saturation.

The precipitation is made with magnesia mixture, well washed with ammonia, and the latter completely removed by washing with alcohol of 50 or 60 per cent. The precipitate is then dissolved in a measured excess of $\frac{N}{10}$ acid, methyl orange added, and the amount of acid required found by titration with $\frac{N}{10}$ alkali. Care must be taken that all free ammonia is removed from the filter and precipitate, and that the whole of the double salt is decomposed by the acid before titration, which may always be insured by using a rather large excess and warming. The titration is carried on cold.

This method has given me very good results in comparison with the gravimetric method. The same process is applicable to the estimation of arsenic acid, and also of magnesia.

1 c.c. of $\frac{N}{10}$ acid = 0·00355 gm. $P^2O^5$
„ „ = 0·00575 gm. $As^2O^3$
„ „ = 0·002 gm. MgO

The reaction in the case of phosphoric acid may be expressed as follows:—

$$Mg\,(NH^4)\,PO^4 + 2HCl = (NH^4)\,H^2PO^4 + MgCl^2.$$

## SULPHURIC ANHYDRIDE.

$SO^3 = 80.$

§ 24. NORDHAUSEN or fuming sulphuric acid consists of a mixture of $SO^3$ and $H^2SO^4$. When it is rich in $SO^3$ it occurs in a solid form, and being very hygroscopic cannot be weighed in the ordinary manner. Its strength is therefore best taken in the way recommended by Messel as follows:—A very thin bulb tube with capillary ends is inserted into a bottle of the melted acid. The ends are bent like the letter *f*, the bulb being in the middle. The bottle should be of such size, that one end of the tube projects out of its mouth. As soon as the bulb is filled, the upper capillary end is sealed, the tube lifted out, wiped, inverted, and the other end sealed; the tube is then carefully wiped with blotting paper till dry and clean, then weighed. A stoppered bottle, just large enough to allow the tube being placed loosely inside it, is then about one-third filled with water, the tube gently inserted, the stopper replaced, held firmly in by the hand, and a vigorous shake given so as to break the tube. A sudden vibration occurs from contact of the acid with the water, but no danger is incurred. A white cloud is seen on the sides of the bottle, which disappears on shaking for a few minutes. After the bottle is cooled the contents are emptied into a measuring flask. An aliquot portion is then taken out and titrated with $\frac{N}{10}$ iodine for $SO^2$, which is always present in small quantity: another portion is titrated with standard alkali and methyl orange for sulphuric acid.

## TARTARIC ACID.

$C^4H^6O^6 = 150.$

§ 25. THE free acid may be readily titrated with normal alkali and phenolphthalein.

1 c.c. alkali = 0·075 gm. tartaric acid.

The amount of tartaric acid existing in tartaric acid liquors is best estimated by precipitation as potassic bitartrate; the same is also the case with crude argols, lees, etc. Manufacturers are highly indebted to Warington and Grosjean for most exhaustive papers on this subject, to which reference should be made by all who desire to study the nature and analysis of all commercial compounds of citric and tartaric acids (Warington, *J. C. S.* 1875, 925—994; Grosjean, *J. C. S.* 1879, 341—356).

Without entering into the copious details and explanations given by these authorities, the methods may be summarized as follows:—

### 1. Commercial Tartrates.

In the case of good clean tartars, even though they may contain sulphates and carbonates, very accurate results may be obtained by indirect methods.

(*a*) The very finely powdered sample is first titrated with normal alkali, and thus the amount of tartaric acid existing as bitartrate is found; another portion of the sample is then calcined at a moderate heat, and the ash titrated. By deducting from the volume of acid so used the volume used for bitartrate, the amount of base corresponding to neutral tartrates is obtained.

(*b*) The whole of the tartaric acid is exactly neutralized with caustic soda, evaporated to dryness, calcined, and the ash titrated with normal acid; the total tartaric acid is then calculated from the volume of standard acid used; any other organic acid present will naturally be included in this amount. In the case of fairly pure tartars, etc., this probable error may be disregarded.

Warington's description of the first process is as follows:—

5 gm. of the finely powdered tartar are heated with a little water to dissolve any carbonates that may be present. If it is wished to guard against crystalline carbonates, 5 c.c. of standard HCl are added in the first instance, and the heating is conducted in a covered beaker. Standard alkali is next added to the extent of about three-fourths of the amount required by a good tartar of the kind examined, plus that equivalent to the acid used, and the whole is brought to boiling; when nearly cold, the titration is finished. From the amount of alkali consumed, minus that required by the HCl, the tartaric acid present as acid tartrate is calculated.

2 gm. of the powdered tartar are next weighed into a platinum crucible with a well-fitting lid; the crucible is placed over an argand burner; heat is first applied very gently to dry the tartar, and then more strongly till inflammable gas ceases to be evolved. The heat should not rise above very low redness. The black ash is next removed with water to a beaker. If the tartar is known to be a good one, 20 c.c. of standard $H^2SO^4$ are now run from a pipette into the beaker, a portion of the acid being used to rinse the crucible. The contents of the beaker are now brought to boiling, filtered, and the free acid determined with standard alkali. As the charcoal on the filter under some circumstances retains a little acid, even when well washed, it is advisable when the titration is completed to transfer the filter and its contents to the neutralized fluid, and add a further amount of alkali if necessary. From the neutralizing power of a gram of burnt tartar is subtracted the acidity of a gram of unburnt tartar, both expressed in c.c. of standard alkali, the difference in the neutralizing power of the bases existing as neutral tartrates, and is then calculated into tartaric acid on this assumption.*

If the tartar is of low quality, 5 c.c. of solution of hydrogen peroxide (1 volume = 10 volumes O) are added to the black ash and water, and immediately afterwards the standard acid; the rest of the analysis proceeds as already described; the small acidity usually belonging to the peroxide solution must, however, be known and allowed for in the calculation. By the use of hydrogen peroxide the sulphides formed during ignition are reconverted into sulphates, and the error of excess which their presence would occasion is avoided.

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* It is obvious that the neutralizing power of the ash of an acid tartrate is exactly the same as the acidity of the same tartrate before burning. In making the calculations, it must be remembered that the value of the alkali in tartaric acid is twice as great in the calculation made from the acidity of the unburnt tartar, as in the calculation of the acid existing as neutral tartrates.

The above method does not give the separate amounts of acid and neutral tartrates in the presence of carbonates, but it gives the correct amount of tartaric acid; it is also correct in cases where free tartaric acid exists, so long as the final results show that some acid existed as neutral salt. Whenever this method shows that the acidity of the original substance is greater than the neutralizing power of the ash, it will be necessary to use the method *b*, which is the only one capable of giving good results when the sample contains much free tartaric acid.

Instead of the alkalimetric estimation in both the above methods, equally good results may be got by a carbonic acid determination in the ash with Scheibler's apparatus (§ 26.6), or any of the usual methods.

### 2. Tartaric Acid Liquors.

Old factory liquors contain a great variety of substances gradually accumulated, from which the actual tartaric acid can only be separated as bitartrate by the following process:—

(*c*) A quantity of liquor containing 2—4 gm. of tartaric acid, and of 30—40 c.c. volume, is treated with a saturated solution of neutral potassic citrate, added drop by drop with constant stirring. If free sulphuric acid is present no precipitate is at first produced; but as soon as the acid is satisfied, the bitartrate begins to appear in streaks on the sides of the vessel. When this is seen, the remainder of the citrate is measured in to avoid an undue excess: 4 c.c. of a saturated solution of potassic citrate will be found sufficient to precipitate the maximum of 4 grams of tartaric acid supposed to be present. If the liquor contain a great deal of sulphuric acid, a fine precipitate of potassic sulphate will precede the formation of bitartrate, but is easily distinguished from it. With liquors rich in sulphuric acid, it is advisable to stir the mixture vigorously at intervals for half an hour, then proceed as in 3 *d*.

Grosjean modifies this process by precipitating the liquor with an excess of calcic carbonate, then boiling the mixture with excess of potassic oxalate. By this means the alumina, iron, phosphoric and sulphuric acids are thrown down with the calcic oxalate, and the precipitate allows of ready filtration. The separation as bitartrate then follows, as in *d*.

### 3. Very impure Lees and Argols.

Grosjean (*J. C. S.* 1879, 341) gives a succinct method for the treatment of these substances, based on Warington's original oxalate process, the principle of which is as follows:—

The finely ground sample (=about 2 gm. tartaric acid) is first moistened with a little water, heated to 100° C., then digested for 15 minutes or so with an excess of neutral potassic oxalate (the excess must not be less than 1·5 gm.), and nearly neutralized with potash. After repeated stirring, the mixture is transferred to a vacuum filter, and the residue washed; the liquid so obtained contains all the tartaric acid as neutral potassic tartrate; excess of citric acid is added, which precipitates the whole of the tartaric acid as bitartrate, and the amount is found by titration with standard alkali in the usual way.

One of the chief difficulties in treating low qualities of material is the filtration of the nearly neutral mixture above mentioned. Grosjean adopts the principle of Casamajor's filter (*C. N.* xxxii. 45), using an ordinary funnel with either platinum, lead, or pumice disc; but whether this, or Bunsen's, or other form of filter is used, the resulting filtrate and washings (which for 2 gm. tartaric acid should not much exceed 50 c.c.) are ready for the separation of the bitartrate in the following improved way:—

(*d*) To the 50 c.c. or so of cold solution 5 gm. of powdered potassic chloride is added, and stirred till dissolved: this renders the subsequent precipitation of bitartrate very complete. A 50-per-cent. solution of citric acid is then mixed with the liquid in such proportion, that for every 2 gm. of tartaric acid an equal, or slightly greater amount of citric acid is present. By continuously stirring, the whole of the bitartrate comes down in ten minutes (Grosjean); if the temperature is much above 16°, it is preferable to wait half an hour or so before filtering. This operation is best done on the vacuum filter, and the washing is made with a 5-per-cent. solution of potassic chloride, saturated at ordinary temperature with potassic bitartrate; if great accuracy is required, the exact acidity of the solution should be found by $\frac{N}{10}$ alkali, and the washing continued until the washings show no greater acidity, thus proving the absence of citric acid. Finally, the washed precipitate is gently pressed into a cake to free it from excess of liquid, transferred to a beaker with the filter, hot water added, and titrated with standard alkali.

The troublesome filtration can be avoided in many cases by taking 30—40 gm. of substance, and after decomposition by oxalate, and neutralizing with potash, making up the volume to 150 or 200 c.c., adding water in corresponding proportion to the bulk of the residue, then taking an aliquot portion for precipitation. A blank experiment made by Grosjean in this way, gave a volume of 3·75 c.c. for the residue in 10 gm. lees. Other things being equal, therefore, 30 or 40 gm. may respectively be made up to 161 and 215 c.c., then 50 c.c. taken for precipitation.

## CARBONIC ACID AND CARBONATES.

§ 26. All carbonates are decomposed by strong acids; the carbonic acid which is liberated splits up into water and carbonic anhydride ($CO^2$), which latter escapes in the gaseous form.

It will be readily seen from what has been said previously as to the estimation of the alkaline earths, that carbonic acid in combination can be estimated volumetrically with a very high degree of accuracy (see § 17).

The carbonic acid to be estimated may be brought into combination with either calcium or barium, these bases admitting of the firmest combination as neutral carbonates.

If the carbonic acid exist in a soluble form as an alkaline monocarbonate, the decomposition is effected by the addition of baric or calcic chloride as before directed; if as bicarbonate, or a compound between the two, ammonia must be added with either of the chlorides.

As solution of ammonia frequently contains carbonic acid, it must be removed by the aid of baric or calcic chloride, previous to use.

### 1. Carbonates Soluble in Water.

It is necessary to remember, that when calcic chloride is used as the precipitant in the cold, amorphous calcic carbonate is first formed; and as this compound is sensibly soluble in water, it is necessary to convert it into the crystalline form. In the absence of free ammonia this can be accomplished by boiling. When ammonia is present, the same end is obtained by allowing the mixture to stand for eight or ten hours in the cold, or by heating for an hour or two to 70—80° C. With barium the precipitation is regular.

Another fact is, that when ammonia is present, and the precipitation occurs at ordinary temperatures, ammonic carbamate is formed, and the baric or calcic carbonate is only partially precipitated. This is overcome by heating the mixture to near boiling for a couple of hours, and is best done by passing the neck of the flask through a retort ring, and immersing the flask in boiling water.

When caustic alkali is present in the substance to be examined, it is advisable to use barium as the precipitant; otherwise, for all volumetric estimations of $CO^2$ calcium is to be preferred, because the precipitate is much more quickly and perfectly washed than the barium compound.

*Example:* 1 gm. of pure anhydrous sodic carbonate was dissolved in water, precipitated while hot with baric chloride, the precipitate allowed to settle well, the clear liquid decanted through a moist filter, more hot water containing a few drops of ammonia poured over the precipitate, which was repeatedly done so that the bulk of the precipitate remained in the flask, being washed by decantation through the filter; when the washings showed no trace of chlorine, the filter was transferred to the flask containing the bulk of the precipitate, and 20 c.c. of normal nitric acid added, then titrated with normal alkali, of which 1·2 c.c. was required=18·8 c.c. of acid; this multiplied by 0·022, the coefficient for carbonic acid, gave 0·4136 gm. $CO^2$= 41·36 per cent., or multiplied by 0·053, the coefficient for sodic carbonate, gave 0·9964 gm. instead of 1 gm.

### 2. Carbonates Soluble in Acids.

It sometimes occurs that substances have to be examined for carbonic acid, which do not admit of being treated as above described; such, for instance, as the carbonates of the metallic oxides (white lead, calamine, etc.), carbonates of magnesia, iron, and copper, the estimation of carbonic acid in cements, mortar, and many other substances. In these cases the carbonic acid must be evolved from the combination by means of a stronger acid, and conducted into an absorption apparatus containing ammonia, then precipitated with calcic chloride, and titrated as before described.

The following form of apparatus (fig. 22) affords satisfactory results.

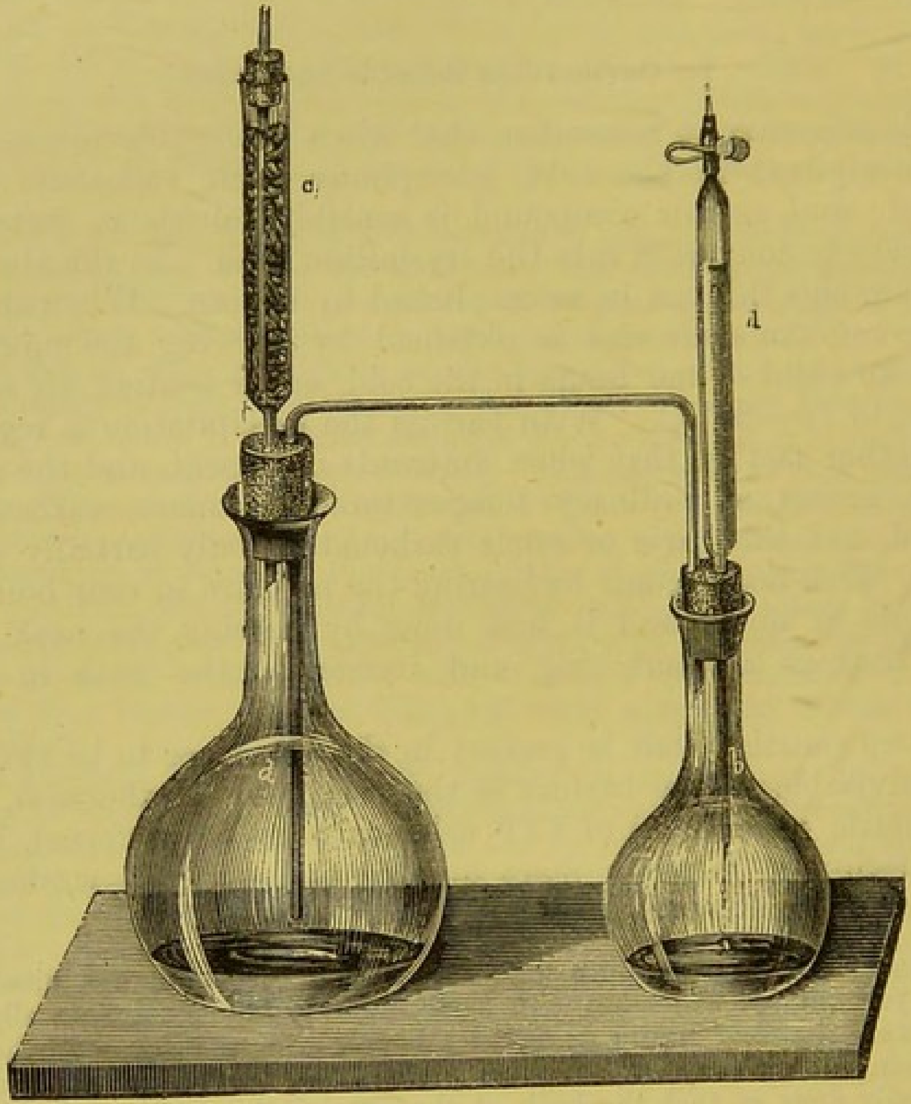

Fig. 22.

The weighed substance from which the carbonic acid is to be evolved is placed in *b* with a little water; and the tube *d* contains strong hydrochloric acid, and *c* broken glass wetted with ammonia free from carbonic acid. The flask *a* is about one-eighth filled with the same ammonia: the bent tube must not enter the liquid. When all is ready and the corks tight, warm the flask *a* gently so as to fill it with vapour of ammonia, then open the clip and allow the acid to flow circumspectly upon the material, which may be heated until all carbonic acid is apparently driven off; then by boiling and shaking the last traces can be evolved, and the operation ended. When cool, the apparatus may be opened, the end of the bent tube washed into *a*, and also a good quantity of boiled distilled water passed through *c*, so as to carry down any ammonic carbonate that may have formed. Then add solution of calcic chloride, boil, filter, and titrate the precipitate as before described.

During the filtration, and while ammonia is present, there is a great avidity for carbonic acid, therefore boiling water should be used for washing, and the funnel kept covered with a small glass plate.

In many instances $CO^2$ may be estimated by its equivalent in chlorine with $\frac{N}{10}$ silver and potassic chromate, as shown in § 38.

### 3. Carbonic Acid Gas in Waters, etc.

The carbonic acid existing in waters as neutral carbonates of the alkalies or alkaline earths may very elegantly and readily be titrated directly by $\frac{N}{10}$ acid (see § 17).

Well or spring water, and also mineral waters, containing free carbonic acid gas, can be examined by collecting measured quantities of them at their source, in bottles containing a mixture of calcic and ammonic chloride, afterwards heating the mixture in boiling water for one or two hours, and titrating the precipitate as before described.

Pettenkofer's method with caustic baryta or lime is decidedly preferable to any other. Lime water may be used instead of baryta with equally good results, but care must be taken that the precipitate is crystalline.

The principle of the method is that of removing all the carbonic acid from a solution, or from a water, by excess of baryta or lime water of a known strength; and, after absorption, finding the excess of baryta or lime by titration with weak standard acid.

The following is the best method to be pursued for ordinary drinking waters not containing large quantities of carbonic acid:—

100 c.c. of the water are put into a flask with 3 c.c. of strong solution of calcic or baric chloride, and 2 c.c. of saturated solution of ammonic chloride; 45 c.c. of baryta or lime water, the strength of which is previously ascertained by means of decinormal acid, are then added, the flask well corked and put aside to settle; when the precipitate is fully subsided, take out 50 c.c. of the clear liquid with a pipette, and let this be titrated with decinormal acid. The quantity required must be multiplied by 3 for the total baryta or lime solution, there being 50 c.c. only taken; the number of c.c. so found must be deducted from the original quantity required for the baryta solution added; the remainder multiplied by 0·0022 (the acid being decinormal) will give the weight of carbonic acid existing free and as bicarbonate in the 100 c.c.

The addition of the baric or calcic chloride and ammonic chloride is made to prevent any irregularity which might arise from alkaline carbonates or sulphates, and also magnesia.

If it be desirable to ascertain the volume of carbonic acid from the weight, 1000 c.c. of gas, at 0° and 0·76 m.m., weigh 1·96663 gm. 100 cubic inches weigh 47·26 grains.

### 4. Carbonic Acid in Aërated Beverages, etc.

For ascertaining the quantity of carbonic acid in bottled aërated waters, such as soda, seltzer, potass, and others, the following apparatus is useful.

Fig. 23 is a brass tube made like a cork-borer about five inches long, having four small holes, two on each side, and about two inches from its cutting end; the upper end is securely connected with the bent tube from the absorption flask (fig. 24) by means of a vulcanized tube; the flask contains a tolerable quantity of pure ammonia, into which the delivery tube dips; the tube *a* contains broken glass moistened with ammonia.

Everything being ready the brass tube is greased, and the bottle being held in the right hand, the tube is screwed a little aslant through the cork by turning the bottle round, until the holes appear below the cork and the gas escapes into the flask. When all visible action has ceased, after the bottle has been well shaken two or three times to evolve all the gas that can be possibly eliminated, the vessels are quietly disconnected, the tube *a* washed out into the flask, and the contents of the bottle added also; the whole is then precipitated with calcic chloride and boiled, and the precipitate titrated as usual. This gives the total carbonic acid free and combined.

Fig. 23.

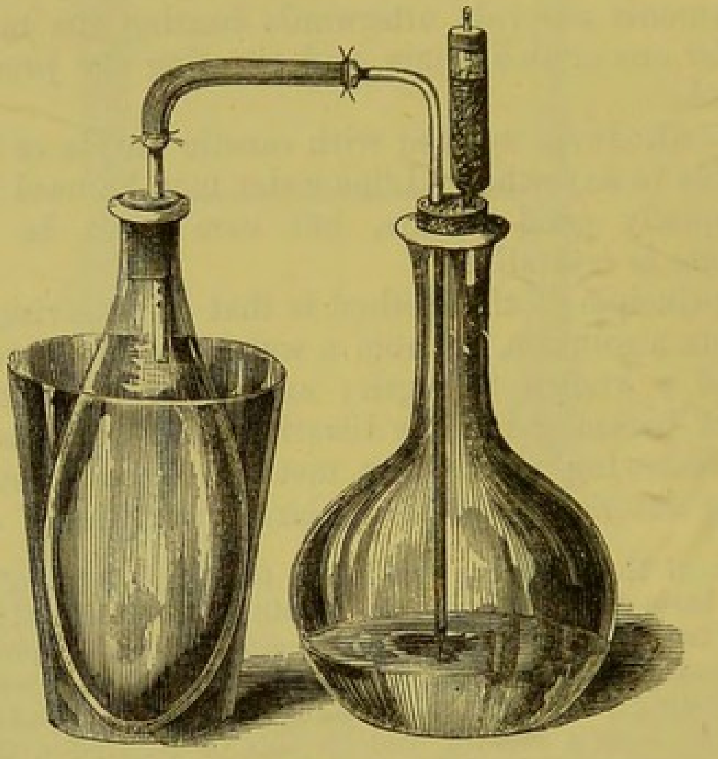

Fig. 24.

To find the quantity of the latter, another bottle of the same manufacture must be evaporated to dryness, and the residue gently ignited, then titrated with normal acid and alkali; the amount of carbonic acid in the monocarbonate deducted from the total, will give the weight of free gas originally present.

The volume may be found as follows:—1000 c.c. of carbonic acid at 0°, and 76 m.m., weigh 1·96663 gm. Suppose, therefore, that the total weight of carbonic acid found in a bottle of ordinary soda water was 2·8 gm., and the weight combined with alkali 0·42 gm., this leaves 2·38 gm. $CO^2$ in a free state—

$$1{\cdot}96663 : 2{\cdot}38 : : 1000 : x = 1210 \text{ c.c.}$$

If the number of c.c. of carbonic acid found is divided by the number of c.c. of soda water contained in the bottle examined, the quotient will be the volume of gas compared with that of the soda water. The volume of the contents of the bottle is ascertained by marking the height of the fluid previous to making the experiment; the bottle is afterwards filled to the same mark with water, emptied into a graduated cylinder and measured; say the volume was 292 c.c., therefore

$$\frac{1210}{292} = 4{\cdot}14 \text{ vols. } CO^2.$$

### 5. Carbonic Acid in Air.

A glass globe or bottle capable of being securely closed by a stopper or otherwise, and holding 4 to 6 liters, is filled with the air to be tested by means of a bellows aspirator; baryta water is then introduced in convenient quantity and of known strength as compared with $\frac{N}{10}$ acid. The vessel is securely closed, and the liquid allowed to flow round the sides at intervals during half an hour; if at the end of that time no great amount of cloudiness in the baryta has occurred, it may be advisable to refill the bottle with air one or more times. This can of course be done with the aspirator as at first, taking care on each occasion to agitate the vessel, so as to bring the baryta in contact with all parts of its surface during the space of half an hour. When sufficient air has thus been treated, the baryta is emptied out quickly into a beaker, the bottle rinsed out with distilled water free from $CO^2$, the rinsings added to the baryta, and the excess of the latter at once ascertained by $\frac{N}{10}$ hydrochloric acid and turmeric paper as described in § 14.9; or, instead of taking the whole of the baryta, that and the rinsings may be emptied into a stoppered cylinder, made up to a definite measure, and half or one-third taken for titration. The final calculation is of course made on the total baryta originally used, and upon the exact measurement of the air-collecting vessel.

It is above all things necessary to prevent the absorption of $CO^2$ from extraneous sources during the experiment. The error may be reduced to a minimum by carrying on the titration in the vessel itself, which is done by fixing an accurately graduated pipette through the cork or caoutchouc stopper of the air vessel, to the upper end of which is attached a stout piece of elastic tube, closed with a pinch-cock; and this being filled to the O mark with dilute standard acid acts as a burette. The baryta solution is placed in the air bottle with a drop or two of phenolphthalein, and after absorption of all $CO^2$, the excess of baryta is found by running in the acid until the colour disappears.

The cork or stopper must have a second opening to act as ventilator; a small piece of glass tube does very well.

$\frac{N}{100}$ acid should be used as the standard; the proportionate strength of the baryta must be found by a blank experiment.

If a freshly made solution of oxalic acid is used containing 0·2863 gm. per liter, each c.c. represents 1 mgm. $CO^2$. The liquid holds its strength correctly for a day, and can be made as required from a strong solution, say 28·636 gm. per liter.

Another method of calculation is, to convert the volume of baryta solution decomposed into its equivalent volume in $\frac{N}{10}$ acid, 1 c.c. of which $=0·0022$ gm. $CO^2$, or by measurement at 0° C. and 760 m.m. pressure represents 1·119 c.c.

*Expired Air.*—Marcet uses a special vessel for the treatment of air for carbonic acid from the lungs (*J. C. S.* 1880, 495).

The absorption by baryta, and the analysis, however, do not essentially differ from the method described above.

### 6. Scheibler's Apparatus for the estimation of Carbonic Acid by Volume.

This apparatus is adapted for the estimation of the $CO^2$ contained in native carbonates, as well as in artificial products, and has been specially contrived for the purpose of readily estimating the $CO^2$ in the bone-black used in sugar refining. The principle upon which the apparatus is founded is simply this:—That the quantity of $CO^2$ contained in calcic carbonate can be used as a measure of the quantity of that salt itself; and instead of determining, as has been usually the case, the quantity of gas by weight, this apparatus admits of its estimation by volume; and it is by this means possible to perform, in a few minutes, operations which would otherwise take hours to accomplish, while, moreover, the operator need scarcely possess any knowledge of chemistry. The results obtained by this apparatus are correct enough for technical purposes.

The apparatus is shown in fig. 25, and consists of the following parts:—The glass vessel, A, serves for the decomposition of the material to be tested for $CO^2$, which for that purpose is treated with dilute HCl; this acid is contained, previous to the experiment, in the gutta-percha vessel *s*. The glass stopper of A is perforated, and through it firmly passes a glass tube, to which is fastened the india-rubber tube *r*, by means of which communication is opened with B, a bottle having three openings in its neck. The central opening of this bottle contains a glass tube (*r*) firmly fixed, which is in communication, on the one hand, with A, by means of the flexible india-rubber tube already alluded to, and, on the other hand, *inside* of B, with a very thin india-rubber bladder, K. The neck (*q*) of the vessel B is shut off during the experiment by means of a piece of india-rubber tubing, kept firmly closed with a spring clamp. The only use of this opening of the bottle B, arranged as described, is to give access of atmospheric air to the interior of the bottle, if required. The other opening is in communication with the measuring apparatus C, a very accurate cylindrical glass tube of 150 c.c. capacity, divided into 0·5 c.c.; the lower portion of this tube C is in communication with the tube D, serving the purpose of controlling the pressure of the gas. The lower part of this tube D ends in a glass tube of smaller diameter, to which is fastened the india-rubber tube *p*, leading to E, but the communication between these parts of the apparatus is closed, as seen at *p*, by means of a spring clamp. E is a water reservoir, and on removal of the clamp at *p*, the water contained in C and D runs off towards E; when it is desired to force the water contained in E into C and D, this can be readily done by blowing with the mouth into V, and opening the clamp at *p*.

The main portion of the apparatus above described, with the exception, however, of the vessel A, is fixed by means of brass fittings to a wooden board; a thermometer is also attached. The filling of the apparatus with water is very readily effected by pouring it through a suitable funnel placed in the open end of the tube D, care being taken to remove, or at least to unfasten, the spring clamp at *p;* in this manner the water runs into E, which should be almost entirely filled. Distilled water is preferable for this purpose, especially as the filling only requires to be done once, because the water always remains in E as long as the apparatus is

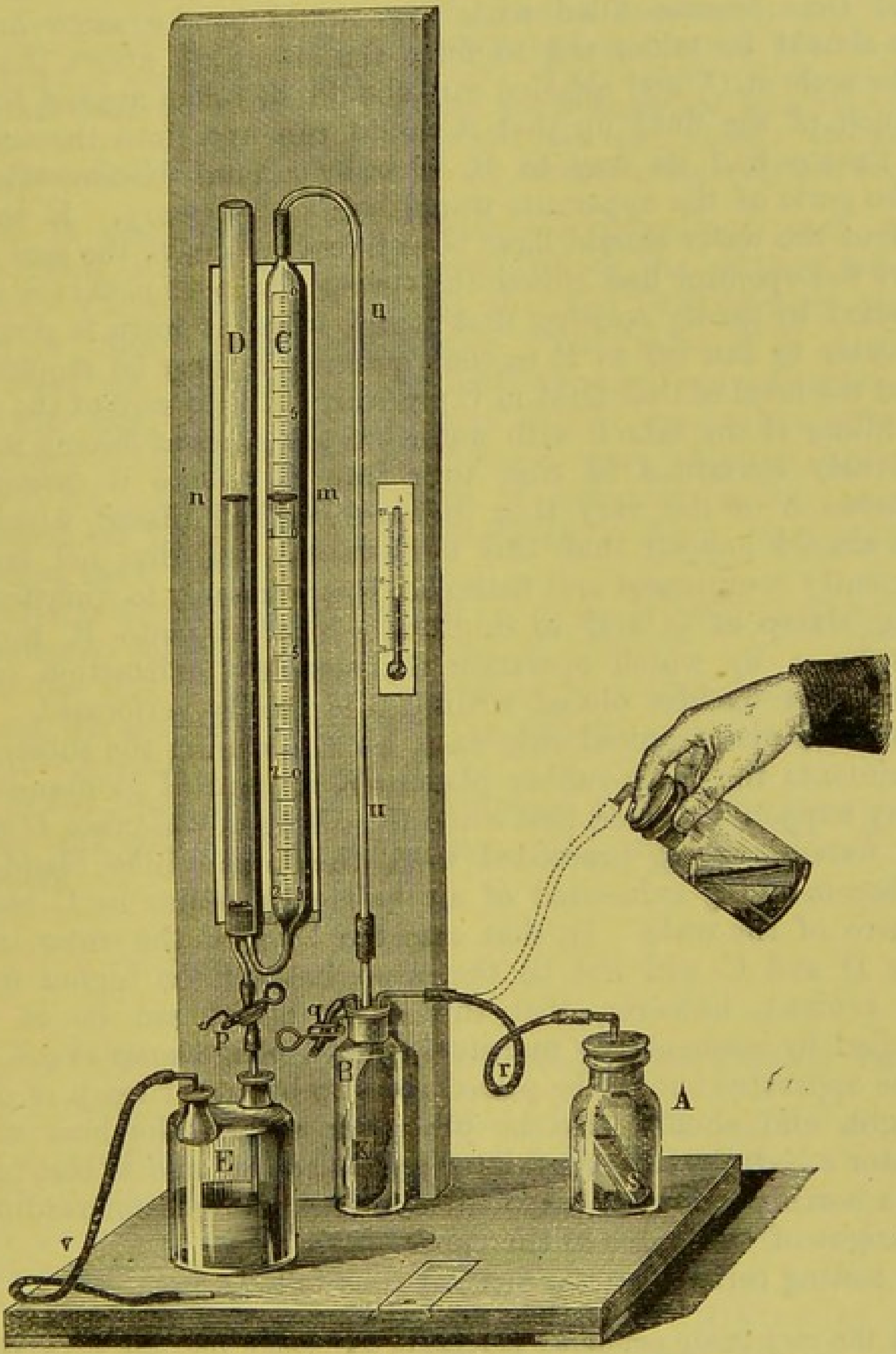

Fig. 25.

intended to be kept ready for use. When it is required to fill the tubes C and D with water, so as to reach the zero of the scale of the instrument, it is best to remove the glass stopper from A. The spring clamp at *p* is next unfastened, and air is then blown by means of the mouth into the tube V, which communicates with E; by this operation the water rises up into the tubes C and D, which thus become filled with that liquid to the same height. Care should be taken not to force the water up above the zero of the scale at C, and especial care should be taken against forcing so much of the fluid up that it would run over into the tube *u*, and thence find its way to B, whereby a total disconnection of all the parts of the apparatus would become necessary. If by any accident the water should have been forced up above the zero at C, before the operator had closed the spring clamp at *p*, this is easily remedied by gently opening that clamp, whereby room is given for the water to run off to E in such quantity as may be required to adjust the level of that fluid in C precisely with the zero of the scale. The filling of the tube C with water has the effect of forcing the air previously contained in that tube into B, where it causes the compression of the very thin india-rubber ball placed within B. If it should happen that this india-rubber ball has not become sufficiently compressed and flattened, it is necessary to unfasten the spring clamp at *q*, and to cautiously blow air into B, through the tube *q*, by which operation the complete exhaustion of the india-rubber bladder placed within B is readily performed. This operation is also required only once, because during the subsequent experiments the india-rubber bladder K is emptied spontaneously. It may happen, however, that while the filling of the tubes D and C with water is being proceeded with, the india-rubber bladder K has become fully exhausted of air before the water in C reaches the zero of the scale. In that case the level of the water in the tubes D and C will not be the same, but will be higher in D: it is evident, however, that this slight defect can be at once remedied by momentarily unfastening the spring clamp at *q*.

The apparatus should be placed so as to be out of reach of direct sunlight, and should also be protected against the heat of the operator's body by intervention of a glass screen, and is best placed near a north window, so as to afford sufficient light for reading off the height of the water in the tubes.

In testing carbonates the method is as follows :—

Put the very finely powdered portion of carbonate into the perfectly dry decomposing glass A, fill the gutta-percha tube with 10 c.c. hydrochloric acid of 1·12 sp. gr., place the tube cautiously in the decomposing glass, and then close the bottle with the well-tallowed stopper. Here the water will sink a little in C and rise in D; open *q* for a moment, and the equilibrium will be restored. Now note the thermometer and barometer, grasp the bottle with the right hand round the neck to avoid warming, raise it, incline it slightly so that the hydrochloric acid may mix with the substance gradually, and at the same time with the left hand regulate *p*, so that the water in the two tubes may be kept at exactly the same height; continue these operations without intermission, till the level of the water in C does not change for a few seconds. Now bring the columns in C and D to exactly the same height, read off the height of the water, and note whether the temperature has remained constant. If it has, the number of c.c. read off indicates the liberated $CO^2$, but as a small quantity has been dissolved by the hydrochloric acid, it is necessary to make a correction. Scheibler has determined the small amount of carbonic acid which remains dissolved in the 10 c.c. hydrochloric acid at the mean temperature, and he directs to add 0·8 c.c. to the volume of the carbonic acid read off. Warington (*C. N.* xxxi. 253) states that this is not a constant quantity, but is dependent upon the volume of gas evolved, and this ratio he fixes at 7 per cent. Lastly, the volume being reduced to 0°, 760 m.m., and the dry condition, the weight is found.

If it is desired to dispense with all corrections, each set of experiments may be begun by establishing the relation between the $CO^2$ obtained in the process (*i.e.* the $CO^2$ actually yielded $+ 0{\cdot}8$ c.c.) and pure calcic carbonate. This relation is, of course, dependent on the temperature and pressure prevailing on the particular day. For example, from 0·2737 gm. calcic carbonate containing 0·120428 gm. $CO^2$, 63·8 c.c. were obtained, including the 0·8 c.c.; and in an analysis of dolomite under the same circumstances from 0·2371 gm. substance, 57·3 c.c. were obtained, including the 0·8 c.c.

Therefore $63{\cdot}8 : 57{\cdot}3 :: 0{\cdot}120428 : x$, or $x = 0{\cdot}10816$, consequently the dolomite contains 45·62 per cent. of $CO^2$.

For the special procedure in testing bone-black, used in sugar refining, the reader is referred to the printed instructions supplied with the apparatus.*

Wigner (*Analyst*, i. 158) has obtained exceedingly good results in the analysis of lead carbonates, etc., with Mc Leod's gas apparatus.

## ESTIMATION OF COMBINED ACIDS IN NEUTRAL SALTS.

§ 27. This comprehensive method of determining the quantity of acid in neutral compounds (but not the nature of the acid), is applicable only in those cases where the base is perfectly precipitated by an excess of caustic alkali or its carbonate. The number of bodies capable of being so precipitated is very large, as has been proved by the researches of Langer and Wawnikiewicz (*Ann. Chem. u. Phar.* 1861, 239), who seem to have worked out the method very carefully. These gentlemen attribute its origin to Bunsen; but it does not seem certain who devised it. The best method of procedure is as follows:—

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* It is perhaps almost needless to say that the modern apparatus designed by Hempel, Lunge, and others, for technical gas analysis, practically supersedes that of Scheibler. The methods are all, however, open to the objection that an uncertain portion of $CO^2$ is lost by aqueous absorption.

The substance is weighed, dissolved in water in a 300-c.c. flask, heated to boiling or not, as may be desirable; normal alkali or its carbonate, according to the nature of the base, is then added from a burette, until the whole is decidedly alkaline. It is then diluted to 300 c.c. and put aside to settle, and 100 c.c. are taken out and titrated for the excess of alkali; the remainder multiplied by 3, gives the measure of the acid combined with the original salt, *i.e.* supposing the precipitation is complete.

*Example:* 2 gm. crystals of baric chloride were dissolved in water, heated to boiling, and 20 c.c. normal sodic carbonate added, diluted to 300 c.c., and 100 c.c. of the clear liquid titrated with normal nitric acid, of which 1·2 c.c. were required: altogether, therefore, the 2 gm. required 16·4 c.c. normal alkali; this multiplied by 0·122 gave 2·0008 gm. $BaCl^2\ 2H^2O$ instead of 2 gm.; multiplied by the factor for chlorine 0·03537, it yielded 0·58007 gm. Theory requires 0·5809 gm. chlorine.

The following substances have been submitted to this mode of examination with satisfactory results :—

Salts of the alkaline earths precipitated with an alkaline carbonate while boiling hot.

Salts of magnesia, with pure or carbonated alkali.

Alum, with carbonate of alkali.

Zinc salts, boiling hot, with the same.

Copper salts, boiling hot, with pure potash.

Silver salts, with same.

Bismuth salts, half an hour's boiling, with sodic carbonate.

Nickel and cobalt salts, with the same.

Lead salts, with the same.

Iron salts, boiling hot, with pure or carbonated alkali.

Mercury salts, with pure alkali.

Protosalts of manganese, boiling hot, with sodic carbonate.

Chromium persalts, boiling hot, with pure potash.

Where the compound under examination contains but one base precipitable by alkali, the determination of the acid gives, of course, the quantity of base also.

Wolcott Gibbs (*C. N.* 1868, i. 151) has enunciated a new acidimetric principle applicable in cases where a base is precipitable at a boiling temperature by hydric sulphide, and the acid set free so as to be estimated with standard alkali. Of course the method can only be used where complete separation can be obtained, and where the salt to be analyzed contains a fixed acid which has no effect upon hydric sulphide. A weighed portion is dissolved in water, brought to boiling, and the gas passed in until the metal is completely precipitated; which is known by testing a drop of the clear liquid upon a porcelain tile with sulphuretted hydrogen water, or any other appropriate agent adapted to the metallic salt under examination.

The liquid is filtered from the precipitate, and the latter well washed, and the solution made up to a definite measure. An aliquot portion is then titrated with normal alkali as usual, with one of the phenol indicators.

In the case of nitrates or chlorides, where nitric or hydrochloric acid would interfere with the hydric sulphide, it was found that the addition in tolerable quantity of a neutral salt containing an organic acid (*e.g.* sodic or potassic tartrate, or the double salt) obviated all difficulty.

The results obtained by Gibbs in the case of copper, lead, bismuth, and mercury, as sulphate, nitrate, and chloride, agreed very closely with theory; but the process would be very objectionable to many, on account of the offensive and poisonous character of the gas necessarily employed in the precipitation.

## EXTENSION OF ALKALIMETRIC METHODS.

§ 28. Bohlig (*Z. a. C.* 1870, 310) has described a method for the estimation of sulphuric acid, baryta, chlorine, iodine, and bromine, which appears worthy of some consideration, since the only standard solutions required are an acid and an alkali.

Alkaline sulphates are known to be partially decomposed, in contact with baric carbonate, into alkaline carbonates and baric sulphate. The decomposition is complete in the presence of free carbonic anhydride; acid carbonates of the alkali-metals are left in solution, together with some acid baric carbonate, which can be removed by boiling. The solution is filtered, and the alkaline carbonate determined by means of a standard acid solution, and the amount of sulphuric acid or alkaline sulphate calculated from the amount of normal acid required. This process has been satisfactorily used by Haubst for sulphates in waters (*C. N.* xxxvi. 227), and by Grossmann for salt cake (*C. N.* xli. 114). See also § 16.14.

Neutral chlorides, bromides, and iodides, more especially of the alkali-metals, are most readily decomposed by pure silver oxide into insoluble silver salts, leaving the alkali-metal in solution as hydrate (ammonia salts always excepted), which can then be determined as usual by standard acid.

The author treats solutions containing sulphates of the heavy metals, of the earths or alkaline earths, and free from acids whose presence would influence the method, viz., phosphoric, arsenic, oxalic, etc., with a solution of potassic carbonate, so as to precipitate the bases and leave about double or treble the amount of alkaline carbonate in solution. From 1 to 1½ gm. of substance is operated upon in a flask. The solution is made up to 500 c.c., well shaken, and the precipitate allowed to subside. 50 c.c. are then filtered, and titrated with standard acid and methyl orange. Another 100 c.c. are filtered in like manner into a strong quarter-liter flask, and diluted with about 100 c.c. of hot water; the requisite quantity of normal acid is then run in at once from a burette; the solution diluted to 250 c.c.; and about a gram of dry baric carbonate (free from alkali) added. The flask is next closed, and the liquid well agitated. The decomposition of the alkaline sulphate is complete in a few minutes. The flask should be opened now and then to allow the carbonic anhydride to escape. Finally, about $\frac{1}{2}$ gm. of pulverized baric hydrate is added, the whole well shaken, and a portion of the rapidly clearing liquid tested qualitatively for barium and sulphuric acid. The result should be a negative one. 50 c.c. corresponding to 20 c.c. of the original solution are then filtered and titrated with normal acid, and the quantity of sulphuric acid (sulphate) calculated as usual.

The source of carbonic anhydride is thus placed in the liquid itself, provided the quantity of potassic carbonate be not too small.

Equivalent quantities of $K^2SO^4 + 2K^2CO^3 + 2HCl + BaCO^3$ when mixed with sufficient water, change into $BaSO^4 + 2KHCO^3 + 2KCl$, and it is therefore more than sufficient to add twice the quantity of potassic carbonate compared with the alkaline sulphate operated upon.

Baric hydrate is added with a view of removing any carbonic anhydride left in the liquid after boiling, which would otherwise dissolve some of the excess of baric carbonate contained in the precipitate.

Any baric hydrate not required to remove $CO^2$ is acted upon by the acid potassic carbonate, but does not influence the final result.

Phosphoric and oxalic acids the author proposes to remove by means of calcic chloride; chromic acid by deoxidizing agents, such as alcohol and hydrochloric acid. Bohlig recommends this method for estimating sulphuric acid in ashes, crude soda, Stassfurth salts, etc.

Solutions containing baryta are estimated in like manner by precipitation as carbonate, and decomposition with potassic sulphate in a solution containing free carbonic acid. Chlorine is determined in solutions by first precipitating any metallic chloride with potassic carbonate added in moderate excess. The filtrate is made up to 250 c.c., and the excess of potassic carbonate determined in 50 c.c. by means of a normal solution of HCl. 125 c.c. of the solution are next treated with excess of silver oxide and made up to 250 c.c., well shaken (out of contact with the light) and filtered. 100 c.c. of the filtrate are titrated with normal hydrochloric acid. The difference between the quantity of acid required in the last and that of the first experiment, multiplied by 5, gives the amount of chlorine contained in the original solution. A portion of the filtrate should be tested for chlorine by means of mercurous nitrate.

The filtrate is obtained perfectly clear only in the presence of some potassic or sodic carbonate, and by employing argentic oxide free from argentous oxide. A few drops of pure potassic permanganate added to the argentic oxide preserved in water prevent formation of the latter. The oxide to be employed for each experiment is filtered when required, and thoroughly washed.

Bromine and iodine are determined in like manner. The author has not been able, however, to estimate the mixtures of the halogen salts; but he has made the interesting observation that potassic iodide, when boiled with potassic permanganate, is completely oxidized into iodate. This facilitates the detection of small quantities of chlorine and bromine, in the presence of much iodide. The greater part of iodate may be separated also by precipitation with baric nitrate before determining chlorine. The standard acid solutions which Bohlig employed contained not more than one-third of the equivalent of HCl or $SO^3$ per liter.

For further particulars the reader is referred to the original paper (*Arch. Pharm.* 3. cxlv. 113).

Siebold (*Year Book of Pharmacy*, 1878, 518) describes a very ingenious process, devised by himself, for the titration of caustic and carbonated alkalies by means of prussic acid, the principle of which is explained in § 55. The process is useful in the case of carbonates, since $CO^2$ is no hindrance.

0·5 to 1 gm. of the alkali or alkaline carbonate is dissolved in about 100 c.c. of water, and an excess of hydrocyanic acid (say 10 or 20 c.c.) of 5 per cent. solution added; then $\frac{N}{10}$ silver solution cautiously added with constant stirring until a faint permanent turbidity occurs. Each c.c. of $\frac{N}{10}$ silver $=0{\cdot}0138$ gm. $K^2CO^3$, or 0·0106 gm. $Na^2CO^3$.

In the case of chlorides being present, their quantity may be determined by boiling down the mixture to about half its volume to expel all free prussic acid, adding a drop or two of potassic chromate as indicator, then titrating with $\frac{N}{10}$ silver. Any excess above that required in the first titration will be due to chlorine, and may be calculated accordingly.

# PART III.

## ANALYSIS BY OXIDATION OR REDUCTION.

§ 29. The series of analyses which occur under this system are very extensive in number, and not a few of them possess extreme accuracy, such in fact, as is not possible in any analysis by weight. The completion of the various processes is generally shown by a distinct change of colour; such, for instance, as the occurrence of the beautiful rose-red permanganate, or the blue iodide of starch; and as the smallest quantity of these substances will colour distinctly large masses of liquid, the slightest excess of the oxidizing agent is sufficient to produce a distinct effect.

The principle involved in the process is extremely simple. Substances which will take up oxygen are brought into solution, and titrated with a substance of known oxidizing power; as, for instance, in the determination of ferrous salts by permanganic acid. The iron is ready and willing to receive the oxygen, the permanganate is equally willing to part with it; while the iron is absorbing the oxygen, the permanganate loses its colour almost as soon as it is added, and the whole mixture is colourless; but immediately the iron is satisfied, the rose colour no longer disappears, there being no more oxidizable iron present. In the case of potassic permanganate the reaction is: $10FeO + 2MnKO^4 = 5Fe^2O^3 + 2MnO + K^2O$. Oxalic acid occupies the same position as the ferrous salts; its composition is $C^2O^4H^2 + 2H^2O = 126$. If permanganate is added to it in acid solution, the oxalic acid is oxidized to carbonic acid, and the manganic reduced to manganous oxide, thus $Mn^2O^7 + 5C^2O^4H^2 + 2H^2SO^4 = 10CO^2 + 2MnSO^4 + 7H^2O$. When the oxalic acid is all decomposed, the colour of the permanganate no longer disappears. On the other hand, substances which will give up oxygen are deoxidized by a known excessive quantity of reducing agent, the amount of which excess is afterwards ascertained by residual titration with a standard oxidizing solution; the strength of the reducing solution being known, the quantity required is a measure of the substance which has been reduced by it.

The oxidizing agents best available are—potassic permanganate, iodine, potassic bichromate, and red potassic prussiate.

The reducing agents are—sulphurous acid, sodic hyposulphite,* sodic thiosulphate, oxalic acid, ferrous oxide, arsenious anhydride, stannous chloride, yellow potassic prussiate, and zinc.

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* Schützenberger's preparation is here meant.

With this variety of materials a great many combinations may be arranged so as to make this system of analysis very comprehensive; but the following are given as sufficient for almost all purposes, and as being susceptible of the greatest amount of purity and stability of material, with exceedingly accurate results:—

1. Permanganate and ferrous salts (with the rose colour as indicator); permanganate and oxalic acid (with the rose colour as indicator).
2. Potassic bichromate and ferrous salts (with cessation of blue colour when brought in contact with red potassic prussiate, as indicator).
3. Iodine and sodic thiosulphate (with starch as indicator); iodine and sodic arsenite (with starch as indicator).

# PREPARATION OF STANDARD SOLUTIONS.

## PERMANGANIC ACID AND FERROUS OXIDE.

### 1. Potassic Permanganate.

$Mn^2K^2O^8 = 315{\cdot}6$. Decinormal Solution = 3·156 gm. per liter.

§ 30. The solution of this salt is best prepared for analysis by dissolving the pure crystals in fresh distilled water of such a strength, that 17·85 c.c. will peroxidize 1 decigram of iron. The solution is then decinormal. If well kept, and shaded from sunlight, it will retain its strength for several months.

If the salt can be had perfectly pure and dry, 3·156 gm. dissolved in a liter of water at 16° C. will give an exactly decinormal solution; but, nevertheless, it is always well to titrate it upon a definite quantity of iron or one of the following re-agents.

The solution may be kept in any well-stoppered bottle, and while it is quite free from sediment, it may be taken for granted that its strength is not much altered.

In all cases where accuracy is required, it is imperative that the exact strength should be proved by titration in one of the following ways:—

### 2. Titration of Permanganate.

(*a*) *With Metallic Iron.*—The purest iron to be obtained is thin annealed binding-wire free from rust, generally known as flower wire.

About 0·1 gm. of this is to be dissolved in dilute sulphuric acid, by the aid of heat, in a small flask closed with a cork, through which a fine glass tube is passed, so that the hydrogen which is evolved escapes under pressure, thus preventing the access of air; or the apparatus shown in § 59 may be used. When the iron is all dissolved the flask may be two-thirds filled with cold distilled water, and the titration with permanganate commenced and concluded as in the case of the double sulphate.

The decomposition which ensues from titrating ferrous oxide by permanganic acid may be represented as follows :—

$$10FeO \text{ and } Mn^2O^7 = 2MnO \text{ and } 5Fe^2O^3.$$

(*b*) *With Ammonio-ferrous Sulphate.* In order to ascertain the strength of the permanganate, it may be titrated with a weighed quantity of this salt instead of metallic iron.

This salt is a convenient substance for titrating the permanganate, as it saves the time and trouble of dissolving the iron, and when perfectly pure, it can be depended on without risk. To prepare it, 139 parts of the purest crystals of ferrous sulphate, and 66 parts of pure crystallized ammonic sulphate are separately dissolved in the least possible quantity of distilled water of about 40° C. (if the solutions are not perfectly clear they must be filtered); mix them at the same temperature in a porcelain dish, adding a few drops of pure sulphuric acid, and stir till cold. During the stirring the double salt will fall in a finely granulated form. Set aside for a few hours, then pour off the supernatant liquor, and empty the salt into a clean funnel with a little cotton wool stuffed into the neck, so that the mother-liquor may drain away; the salt may then be quickly and repeatedly pressed between fresh sheets of clean filtering paper. Lastly, place in a current of air to dry thoroughly, so that the small grains adhere no longer to each other, or to the paper in which they are contained, then preserve in a stoppered bottle for use.

The formula of the salt is—$Fe\,(NH^4)^2\,(SO^4)^2,\ 6H^2O = 392$.

Consequently it contains exactly one-seventh of its weight of iron; therefore 0·7 gm. represents 0·1 gm. of iron, and this is a convenient quantity to weigh for the purpose of titrating the permanganate.

0·7 gm. being brought into dilute solution in a flask or beaker, and 5 or 6 c.c. of dilute sulphuric acid (1 to 5) added (the titration of permanganate, or any other substance by it, should always take place in the presence of free acid, and preferably sulphuric), the permanganate is delivered from a burette with glass tap divided in $\frac{1}{5}$ or $\frac{1}{10}$ c.c., until a point occurs when the rose colour no longer disappears on shaking. A drop or two of the permanganate in excess suffices to produce this effect. The titration is now ended, and should the quantity not be strictly correct, the number of c.c. used may be marked upon the bottle as the quantity for 0·1 gm. Fe, or the factor found, which is necessary to reduce it to decinormal strength, or if too strong, it may be diluted to that strength at once.

(*c*) *With Oxalic Acid.*—0·63 gm. of the pure acid is to be weighed, or 10 c.c. of normal solution measured with a pipette, brought into a flask with dilute sulphuric acid, as in the case of the iron salt, and considerably diluted with water, then warmed to about 58° C., and the permanganate added from the burette. The colour disappears slowly at first, but afterwards more rapidly, becoming first brown, then yellow, and so on to colourless. More care must be exercised in this case than in the titration with iron, as the action is less decisive and rapid.

(*d*) *With Lead Oxalate.*—Stolba prefers this salt to oxalic acid, for the reasons that it contains no water, nor is liable to absorb any from exposure, and because of its high molecular weight, 1 part of the salt representing 0·42799 of oxalic acid, or 63 oxalic acid = 147·2 lead oxalate.

The method of titration is similar to that with oxalic acid, using dilute sulphuric acid, and warming the mixture to insure the complete decomposition of the salt into lead sulphate and free oxalic acid. Sodic oxalate is also anhydrous and equally serviceable.

The lead oxalate is prepared by precipitating pure lead acetate with oxalic acid in excess, and washing the precipitate by decantation with warm water till all free acid is removed; the precipitate is then dried at 120° C., and preserved for use.

(*e*) *With Ammonic Sulphocyanate.*—A standard solution of sulphocyanate holds its strength well for a long period, and is very convenient for the rapid verification of permanganate solution. The reaction is such, that when sulphocyanate is added to an acid solution of permanganate, sulphuric and hydrocyanic acids are produced, and colourless manganese salts are left in solution. The reaction may be expressed thus:—$CNSH + 3O = SO^3 + CNH$. Each c.c. of $\frac{N}{10}$ sulphocyanate = 0·0048 gm. oxygen.

The standard sulphocyanate is described in § 39, but for this purpose it is advisable to use $\frac{N}{100}$ solution.

10 c.c. of the permanganate are freely diluted, sulphuric acid added, and the sulphocyanate delivered in with shaking, and waiting a few moments between each addition, until the red colour entirely disappears. A strictly decinormal permanganate should require 16·7 c.c. of a strictly centinormal sulphocyanate.

The operation requires some practice to ensure good results, as the colour does not disappear so rapidly or distinctly as with ferrous salts. The sharpest results are obtained by running the permanganate into the sulphocyanate, 50 c.c. of which should require 30 c.c. $\frac{N}{10}$ permanganate to give the faint pink colour. Owing to the great dilution of the solutions, and the probable traces of impurity in the water or sulphuric acid used, these exact numbers may not be obtained; but it will be found, that having established the relationship between the two solutions with pure water and a known volume of $H^2SO^4$, a repetition of the titration under the same conditions will show whether the permanganate has varied.

(*f*) *With Vanadic Pentoxide.*—Gerland (*C. N.* xxxvi. 272) adopts this method of verification for permanganate; and the process is certainly elegant, and easily carried out. It can, however, only be recommended in the same manner as the foregoing, for the occasional titration of a permanganate solution, to ascertain whether it has lost strength, and not for the original standardizing of the solution.

It is first necessary to have a solution of pure vanadic pentoxide containing, say, about 1 or 2 gm.; this is dissolved by heat in pure dilute sulphuric acid, producing a clear yellow solution. When this is boiled with aqueous sulphurous acid it is reduced to blue vanadic tetroxide, which is perfectly unchangeable in acid solution, in the absence of alcohol or carbonaceous matters, and may be boiled to expel excess of $SO^2$. The addition of permanganate brings it back to pentoxide, and hence the process as follows:—

The pure sulphuric acid solution of pentoxide being obtained in a capacious flask, an excess of aqueous sulphurous acid is added and boiled till it becomes blue, and all excess of $SO^2$ is dissipated; the solution is then cooled and titrated with permanganate till the red colour is just apparent.

The quantity of permanganate is then noted and marked on the flask, which should be set aside, and absolutely closed against dust or other reducing matter (which might cause the formation of trioxide).

The solution so obtained may at any time be used again and again by simply reducing with sulphurous acid by boiling, taking care that all excess is removed, then cooling and titrating as before described.

Gerland states that he has solutions of various strengths preserved in flasks, which have repeatedly been titrated in the course of years, and which continue to give the reaction as delicately as when first prepared.

### 3. Precautions in Titrating with Permanganate.

It must be borne in mind that free acid is always necessary in titrating a substance with permanganate, in order to keep the resulting manganous oxide in solution. Sulphuric acid, in a dilute form, has no prejudicial effect on the pure permanganate, even at a high temperature. With hydrochloric acid the solution to be titrated must be very dilute and of low temperature, otherwise chlorine will be liberated and the analysis spoiled. This acid acts as a reducing agent on permanganate in concentrated solution, thus—

$$Mn^2O^7 + 14HCl = 7H^2O + 10Cl + 2MnCl^2.$$

The irregularities due to this reaction may be entirely obviated by the addition of a few grams of manganous or magnesic sulphate before titration.

Organic matter of any kind decomposes the permanganate, and the solution, therefore, cannot be filtered through paper, nor can it be used in Mohr's burette, because it is decomposed by the india-rubber tube. It may, however, be filtered through gun cotton or glass wool.

## TITRATION OF FERRIC SALTS BY PERMANGANATE.

§ 31. All ferric compounds requiring to be estimated by permanganate must, of course, be reduced to the ferrous state. This may be done by sulphurous acid or an alkaline sulphite, but is best accomplished by metallic zinc in sulphuric acid solution. Hydrochloric may also be used with the precautions mentioned.

The reduction occurs by simply adding to the warm diluted solution small pieces of zinc (free from iron, or at least with a known quantity present) until colourless; or until a drop of the solution brought in contact with a drop of potassic sulphocyanide produces no red colour. All the zinc must be dissolved previous to the titration.

The reduction may be hastened considerably as shown in § 59.3.

When the reduction is complete, no time should be lost in titrating the solution.

## CALCULATION OF ANALYSES MADE WITH PERMANGANATE SOLUTION.

§ 32. The calculation of analyses with permanganate, if the solution is not strictly decinormal, can be made by ascertaining its factor, reducing the number of c.c. used for it to decinormal strength, and multiplying the number of c.c. thus found by $\frac{1}{10000}$ of the equivalent weight of the substance sought; for instance—

Suppose that 15 c.c. of permanganate solution have been found to equal 0·1 gm. iron; it is required to reduce the 15 c.c. to decinormal strength, which would require 1000 c.c. of permanganate to every 5·6 gm. iron, therefore $5{\cdot}6 : 1000 :: 0{\cdot}1 : x = 17{\cdot}85$ c.c.; $17{\cdot}85 \times 0{\cdot}0056 = 0{\cdot}09996$ gm. iron, which is as near to 0·1 gm. as can be required. Or the factor necessary to reduce the number of c.c. used may be found as follows:—$0{\cdot}1 : 15 :: 5{\cdot}6 : x = 84$ c.c., therefore $\frac{100}{84} = 1{\cdot}19$. Consequently 1·19 is the factor by which to reduce the number of c.c. of that special permanganate used in any analysis to the decinormal strength, from whence the weight of substance sought may be found in the usual way.

Another plan is to find the quantity of iron or oxalic acid represented by the permanganate used in any given analysis, and this being done the following simple equation gives the required result:—

$$\begin{array}{ccccccc} \text{Fe (56)} & & \text{eq. weight of} & & \text{the weight} & & \text{the weight of} \\ \text{or} & : & \text{the substance} & :: & \text{of Fe or} & : & \text{substance} \\ \overline{\text{O}}\text{ (63)} & & \text{sought} & & \overline{\text{O}}\text{ found} & & \text{sought} \end{array}$$

In other words, if the equivalent weight of the substance analyzed be divided by 56 or 63 (the respective equivalent weights of iron or oxalic acid), a factor is obtained by which to multiply the weight of iron or oxalic acid, equal to the permanganate used, and the product is the weight of the substance analyzed.

For example: sulphuretted hydrogen is the substance sought, the eq. weight of $H^2S$ corresponding to 2 eq. Fe is 17; let this number therefore be divided by 56, $\frac{17}{56} = 0{\cdot}3036$, therefore, if the quantity of iron represented by the permanganate used in an estimation of $H^2S$ be multiplied by 0·3036, the product will be the weight of the sulphuretted hydrogen sought.

Again: in the case of manganic peroxide whose equivalent weight is 43·4.

$$\frac{43·4}{56} = 0·775$$

The weight of iron therefore found by permanganate in any analysis multiplied by the factor 0·775 will give the amount of manganic peroxide, $MnO^2$. Again: if $m$ gm. iron $= k$ c.c. permanganate, then 1 c.c. permanganate $= \frac{m}{k}$ gm. metallic iron.

The equivalents here given are on the hydrogen scale, in accordance with the normal system of solutions adopted; and thus it is seen that two equivalents of iron are converted from the ferrous to the ferric state by the same quantity of oxygen, as suffices to oxidize one equivalent of oxalic acid, sulphuretted hydrogen, or manganic peroxide.

1 c.c. decinormal permanganate is equivalent to

| | | | | | |
|---|---|---|---|---|---|
| 0·0056 | gm. | Fe | estimated in the ferrous state | | |
| 0·0072 | ,, | FeO | ,, | ,, | ,, |
| 0·008 | ,, | $Fe^2O^3$ | ,, | ,, | ,, |
| 0·003733 | ,, | Fe | ,, | from | FeS |
| 0·0059 | ,, | Sn | ,, | ,, | $SnCl^2$ |
| 0·00295 | ,, | Sn | ,, | ,, | $SnS^2$ |
| 0·00315 | ,, | Cu | ,, | ,, | CuS |
| 0·00274 | ,, | Mn | ,, | ,, | MnS |
| 0·00315 | ,, | Cu | ,, | ,, | $Cu + Fe^2Cl^6$ |
| 0·0063 | ,, | Cu | ,, | ,, | $CuO + Fe$ |
| 0·0017 | ,, | $H^2S$ | ,, | ,, | |
| 0·0008 | ,, | O | | | |
| 0·0063 | ,, | $\bar{O}$ | | | |
| 0·002 | ,, | Ca from $CaC^2O^4$ | | | |
| 0·0120 | ,, | Ur | ,, | UrO, etc., etc. | |

When possible the necessary factors will be given in the tables preceding any leading substance.

## CHROMIC ACID AND FERROUS OXIDE.

§ 33. Potassic bichromate, which appears to have been first proposed by Penny, possesses the advantage over permanganate, that it is absolutely permanent in solution, may easily be obtained in a pure state, and its solution may be used in Mohr's burette without undergoing the change peculiar to permanganate: on the other hand, the end of the reaction in the estimation of iron can only be known by an external indicator; that is to say, a drop of the mixture is brought in contact with a drop of solution of red potassic prussiate (freshly prepared) upon a white slab or plate. While the ferrous oxide is in tolerable excess, a rich blue colour occurs at the point of contact between the drops; but as this excess continues to lessen by the addition of the bichromate, the blue becomes somewhat turbid, having first a green, then a grey, and lastly a brown shade. When the greenish-blue tint has all disappeared, the process is finished. This series of changes in the colour admits of tolerably sure reading of the burette, after some little practice is obtained.

The reaction between chromic acid and ferrous oxide may be represented by the formula:—

$$2CrO^3 + 6FeO = Cr^2O^3 + 3Fe^2O^3.$$

The decomposition takes place immediately, and at ordinary temperatures, in the presence of free sulphuric or hydrochloric acid. Nitric acid is of course inadmissible.

The reduction of ferric compounds to the ferrous state may be accomplished by zinc,* sodic sulphite, ammonic bisulphite, or sulphurous acid as for permanganate; or, instead of these, stannous chloride may be used, which acts very rapidly as a reducing agent upon ferric oxide, the yellow colour of the solution disappearing almost immediately.

In the analysis of iron ores this method of reduction is serviceable; the greatest care, however, is necessary that the stannous chloride is not present in excess, as this would consume the bichromate solution equally with the ferrous oxide, and so lead to false results.

The discharge of the yellow colour of the iron solution may with care be made a very sure indicator of the exact point of reduction. The concentrated hydrochloric solution of iron is heated to gentle boiling, and the moderately dilute tin solution added with a pipette, waiting a moment for each addition till the last traces of colour have disappeared; the solution is then poured into a beaker, diluted with boiled and cooled water, and titrated with the bichromate as usual. An extra security is obtained by adding a few drops of potassic sulphocyanide to the solution, the disappearance of the blood-red colour indicating that no more ferric oxide is present.

In order to obviate the inaccuracy which would be produced by an excess of tin in the state of protosalt, Mohr recommends that chlorine water should be added by drops to the mixture, until a rod moistened with it and brought in contact with blue iodide of starch paper no longer removes the colour; the excess of stannous chloride is then all converted into stannic chloride, and the titration with bichromate may proceed as usual.

It is absolutely necessary that the solution of potassic ferricyanide used as the indicator with bichromate, should be free from ferrocyanide; and as a solution when kept for some long time becomes in some measure converted into the latter, it is best to use a freshly prepared liquid.

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* When zinc is used, the zinc ferricyanide somewhat obscures the critical poin in testing with the indicator.

### 1. Preparation of the Decinormal Solution of Bichromate.

4·913 gm. per liter.

The reaction which takes place between potassic bichromate and ferrous oxide is as follows :—

$$6FeO + Cr^2K^2O^7 = 3Fe^2O^3 + Cr^2O^3 + K^2O$$

It is therefore necessary that $\frac{1}{6}$ eq. in grams should be used for the liter as a normal solution, and $\frac{1}{60}$ for the decinormal; and as it is preferable on many accounts to use a dilute solution, the latter is the most convenient for general purposes.

According to the latest and most reliable researches, the equivalent number of chromium is 52·4, and consequently that of potassic bichromate is 294·8; if, therefore, $\frac{1}{60}$ of this latter number = 4·913 gm. be dissolved in a liter of water, the decinormal solution is obtained. On the grain system, 49·13 grains to 10,000 grains of water will give the same solution.*

1 c.c. of this solution is capable of yielding up $\frac{1}{10000}$ eq. in grams of oxygen, and is therefore equivalent to the $\frac{1}{10000}$ eq. of any substance which takes up 1 equivalent of oxygen.

### 2. Solution of Stannous Chloride.

About 10 gm. of pure tin in thin pieces are put into a large platinum capsule, about 200 c.c. strong hydrochloric acid poured over it, and heated till it is dissolved; or it may be dissolved in a porcelain capsule or glass flask, adding pieces of platinum foil to excite a galvanic current. The solution so obtained is diluted to about a liter with distilled water, and preserved in the bottle (fig. 17) to which the air can only gain access through a strongly alkaline solution of pyrogallic acid. When kept in this manner, the strength will not alter materially in a month. If not so preserved, the solution varies considerably from day to day, and therefore should always be titrated before use as described in § 60.1.

*Examples of Iron Titration:* 0·7 gm. of pure and dry ammonio-ferrous sulphate = 0·1 gm. iron, was dissolved in water, and titrated with decinormal bichromate, of which 17·85 c.c. were required; this multiplied by 0·0392 gave 0·699 gm. instead of 0·7 gm.

0·56 gm. of iron wire required 99·8 c.c. = 0·5588 gm.; as it is impossible to obtain iron wire perfectly pure, the loss is undoubtedly owing to the impurities.

If the bichromate solution should from any accidental cause be found not strictly of decinormal strength, the factor necessary for converting it must be found as previously described.

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* Pure bichromate powdered and dried in the air bath should be used, and not the fused salt.

## IODINE AND SODIC THIOSULPHATE.

§ 34. THE principle of this now beautiful and exact method of analysis was first discovered by Dupasquier, who used a solution of sulphurous acid instead of sodic thiosulphate. Bunsen improved his method considerably by ascertaining the sources of failure to which it was liable, which consisted in the use of a too concentrated solution of sulphurous acid. The reaction between iodine and very dilute sulphurous acid may be represented by the formula—

$$SO^2 + I^2 + 2H^2O = 2HI + H^2SO^4.$$

If the sulphurous acid is more concentrated, *i.e.* above 0·04 per cent., in a short time the action is reversed, the irregularity of decomposition varying with the quantity of water present, and the rapidity with which the iodine is added.* Under proper regulation, therefore, we see that free iodine converts sulphurous into sulphuric acid by decomposing water, the oxygen of which goes to the sulphurous, and produces sulphuric acid; the hydrogen being taken by the iodine, forming hydriodic acid.

Sulphurous acid, however, very rapidly changes by keeping even in the most careful manner, and as it must be exceedingly dilute, it necessitates the use of special vessels and burettes. Taking these things into account, therefore, the substitution of sodic thiosulphate is a great advantage, inasmuch as the salt is easily obtained in a pure state, and may be directly weighed for the standard solution. The reaction is as follows:—

$$2Na^2S^2O^3 + 2I = 2NaI + Na^2S^4O^6,$$

the result being that thiosulphuric acid takes oxygen from the water, with the production of tetrathionic and hydriodic acids in combination with soda.

In order to ascertain the end of the reaction in analysis by this method an indicator is necessary, and the most delicate and sensitive for the purpose is starch, which produces with the slightest trace of free iodine in cold solution the well-known blue iodide of starch. Hydriodic or mineral acids and iodides have no influence upon the colour. Caustic alkalies destroy it.

The principle of this method, namely, the use of iodine as an indirect oxidizing body by its action upon the elements of water, forming hydriodic acid with the hydrogen, and liberating the oxygen

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* This irregularity is obviated by the use of ammonic sesquicarbonate, or the bicarbonates of soda or potash. Mohr finds that these salts added in moderate quantity to the liquid sulphurous acid, or in the case of sulphites dissolving them in the alkaline solution previous to titration with iodine, entirely overcomes the difficulty hitherto found in concentrated solutions. Fleischer recommends borax for the same purpose.

in an active state, can be applied to the determination of a great variety of substances with extreme accuracy.

Bodies which take up oxygen, and decolorize the iodine solution, such as sulphurous acid, sulphites, sulphuretted hydrogen, alkaline thiosulphates and arsenites, stannous chloride, etc., are brought into dilute solution, starch added, and the iodine delivered in with constant shaking or stirring until a point occurs at which a final drop of iodine colours the whole blue—a sign that the substance can take up no more iodine, and that the drop in excess has shown its characteristic effect upon the starch.

Free chlorine, or its active compounds, cannot, however, be titrated with thiosulphate directly, owing to the fact that, instead of tetrathionic acid being produced as with iodine, sulphuric acid occurs, as may be readily seen by testing with baric chloride. In such cases, therefore, the chlorine must be evolved from its compound and passed into an excess of solution of pure potassic iodide, where it at once liberates its equivalent of iodine, which can then, of course, be estimated with thiosulphate.

All bodies which contain available oxygen, and which evolve chlorine when boiled with strong hydrochloric acid, such as the chromates, manganates, and all metallic peroxides, can be readily and most accurately estimated by this method.

### 1. Preparation of the Decinormal Solution of Iodine.

$I=126{\cdot}5$; 12·65 gm. per liter.

Chemically pure iodine may be obtained by intimately mixing dry commercial iodine with about one-fourth of its weight of potassic iodide, and gently heating the mixture between two large watch-glasses or porcelain capsules; the lower one being placed upon a heated iron plate, the iodine sublimes in brilliant plates, which are absolutely pure.

The watch-glass or capsule containing the iodine is placed under the exsiccator to cool, and also to deprive it of any traces of watery vapour; then 12·65 gm. are accurately weighed, and together with about 18 gm. of pure white potassic iodide (free from iodate) dissolved in about 250 c.c. of water, and diluted to exactly one liter. The same solution may be obtained by dissolving 126·5 grains of iodine, and 180 of potassic iodide, in 10,000 grains of water; in either case the solution is strictly decinormal. The flask must not be heated in order to promote solution, and care must be taken that iodine vapours are not lost in the operation.

The solution is best preserved in stoppered bottles, kept in the dark, and which should be completely filled; but under any circumstances it does not hold its strength well for any length of time, and consequently should be titrated before use in analysis.

### 2. Decinormal Sodic Thiosulphate.

$Na^2S^2O^3,5H^2O = 248 = 24{\cdot}8$ gm. per liter.

As it is not difficult either to manufacture or procure pure sodic thiosulphate, this quantity, powdered and dried between blotting-paper, may be weighed directly, and dissolved in a liter of distilled water, and then titrated with the iodine solution and a little starch liquor: or the solution may be checked with $\frac{N}{10}$ bichromate as recommended by Mohr, by digesting a measured volume of the bichromate, with an excess of potassic iodide, and hydrochloric acid in the stoppered flask (fig. 28) or similar well-closed vessel. When the mixture has cooled, the liberated iodine is measured by the thiosulphate, and its power ascertained. If impure thiosulphate should have been used, or the sample was not entirely free from accidental moisture, it will be necessary to find a factor by which to reduce it to decinormal strength, as described for previous solutions; or the amount of impurity being known, a fresh quantity may be prepared of proper strength. It is advisable to preserve the solution in the dark. After a time all solutions of thiosulphate undergo a slight amount of oxidation, and sulphur deposits upon the bottle; it is therefore always better to examine it previous to use. Mohr states that the tendency to deposit sulphur in the solution may be entirely obviated by adding to the $\frac{N}{10}$ solution sesquicarbonate of ammonia, in the proportion of 2 grams to the liter: this does not in the least interfere with the colour produced with the starch indicator. Harcourt and Esson (*Phil. Trans.* [5] clvi. 205) state that a little caustic soda greatly increases the stability.

Beside the decinormal iodine and thiosulphate, it is convenient in some cases to use centinormal solutions, which can readily be prepared by diluting 100 c.c. of each decinormal solution to 1 liter.

In using the iodine solution Mohr's burette may be employed, but care must be taken that the solution is not left in it for any length of time, as decomposition slowly takes place, and the tube becomes hard; the tap burette is on this account preferable.

### 3. Starch Indicator.

One part of clean arrowroot, or potato starch, is first mixed smoothly with cold water into a thin paste, then gradually poured into about 150 or 200 times its weight of boiling water, the boiling continued for a minute, then allowed to stand and settle; the clear liquor only is to be used as the indicator, of which a few drops only are necessary. The liquor may be preserved for some time by adding to it about one per cent. of salicylic acid, or saturating it with common salt; this, however, is not so sensitive as the freshly prepared solution.

A very convenient form of soluble starch is made by mixing 6 gm. starch with 100 gm. pure glycerine, heating for an hour to 100° C., pouring into about double its volume of water, then adding sufficient strong alcohol to precipitate the soluble starch, which is filtered off and preserved in a moist pasty state. When required, a minute quantity is taken with a glass rod.

A concentrated solution of starch, which will keep almost any length of time, may be made by rubbing about 5 gm. starch to a smooth emulsion, with about 50 c.c. water, then add 25 c.c. of 50 per cent. solution of caustic potash and shake well, dilute with half a liter of water, boil, cool, and filter, or allow to settle. This indicator answers very well in cases where the alkali is of no consequence, but is not available for the delicate acidimetric method by iodic acid unless the alkali is exactly corrected. It answers well, however, with the addition of 2 gm. of potassic iodide as a reagent for nitrites, and keeps perfectly though exposed to light.

## ANALYSIS OF SUBSTANCES BY DISTILLATION WITH HYDROCHLORIC ACID.

§ 35. There are a great variety of substances containing oxygen, which when boiled with hydrochloric acid yield chlorine, equivalent to the whole or a part only of the oxygen they contain according to circumstances. Upon this fact are based the variety of analyses

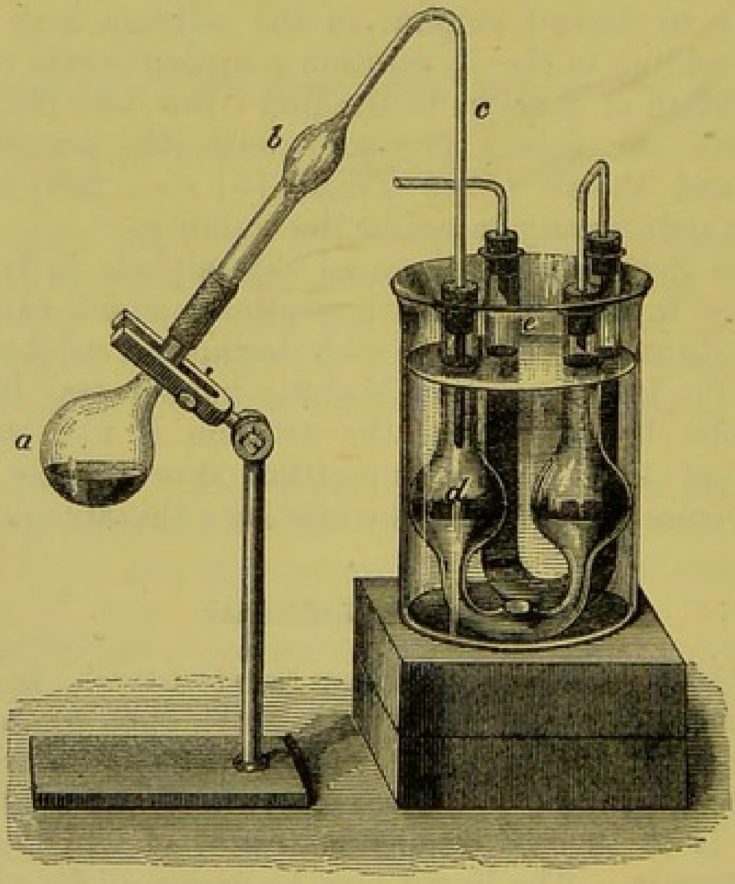

Fig. 26.

which may be accomplished by means of iodine and sodic thiosulphate, or arsenite; the chlorine so evolved, however, is not itself estimated, but is conveyed by means of a suitable apparatus into a solution of potassic iodide, thereby liberating an equivalent quantity of iodine. This latter body is then estimated by thiosulphate; the quantity so found is, therefore, a measure of the oxygen existing in the original substance, and consequently a measure of the substance itself. Analyses of this class may be made the most exact in the whole range of volumetric analysis, far outstripping any process by weight.

The apparatus used for distilling the substances, and conveying the liberated chlorine into the alkaline iodide, may possess a variety of forms, the most serviceable, however, being the three kinds devised respectively by Bunsen, Fresenius, and Mohr.

Bunsen's arrangement consists of an inverted retort, into the neck of which the tube from the small distilling flask is passed.

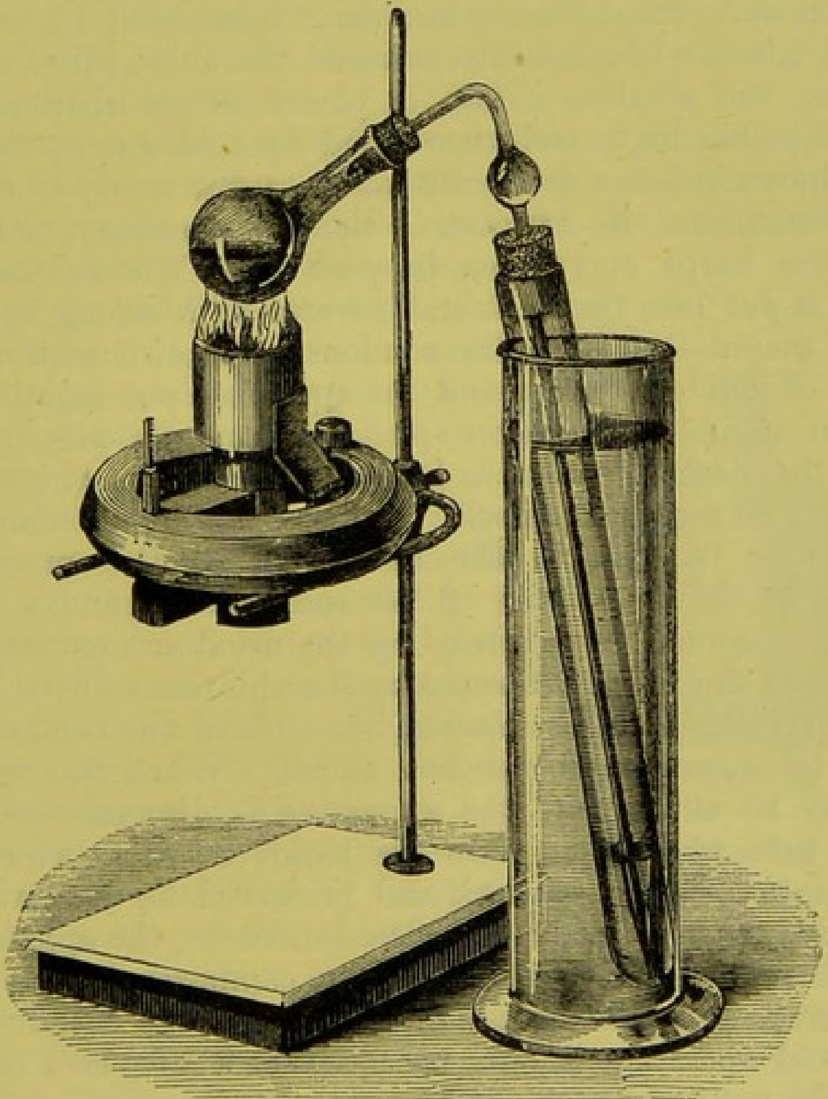

Fig. 27.

A drawing of the entire apparatus may be seen in most treatises on chemical analysis.

Owing to the great solubility of HCl in the form of gas, the apparatus must be so constructed that when all Cl is liberated and HCl begins to distil, a vacuum is not formed so that the liquid may rush back to the flask.

The best preventive of this regurgitation is, however, suggested by Fresenius, and applicable to each kind of apparatus; namely, the addition of a few pieces of pure magnesite. This substance dissolves but slowly in the hydrochloric acid, and so keeps up a constant flow of $CO^2$, the pressure of which is sufficient to prevent the return of the liquid.

The apparatus contrived by Fresenius is shown in fig. 26, and is exceedingly useful as an absorption apparatus for general purposes.

Mohr's apparatus is shown in fig. 27, and is, on account of its simplicity of construction, very easy to use.

The distilling flask is of about 2 oz. capacity, and is fitted with a cork soaked to saturation in melted paraffine; through the cork the delivery tube containing one bulb passes, and is again passed through a common cork, fitted loosely in a stout tube about 12 or 13 inches long and 1 inch wide, closed at one end like a test tube. This tube, containing the alkaline iodide, is placed in an hydrometer glass, about 12 inches high, and surrounded by cold water; the delivery tube is drawn out to a fine point, and reaches nearly to the bottom of the condenser. No support or clamp is necessary, as the hydrometer glass keeps everything in position. The substance to be distilled is put into the flask and covered with strong hydrochloric acid, the magnesite added, the condenser supplied with a sufficient quantity of iodide solution, and the apparatus put together tightly. Either an argand or common spirit lamp, or gas, may be used for heating the flask, but the flame must be manageable, so that the boiling can be regulated at will. In the case of the common spirit lamp it may be held in the hand, and applied or withdrawn according to the necessities of the case: the argand spirit or gas lamp can, of course, be regulated by the usual arrangements for the purpose. If the iodine liberated by the chlorine evolved should be more than will remain in solution, the cork of the condensing tube must be lifted, and more solution added. When the operation is judged to be at an end, the apparatus is disconnected, and the delivery tube washed out into the iodide solution, which is then emptied into a beaker or flask and preserved for analysis, a little fresh iodide solution is put into the condenser, the apparatus again put together, and a second distillation commenced, and continued for a minute or so, to collect every trace of free chlorine present. This second operation is only necessary as a safeguard in case the first should not have been complete.

The solutions are then mixed together and titrated in the manner previously described. In all cases the solution must be cooled before adding the thiosulphate, otherwise sulphuric acid might be formed.

Instead of the large test tube, some operators use a U tube to contain the potassic iodide, having a bulb in each limb, but the latter is not necessary if magnesite is used.

The solution of potassic iodide may conveniently be made of such a strength that $\frac{2}{10}$ eq. or 33·2 gm. are contained in the liter. 1 c.c. will then be sufficient to absorb the quantity of free iodine, representing 1 per cent. of oxygen in the substance analyzed, supposing it to be weighed in the metric system. In examining peroxide of manganese, for instance, 0·436 gm. or 4·36 grn. would be used, and supposing the percentage of peroxide to be about sixty, 60 c.c. or dm. of iodide solution would be sufficient to absorb the chlorine and keep in solution the iodine liberated by the process; it is advisable, however, to have an excess of iodide, and, therefore, in this case, about 70 c.c. or dm. should be used. A solution of indefinite strength will answer as well, so long as enough is used to absorb all the iodine. It may sometimes happen that not enough iodide is present to keep all the liberated iodine in solution, in which case it will separate out in the solid form; more iodide, however, may be added to dissolve the iodine, and the titration can then be made as usual.

The process of distillation above described may be avoided in many cases. There are a great number of substances which, by mere digestion with hydrochloric acid and potassic iodide at an elevated temperature, undergo decomposition quite as completely as by distillation. For this purpose a strong bottle with a very accurately ground stopper is necessary; and as the ordinary stoppered bottles of commerce are not sufficiently tight, it is better to re-grind the stopper with a little *very fine* emery and water. It must then be tested by tying the stopper tightly down and immersing in hot water; if any bubbles of air find their way through the stopper the bottle is useless. The capacity may vary from 30 to 150 c.c., according to the necessities of the case.

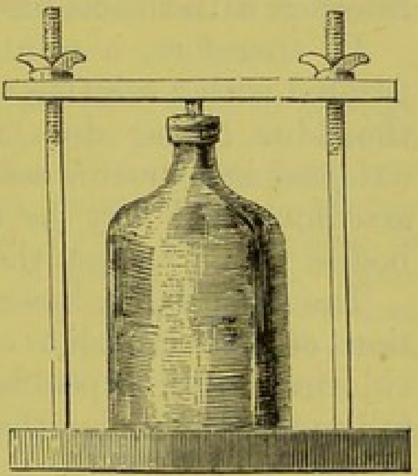
Fig. 28.

The stopper may be secured by fine copper binding-wire, or a kind of clamp contrived by Mohr may be used, as shown in fig. 28; by means of the thumb-screws the pressure upon the stopper may be increased to almost any extent.

The substance to be examined, if in powder, is put into the bottle with pure flint pebbles or small garnets, so as to divide it better, and a sufficient quantity of *saturated* solution of potassic iodide and pure hydrochloric acid added; the stopper is then inserted, fastened down, and the bottle suspended in a water bath, and the water is gradually heated to boiling by a gas flame or hot plate as may be most convenient. When the decomposition is complete the bottle is removed, allowed to cool somewhat, then placed in cold water, and, after being shaken, emptied into a beaker, and the liquid diluted by the washings for titration.

The salts of chloric, iodic, bromic, and chromic acids, together with many other compounds, may be as effectually decomposed by digestion as by distillation; many of them even at ordinary temperatures. Recently precipitated oxides, or the natural oxides, when reduced to fine powder are readily dissolved and decomposed by very weak acid in the presence of potassic iodide (Pickering).

The potassic iodide used in the various analyses must be absolutely free from potassic iodate and free iodine, or if otherwise, the effect of the impurity must be known by blank experiment.

## ARSENIOUS ACID AND IODINE.

§ 36. The principle upon which this method of analysis is based is the fact, that when arsenious acid is brought in contact with iodine in the presence of water and free alkali, it is converted into arsenic acid, the reaction being—

$$As^2O^3 + 4I + 2Na^2O = As^2O^5 + 4NaI.$$

The alkali must be in sufficient quantity to combine with the hydriodic acid set free, and it is necessary that it should exist in the state of bicarbonate, as caustic or monocarbonated alkalies interfere with the colour of the blue iodide of starch used as indicator.

If, therefore, a solution of arsenious acid containing starch is titrated with a solution of iodine in the presence of sodic bicarbonate, the blue colour does not occur until all the arsenious acid is oxidized into arsenic acid. In like manner, a standard solution of arsenious acid may be used for the estimation of iodine or other bodies which possess the power of oxidizing it.

The chief value, however, of this method is found in the estimation of free chlorine existing in the so-called chloride of lime, chlorine water, hypochlorites of lime, soda, etc., in solution; generally included under the term of chlorimetry.

### Preparation of the Decinormal Solution of Sodic Arsenite.

$As^2O^3 = 198$; 4·95 gm. per liter.

The iodine solution is the same as described in § 34·1.

The corresponding solution of sodic arsenite is prepared by dissolving 4·95 gm. of the purest sublimed arsenious anhydride, in about 250 c.c. of distilled water in a flask, with about 20 gm. of the purest sodic bicarbonate. It is necessary that the acid should be in powder, and the mixture needs boiling and shaking for some time in order to complete the solution; when this is accomplished the mixture is diluted somewhat, then made up to the liter.

In order to test this solution, 10 c.c. are put into a beaker with a little starch liquor, and the iodine solution allowed to flow in from a burette, graduated in $\frac{1}{10}$ c.c., until the blue colour appears. If exactly 10 c.c. are required the solution is strictly decinormal; if otherwise, the necessary factor must be found for converting it to that strength.

*Starch-paper Indicator.*—Starch liquor cannot be used for the direct estimation of free chlorine, consequently resort must be had to an external indicator; and this is very conveniently found in starch-iodide paper, which is best prepared by mixing a portion of starch liquor with a few drops of solution of potassic iodide on a plate, and soaking strips of pure filtering paper therein. The paper so prepared is used in the damp state, and is far more sensitive than when dried.

*The Analysis:* In all cases the chlorine to be estimated must exist in an alkaline solution. In the case of bleaching powder this is already accomplished by the caustic lime which invariably exists in the compound.

The substance being brought under the burette containing the arsenious acid solution, the latter is suffered to flow until a drop of the mixture taken out with a glass rod and brought in contact with the prepared paper, no longer produces a blue spot. As the colour becomes gradually lighter towards the end of the process, it is not difficult to hit the exact point; should it, however, by any accident be overstepped, starch liquor may be added to the mixture, and iodine solution added until the blue colour is produced; the quantity so used is then deducted from the total arsenic solution.

*Examples:* 50 c.c. of chlorine water were mixed with solution of sodic carbonate, and brought under the arsenic burette, and 20 c.c. of solution added; on touching the prepared paper with the mixture no colour was produced, consequently the quantity used was too great; starch liquor was therefore added, and decinormal iodine, of which 3·2 c.c. were required to produce the blue colour. This gave 16·8 c.c. of arsenic solution, which multiplied by 0·003537, gave 0·05942 gm. of Cl in the 50 c.c. A second operation with the same water required 16·8 c.c. of arsenic solution direct, before the end of the reaction with iodized starch-paper was reached.

The arsenic solution is equally as serviceable as thiosulphate for the general estimation of iodine, sulphuretted hydrogen, chromates, etc., by distillation with hydrochloric acid, and possesses the great advantage of being permanent in strength for almost any period of time.

# PART IV.

# ANALYSIS BY PRECIPITATION.

§ 37. The general principle of this method of determining the quantity of any given substance is alluded to in § 1, and in all instances is such that the body to be estimated forms an insoluble precipitate with a titrated re-agent. The end of the reaction is, however, determined in three ways.

1. By adding the re-agent until no further precipitate occurs, as in the determination of chlorine by silver.
2. By adding the re-agent in the presence of an indicator contained either in the liquid itself, or brought externally in contact with it, so that the slightest excess of the re-agent shall produce a characteristic reaction with the indicator; as in the estimation of silver with salt by the aid of potassic chromate, or with sulphocyanate and ferric sulphate, or that of phosphoric acid with uranium by yellow potassic prussiate.
3. By adding the re-agent to a clear solution, until a precipitate occurs, as in the estimation of cyanogen by silver.

The first of these endings can only be applied with great accuracy to silver and chlorine estimations. Very few precipitates have the peculiar quality of chloride of silver; namely, almost perfect insolubility, and the tendency to curdle closely by shaking, so as to leave the menstruum clear. Some of the most insoluble precipitates, such as baric sulphate and calcic oxalate, are unfortunately excluded from this class, because their finely divided or powdery nature prevents their ready and perfect subsidence.

In all these cases, therefore, it is necessary to find an indicator, which brings them into class 2.

The third class comprises only two processes; viz., the determination of cyanogen by silver, and that of chlorine by mercuric nitrate.

Since the estimation of chlorine by precipitation with silver, and that of silver by sulphocyanic acid, can be used in many cases for the indirect estimation of many other substances with great exactness, the preparation of the necessary standard solutions will now be described.

## SILVER AND CHLORINE.

### 1. Decinormal Solution of Silver.

16·966 gm. $AgNO^3$ per liter.

10·766 gm. of pure silver are dissolved in pure dilute nitric acid with gentle heat in a flask, into the neck of which a small funnel is dropped to prevent loss of liquid by spirting. When solution is complete, the funnel must be washed inside and out with distilled water into the flask, and the liquid diluted to a liter; but if it be desired to use potassic chromate as indicator in any analysis, the solution must be neutral; in which case the solution of silver in nitric acid is evaporated to dryness, and the residue dissolved in a liter; or, what is preferable, 16·966 gm. of pure and dry silver nitrate are dissolved in a liter of distilled water. If the grain system is used, 107·66 grn. of silver or 169·66 grn. of nitrate are dissolved, and the solution diluted to 10,000 grains.

### 2. Decinormal Solution of Salt.

5·837 gm. NaCl per liter.

5·837 gm. of pure sodic chloride are dissolved in distilled water, and the solution made up to a liter, or 58·37 grn. to 10,000 grains.

There are two methods by which the analysis may be ended:

(*a*) By adding silver cautiously, and well shaking after each addition till no further precipitate is produced. For details see § 50.

(*b*) By using a few drops of solution of potassic chromate as indicator, as devised by Mohr.

The method *b* is exceedingly serviceable, on the score of saving both time and trouble. The solutions must be absolutely free from acid or any great excess of alkali; it is best to have them neutral, and cold. When, therefore, acid is present in any solution to be examined, it should be neutralized with pure sodic or calcic carbonate in very slight excess.*

*The Analysis:* To the neutral or faintly alkaline solution, two or three drops of a cold solution of potassic chromate free from chlorine are added, and the silver solution delivered from the burette until the last drop or two produce a faint blood-red tinge, an evidence that all the chlorine has combined with the silver, and the slight excess has formed a precipitate of silver chromate; the reaction is very delicate and easily distinguished. The colour reaction is even more easily seen by gas-light than by daylight. It may be rendered more delicate by adopting the plan suggested by Dupré (*Analyst,* v. 123). A glass cell, about 1 centimeter in depth, is filled with water tinted with chromate to the same colour as the solution to be titrated. The operation is performed in a white porcelain basin. The faintest appearance of the red change is at once detected on looking through the coloured cell. For the analysis of waters weak in chlorine this method is very serviceable (see § 40).

*Example:* 1 gm. of pure sodic chloride was dissolved in 100 c.c. of water, a few drops of chromate added, and titrated with $\frac{N}{10}$ silver, of which 17·1 c.c. were required to produce the red colour; multiplied by the $\frac{N}{10}$ factor for sodic chloride = 0·005837 the result was 0·998 gm. NaCl, instead of 1 gm.

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* Silver chromate is sensibly soluble in the presence of alkaline or earthy nitrates, especially at a high temperature; sodic and calcic nitrates have the least effect; ammonic, potassic, and magnesic nitrates the greatest. See also Carpenter (*J.S.C.I.* v. 286).

## INDIRECT ESTIMATION OF AMMONIA, SODA, POTASH, LIME, AND OTHER ALKALIES AND ALKALINE EARTHS, WITH THEIR CARBONATES, NITRATES, AND CHLORATES, ALSO NITROGEN, etc., BY MEANS OF DECINORMAL SILVER SOLUTION, AND POTASSIC CHROMATE, AS INDICATOR.

1 c.c. $\frac{N}{10}$ silver solution = $\frac{1}{10000}$ H. eq. of each substance.

§ 38. Mohr, with his characteristic ingenuity, has made use of the delicate reaction between chlorine and silver, with potassic chromate as indicator, for the determination of the bodies mentioned above. All compounds capable of being converted into neutral chlorides by evaporation to dryness with hydrochloric acid may be determined with great accuracy. The chlorine in a combined state is, of course, the only substance actually determined; but as the laws of chemical combination are exact and well known, the measure of chlorine is also the measure of the base with which it is combined.

In most cases it is only necessary to slightly supersaturate the alkali, or its carbonate, with pure hydrochloric acid; evaporate on the water bath to dryness, and heat for a time to 120° C. in the air bath, then dissolve to a given measure, and take a portion for titration.

**Alkalies and Alkaline Earths** with organic acids are ignited to convert them into carbonates, then treated with hydrochloric acid, and evaporated as before described.

**Carbonic Acid** in combination may be determined by precipitation with baric chloride, as in § 26. The washed precipitate is dissolved on the filter with hydrochloric acid (covering it with a watch-glass to prevent loss), and then evaporated to dryness repeatedly till all HCl is driven off. In order to titrate with accuracy by the help of potassic chromate, the baryta must be precipitated by means of a solution of pure sodic or potassic sulphate, in slight excess; the precipitated baric sulphate does not interfere with the delicacy of the reaction. If this precaution were not taken, the yellow baric chromate would mislead.

**Free Carbonic Acid** is collected by means of ammonia and baric chloride (as in § 26), and the estimation completed as in the case of combined $CO^2$.

**Chlorates** are converted into chlorides by ignition before titration.

**Nitrates** are evaporated with concentrated hydrochloric acid, and the resulting chlorides titrated, as in the previous case.

**Nitrogen.** The ammonia evolved from guano, manures, oilcakes, and sundry other substances, when burned with soda lime in Will and Varrentrapp's apparatus, is conducted through dilute hydrochloric acid; the liquid is carefully evaporated to dryness before titration.

In all cases the operator will, of course, take care that no chlorine from extraneous sources other than the hydrochloric acid is present; or if it exists in the bodies themselves as an impurity, its quantity must be first determined.

*Example:* 0·25 gm. pure sodic carbonate was dissolved in water, and hydrochloric acid added till in excess; it was then dried on the water bath till no further vapours of acid were evolved; the resulting white mass was heated for a few minutes to about 150° C., dissolved and made up to 300 c.c. 100 c.c. required 15·7 c.c. $\frac{N}{10}$ silver, this multiplied by 3 gave 47·1 c.c., which multiplied by the $\frac{N}{10}$ factor for sodic carbonate=0·0053, gave 0·24963 gm. instead of 0·25 gm.

**Indirect Estimation of Potash and Soda existing as Mixed Chlorides.** It is a problem of frequent occurrence to determine the relative quantities of potash and soda existing in mixtures of the two alkalies—such as occur, for instance, in urine, manures, soils, waters, etc. The actual separation of potash from soda by means of platinum is tedious, and not always satisfactory.

The following method of calculation is frequently convenient, since a careful estimation of the chlorine present in the mixture is the only labour required; and this can most readily be accomplished by $\frac{N}{10}$ silver and potassic chromate, as previously described.

(1) The weight of the mixed pure chlorides is accurately found and noted.

(2) The chlorides are then dissolved in water, and very carefully titrated with $\frac{N}{10}$ silver and chromate for the amount of chlorine present, which is also recorded; the calculation is then as follows:—

The weight of chlorine is multiplied by the factor 2·103; from the product so obtained is deducted the weight of the mixed salts found in 1. The remainder multiplied by 3·6288 will give the weight of sodic chloride present in the mixture.

The weight of sodic chloride deducted from the total as found in 1 will give the weight of potassic chloride.

Sodic chloride × 0·5302 = Soda ($Na^2O$).
Potassic chloride × 0·6317 = Potash ($K^2O$).

The principle of the calculation, which is based on the atomic constitution of the individual chlorides, is explained in most of the standard works on general analysis. It is necessary, however, to bear in mind that this method of calculation can only be relied on when the two bases exist in about equal quantities, or at least not less than one part of one to two of the other.

Another method of calculation in the case of mixed potassic and sodic chlorides is as follows:—

The weight of the mixture is first ascertained and noted; the chlorine is then found by titration with $\frac{N}{10}$ silver, and calculated to NaCl; the weight so obtained is deducted from the original weight of the mixture, and the remainder multiplied by 2·42857 will give potassium K.

It is a remarkable fact that the coefficient required for calculating a certain compound from the weight of two bases is the same, whatever the bases may be, provided that but one acid be present in combination with the two bases, and that the salt having the smaller atomic weight be determined by titration (Fleischer).

## SILVER AND SULPHOCYANIC (THIOCYANIC) ACID.

§ 39. This process has been devised by Volhard and is fully described by the author (*Liebig's Ann. d. Chem.* cxc. 1), and has been favourably noticed by Falck (*Z. a. C.* xiv. 227), Brügelman (*Z. a. C.* xvi. 7), and Drechsel (*Z. a. C.* xvi. 351). It differs from Mohr's chromate method in that the silver solutions may contain free nitric acid.

The process can be used for the estimation of silver in the presence of copper up to 70 per cent.; also in presence of antimony, arsenic, iron, zinc, manganese, lead, cadmium, bismuth, and also cobalt and nickel, unless the proportion of these latter metals is such as to interfere by intensity of colour.

It can further be used for the indirect estimation of chlorine, bromine, and iodine, in presence of each other, existing either in minerals or inorganic compounds, and for copper and zinc; these will be noticed under their respective heads.

### 1. Decinormal Ammonic Sulphocyanate.

This solution cannot be prepared by weighing the sulphocyanate direct, owing to the deliquescent nature of the salt; but, supposing it could be weighed, the quantity would be 7·6 gm. per liter; therefore about 8 gm. of the purified crystals may be dissolved in about a liter of water as a basis for getting an exact solution, which must be finally adjusted by a correct decinormal silver solution.

The standard solution so prepared remains of the same strength for a very long period if preserved from evaporation.

### 2. Decinormal Silver Solution.

This is the same as described in the preceding section, and may contain free nitric acid if made direct from metallic silver.

### 3. Ferric Indicator.

This may consist simply of a saturated solution of iron alum; or may be made by oxidizing ferrous sulphate with nitric acid, evaporating with excess of sulphuric acid to dissipate nitrous fumes, and dissolving the residue in water so that the strength is about 10 per cent.

5 c.c. of either of these solutions are used for each titration, which must always take place at ordinary temperatures.

### 4. Pure Nitric Acid.

This must be free from the lower oxides of nitrogen, secured by diluting the usual pure acid with about a fourth part of water, and boiling till perfectly colourless. It should then be preserved in the dark.

The quantity of nitric acid used in the titration may vary within wide limits, and seems to have no effect upon the precision of the method.

*The Analysis for Silver:* 50 c.c. of $\frac{N}{10}$ silver solution are placed into a flask, diluted somewhat with water and 5 c.c. of ferric indicator added, together with about 10 c.c. of nitric acid. If the iron solution should cause a yellow colour, the nitric acid will remove it. The sulphocyanate is then delivered in from a burette; at first a white precipitate is produced rendering the fluid of a milky appearance, and as each drop of sulphocyanate falls in, it produces a reddish-brown cloud which quickly disappears on shaking. As the point of saturation approaches, the precipitate becomes flocculent and settles easily; finally, a drop or two of sulphocyanate produces a faint brown colour which no longer disappears on shaking. If the solutions are correctly balanced, exactly 50 c.c. of sulphocyanate should be required to produce this effect.

The colour is best seen by holding the flask so as to catch the reflected light of a white wall.

## PRECISION IN COLOUR REACTIONS.

§ 40. Dupré adopts the following ingenious method for colour titrations (*Analyst*, v. 123):—As is well known, the change from pale yellow to red, in the titration of chlorides by means of silver nitrate with neutral chromate as indicator, is more distinctly perceived by gas-light than by daylight; and in the case of potable waters, containing from one to two grains of chlorine per gallon, it is generally considered advisable to concentrate by evaporation previous to titration, or else to perform the titration by gas-light. The adoption of the following simple plan enables the operator to perceive the change of colour as sharply, and with as great a certainty, by daylight as by gas-light.

The water is placed into a white porcelain dish (100 c.c. are a useful quantity), a moderate amount of neutral chromate is added (sufficient to impart a marked yellow colour to the water), but instead of looking at the water directly, a flat glass cell containing some of the neutral chromate solution is interposed between the eye and the dish. The effect of this is to neutralize the yellow tint of the water; or, in other words, if the concentration of the solution in the cell is even moderately fairly adjusted to the depth of tint imparted to the water, the appearance of the latter, looked at through the cell, is the same as if the dish were filled with pure water. If now the standard silver solution is run in, still looking through the cell, the first faint appearance of a red colouration becomes strikingly manifest; and what is more, when once the correct point has been reached the eye is never left in doubt, however long we may be looking at the water. A check experiment in which the water, with just a slight deficiency of silver, or excess of chloride, is used for comparison is therefore unnecessary.

A similar plan will be found useful in other titrations. Thus, in the case of turmeric, the change from yellow to brown is perceived more sharply and with greater certainty when looking through a flat cell containing tincture of turmeric of suitable concentration than with the naked eye. The liquid to be titrated should, as in the former case, be placed into a white porcelain dish. Again, in estimating the amount of carbonate of lime in a water by means of decinormal sulphuric acid and cochineal, the exact point of neutrality can be more sharply fixed by looking through the cell filled with a cochineal solution. In this case the following plan is found to answer best. The water to be tested—about 250 c.c.—is placed into a flat porcelain evaporating dish, part of which is covered over with a white porcelain plate. The water is now tinted with cochineal as usual, and the sulphuric acid run in, the operator looking at the dish through the cell containing the neutral cochineal solution. At first the tint of the water and the tint in which the porcelain plate is seen are widely different; as however, the carbonate becomes gradually neutralized, the two tints approach each other more and more, and when neutrality is reached they appear identical; assuming that the strength of the cochineal solution in the cell, and the amount of this solution added to the water, have been fairly well matched. Working in this manner it is not difficult (taking $\frac{1}{4}$ liter of water) to come within 0·1 c.c. of decinormal acid in two successive experiments, and the difference need never exceed 0·2 c.c. In the cell employed the two glass plates are a little less than half an inch apart.

A somewhat similar plan may be found useful in other titrations, or, in fact, in many operations depending on the perceptions of colour change.

## THE COLORIMETER.

§ 41. Several methods of analysis by colour titration are given in the following pages, and therefore it is only appropriate that any convenient instrument which may facilitate these methods should be described.

Several varieties of form have been devised by operators, but the principle is the same; and as Dr. Mills has given some considerable attention to the subject, and his instrument has found acceptance with chemists generally, the following details are given.

Mills's detached colorimeter is made in two pieces, alike in every respect; one of these is represented in the subjoined figure. It consists of a stout glass tube having a broad flat foot, and graduated into 100 equal parts; its capacity is about 120 c.c. On the top of this is a loosely fitting brass cap, prolonged downwards so as to cover and shade the surface of the liquid, thereby preventing the appearance of a dark meniscus. The surface of the liquid is only visible sideways through the little aperture cut out for that purpose. The cap is perforated centrally: and a short tube rises from the perforation. This tube is soldered laterally to a narrower one, and this again to a small block, from which rises a spring carrying another small block. The narrower tube has, cemented into it, a glass tube, which passes straight downwards, and reappears below the flat surface of the cap, its end amply clearing that surface. This tube is coned outwards at its upper extremity, but is left plain below. Through it there passes, with just sufficient room to move, a rod, bent below twice at right angles, so as to carry a flat circular opal glass disk, to which it is attached by fusion. These disks are turned in the lathe: their surfaces should be polished free from scratches, and their edges show no bevel. The rod is prevented from falling by the easy pressure of a little half-tube, carried by the small block. When the thumb and forefinger are lightly pressed on each side of the cap, the rod can be readily moved up and down, and will then stay in any position in which it may have been left. It is convenient to cone outwards the half-tube at both its ends; but only traces of liquid ever reach this spot.

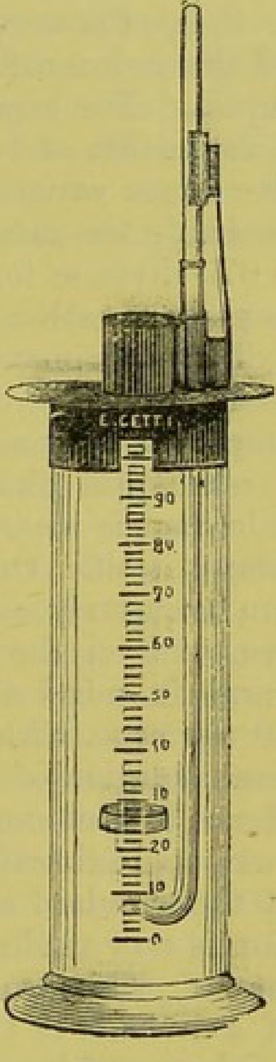

Fig. 29.

The instrument has two accessories which are of considerable service. These consist (1) of a pair of glass disks, lying at the bottom of the tube, one having a suitable red, the other a green colour; there is thus obtained a black ground, on which the opal disk is always seen through the upper opening. An annulus of deeper tint than a given observed colour would otherwise surround the opal disk, and tend to confuse the determination. It is an advantage at times to use other colours, and even to cover the opal disk with a plate of coloured glass. The other accessory is (2) a black hemispherical button. This lies loosely on the opal disk, as shown in the figure. It is used in the estimation of turbidities (*i.e.* precipitates) by lowering it until its point just disappears.

In taking readings, the position of the flat surface with regard to the scale is always the object to be ascertained; and this can be done, as is the case with Erdmann's float, so as entirely to avoid parallax. The level of the liquid's surface is afterwards taken; and the difference between the two readings is the depth required; but if the button be used, the height of the button must be subtracted from that difference.

It is, of course, obvious that any upward or downward movement of the rod must alter somewhat the level of the surface of the liquid. For small variations thus produced (as, for example, by a depression of two or three divisions) no correction need be made. For larger variations a factor is easily found by experiment; it is probably the same in every specimen of the instrument, viz., nearly 0·015 division for every division the rod is moved. This correction is perhaps rather better than direct reading.

The colorimeter has been of late years more extensively used than formerly; but it would probably be much more widely employed if its service were better understood. Thus, for example, a red liquid like a solution of magenta is admirably suited for colorimetric measurement, it having a tint to which the eye readily adapts itself. On the other hand, it is rare to find any one who can accurately estimate yellow. Something thus depends on the eye, and on the employment of the same eye. It must also be borne in mind that very few liquids will stand a dilution of over 20 per cent. without undergoing chemical change. Thus, a very weak solution of magenta differs in actual colour from a strong one. Hence it is obviously necessary to use the first determination as a mere approximation; and, on that as a basis, to alter the strengths of the standard and trial liquid to equality. A second determination is now made, and a still closer approximation obtained by its means. This process being repeated until there is only a difference of a division or two between the two liquids.

The second approximation will in general be found sufficiently exact. All dilutions should, as far as possible, have the same age. With regard to the standard tint selected, the operator has in this colorimeter the means of varying his standard to any extent by shifting one opal disk; he can thus work at the particular depth of tint which he finds most suitable to his own eye. Steady accuracy in any particular measurement can generally be obtained by at most a few days' practice.

*Turbidities.*—A black or coloured disk, lowered through a turbid liquid, eventually vanishes, and the depth at which disappearance takes place is a measure of the amount of turbidity present. In this way, for example, it is easy to estimate the amount of water added to milk. It is obvious, however, that this method admits of quantitative extension to all sorts of precipitates, provided we can find a suitable medium to ensure their suspension as a turbidity, and not in the aggregated state, during a suitable time.

The suspensory liquid consists of 100 gm. of gelatine, 100 gm. at most of glacial acetic acid, and 1 gm. of salicylic acid, dissolved in a liter of distilled water; this is clarified with a little white of egg, and filtered hot. It remains permanently liquid in the cold, and does not putrefy. It may, if desired, be charged with any special re-agent (baric chloride for instance); a volume of the mixture can then be added to a volume of a very weak standard sulphate, and also to a volume of sulphate of unknown strength; by depressing the black buttons, the colorimeters determine the relation between the two. The reacting bodies should in such cases be the same; thus, hydric sulphate should not be compared against potassic sulphate. The key to success in colorimetry is, in fact, equality of condition:

If the precipitant should be alkaline, or an alkaline carbonate, the gelatine solution should first be neutralized, and then mixed with more alkali or carbonate. Such solutions as aqueous magnesic chloride and zinc sulphate can then be added, the whole instantly well shaken, and the result compared with a standard effect in the other tube.

Lime can be determined by adding ammonia and ammonic oxalate to the suspensory liquid, and then a weak solution of calcic salt.

There is probably no substance incapable of suspension for more than half an hour—a period sufficient for thirty comparisons; and most precipitates will refuse to fall for hours, sometimes for days, together. Traces of argentic chloride will remain unprecipitated in this liquid for months. The operator has therefore only to select such a strength of standard precipitate as shall give him not too great an amount to suspend, and an opacity equal to about fifty scale-divisions. If the substance precipitated should be soluble in the solution of gelatine, that solution should be saturated, before use, with the precipitate in question.

The colorimeter is an instrument admirably adapted for use in comparatively unskilled hands, and especially in those industrial analyses where one class of product is constantly tested by a single person.

### Directions for Use.

1. **Clear Liquids.**—The two coloured disks are put in first. The cap is then placed on one of the tubes, and the piston pushed down as far as it will go, the little window being over the scale. A clear coloured solution of known strength is poured in through the brass tube at the top, until the mark 100 is exactly reached. The tube is then placed on a table, preferably behind a ground-glass window, and the piston moved to a position such that, on looking down at it with one eye, the visible depth of tint is easy to remember. The other tube is similarly filled with the solution of unknown strength, and placed beside the first; its piston is raised until, when observed with the same eye, the depth of tint in both tubes appears to be the same. This depth is taken by subtracting the scale-reading opposite the piston's top from the reading at the level of the surface of the liquid. The relative

strengths of the liquids are inversely as the depths. Thus the standard being 50, and containing 2 per cent., the other solution reads 75; its strength was therefore 75 : 50 : : 2°/₀ : 1·33°/₀. It is well to work with different depths of the standard tint, and take the mean of the results. If the strengths differ by more than 10 per cent., they should be adjusted by dilution to less, and re-determined.

2. **Turbid Liquids.**—Milks are examined by diluting them 100 times, and comparing them with a milk of known strength, equally diluted. The comparison is made by lowering a black button through the liquid, until its rounded top just disappears. The calculation is made as above. Colourless metallic solutions are examined by precipitating them with some suitable re-agent, and shaking with an equal volume of a 10-per-cent. acetic solution of gelatine; the turbid liquid thus made is compared with a similar preparation of known strength, by lowering the black buttons.

# PART V.

# APPLICATION OF THE FOREGOING PRINCIPLES OF ANALYSIS TO SPECIAL SUBSTANCES.

## ANTIMONY.

Sb=120.

### 1. Conversion of Antimonious Acid in Alkaline Solution into Antimonic Acid by Iodine (Mohr).

§ 42. ANTIMONIOUS oxide, or any of its compounds, is brought into solution as tartrate by tartaric acid and water; the excess of acid neutralized by sodic carbonate; then a cold saturated solution of sodic bicarbonate added, in the proportion of 20 c.c. to about 0·1 gm. $Sb^2O^3$; to the clear solution starch liquor and $\frac{N}{10}$ iodine are added until the blue colour occurs. The colour disappears after a little time, therefore the first appearance of a permanent blue is accepted as the true measure of iodine required.

1 c.c $\frac{N}{10}$ iodine=0·0060 gm. Sb.

### Estimation of Antimony in presence of Tin (Type and Britannia metal, etc.).

The finely divided alloy is dissolved in strong hydrochloric acid by heat, adding frequently small quantities of potassic chlorate. The liquid is boiled to remove free chlorine, cooled, a slight excess of strong solution of potassic iodide added, and the liberated iodine estimated by standard thiosulphate.

120 Sb liberate 253 I, and the weight of I found multiplied by 0·475=Sb.

If iron or other metal capable of liberating iodine be present, treat the alloy with nitric acid, and evaporate to obtain the oxides of antimony and tin—wash, boil in hydrochloric acid, and proceed as before described. The rationale is, that antimonic chloride is reduced to antimonious chloride, while stannic chloride is not affected.

### 2. Oxidation by Potassic Bichromate or Permanganate (Kessler)

Bichromate or permanganate added to a solution of antimonious chloride, containing not less than $\frac{1}{6}$ of its volume of hydrochloric acid (sp. gr. 1·12), converts it into antimonic chloride.

The reaction is uniform only when the minimum quantity of acid indicated above is present, but it ought not to exceed $\frac{1}{3}$ the volume, and the precautions before given as to the action of hydrochloric acid on permanganate must be taken into account, hence it is preferable to use bichromate.

Kessler (*Poggend. Annal.* cxviii. 17) has carefully experimented upon this method and adopts the following processes.

A standard solution of arsenious acid is prepared containing 5 gm. of the pure acid, dissolved by the aid of sodic hydrate, neutralized with hydrochloric acid, 100 c.c. concentrated hydrochloric acid added, then diluted with water to 1 liter; each c.c. of this solution contains 0·005 gm. $As^2O^3$, and represents exactly 0·007253 gm. $Sb^2O^3$.

Solutions of potassic bichromate and ferrous sulphate of known strength in relation to each other, are prepared in the usual way; and a freshly prepared solution of potassic ferricyanide used as indicator.

The relation between the bichromate and arsenious solution is found by measuring 10 c.c. of the latter into a beaker, 20 c.c. hydrochloric acid of sp. gr. 1·12, and from 80 to 100 c.c. of water (to insure uniformity of action the volume of HCl must never be less than $\frac{1}{6}$ or more than $\frac{1}{3}$); the bichromate solution is then added in excess, the mixture allowed to react for a few minutes, and the ferrous solution added until the indicator shows the blue colour. To find the exact point more closely, $\frac{1}{2}$ or 1 c.c. bichromate solution may be added, and again iron, until the precise ending is obtained.

*The Analysis.* The material, free from organic matter, organic acids, or heavy metals, is dissolved in the proper proportion of HCl, and titrated precisely as just described for the arsenious solution; the strength of the bichromate solution having been found in relation to $As^2O^3$ the calculation as respects $Sb^2O^3$ presents no difficulty. Where direct titration is not possible the same course may be adopted as with arsenic (§ 43.2); namely, precipitation with $H^2S$ and digestion with mercuric chloride.

In the case of using permanganate it is equally necessary to have the same proportion of HCl present in the mixture, and the standard solution must be added till the rose colour is permanent. The permanganate may be safely used with $\frac{1}{4}$ the volume of HCl, with the addition of some magnesic sulphate, and as the double tartrate of antimony and potassium can readily be obtained pure, and the organic acid exercises no disturbing effect in the titration, it is a convenient material upon which to standardize the solution.

### 3. Distillation of Antimonious or Antimonic Sulphide with Hydrochloric Acid, and Titration of the evolved Sulphuretted Hydrogen (Schneider).

When either of the sulphides of antimony is heated with hydrochloric acid in Bunsen's, Fresenius', or Mohr's distilling apparatus (§ 35), for every 1 eq. of antimony present as sulphide, 3 eq. of $H^2S$ are liberated. If, therefore, the latter be estimated, the quantity of antimony is ascertained. The process is best conducted as follows:—

The antimony to be determined is brought into the form of ter- or pentasulphide (if precipitated from a hydrochloric solution, tartaric acid must be previously added to prevent the precipitate being contaminated with chloride), which, together with the filter containing it, is put into the distilling flask with a tolerable quantity of hydrochloric acid not too concentrated. The absorption tube contains a mixture of caustic soda or potash, with a definite quantity of $\frac{N}{10}$ arsenious acid solution (§ 36) in sufficient excess to retain all the sulphuretted hydrogen evolved. The flask is then heated to boiling, and the operation continued till all evolution of sulphuretted hydrogen has ceased; the mixture is then poured into a beaker, and acidified with hydrochloric acid, to precipitate all the arsenious sulphide. The whole is then diluted to, say 300 c.c., and 100 c.c. taken with a pipette, neutralized with sodic carbonate, some bicarbonate added, and the titration for excess of arsenious acid performed with $\frac{N}{10}$ iodine and starch, as directed in § 36. The separation of antimony may generally be insured by precipitation as sulphide. If arsenic is precipitated at the same time, it may be removed by treatment with ammonic carbonate.

## ARSENIC.

$$As=75. \quad As^2O^3=198.$$

### 1. Oxidation by Iodine (Mohr).

§ 43. THE principle upon which the determination of arsenious acid by iodine is based is explained in § 36.

Experience has shown, that in the estimation of arsenious compounds by the method there described, it is necessary to use sodic bicarbonate for rendering the solution alkaline in preference to the neutral carbonate, as there is less chance of the iodine being affected by the bicarbonate than by the neutral salt.

To a neutral or watery solution, therefore, it is best to add about 20 or 25 c.c. of saturated solution of pure bicarbonate to every 0·1 gm. or so of $As^2O^3$, and then titrate with $\frac{N}{10}$ iodine and starch. When the solution is acid, the excess may be removed by neutral sodic carbonate, then the necessary quantity of bicarbonate added, and the titration completed as before.

$$1 \text{ c.c. } \tfrac{N}{10} \text{ iodine} = 0·00495 \text{ gm. } As^2O^3.$$

**Titration of Arseniates.** In the previous edition of this book it was recommended, on the authority of Barnes, to estimate the arsenic acid in commercial arseniates of soda, etc., by reduction with sulphurous acid (passing the gas through the liquid), boiling off the excess of $SO^2$, neutralizing with sodic bicarbonate, and titrating with iodine as described above. This method has not given me satisfactory results. The mere passing the gaseous $SO^2$ through the liquid does not, in all cases, insure the complete reduction to arsenious acid.

Holthof (*Z. a. C.* xxii. 378) and McKay (*C. N.* liii. 221—243) have experimented largely on this method of estimating arsenic, which was really originally suggested by Mohr, but never widely adopted, owing to the defect already mentioned. Holthof proved that various forms of arsenic, on being converted into arsenic acid, would bear evaporation to dryness with HCl without loss, and that arsenic sulphide could be oxidized by strong nitric acid, or with HCl and $KClO^3$ to arsenic acid, and reduced to the lower state of oxidation by copious treatment with $SO^2$, the method being to add 300 or 400 c.c. of strong solution of $SO^2$, digest on the water bath for two hours, then boil down to one-half, and when cool add sodic bicarbonate, and titrate with iodine and starch.

McKay shortens the method considerably by placing the mixture in a well-stoppered bottle, tying down the stopper, and digesting in boiling water for one hour. At the end of that time the bottle is removed and allowed to cool somewhat, then emptied into a boiling flask, diluted with about double its volume of water, and then boiled down by help of a platinum spiral to one-half. The liquid is then cooled, diluted, and either the whole or an aliquot portion titrated in the usual way.

For quantities of material representing about 0·1 gm. As, 30 c.c. of saturated solution of $SO^2$ will suffice, and the reduction may therefore be made in a bottle holding 50 or 60 c.c. (§ 35). The results are very satisfactory. In the case of titrating commercial alkaline arseniates, which often contain small quantities of arsenious acid, this must be estimated first, and the amount deducted from the total obtained after reduction.

### 2. Oxidation by Potassic Bichromate (Kessler).

This method is exactly the same as is fully described in § 42 for antimony.

The arsenious compound is mixed with $\frac{N}{10}$ bichromate in excess in presence of hydrochloric acid and water, in such proportion that at least $\frac{1}{6}$ of the total volume consists of hydrochloric acid (sp. gr. 1·12).

The excess of bichromate is found by a standard solution of pure iron, or of double iron salt, with potassic ferricyanide as indicator; the quantity of bichromate reduced is, of course, the measure of the quantity of arsenious converted into arsenic acid.

$$1 \text{ c.c. } \tfrac{N}{10} \text{ bichromate} = 0·00495 \text{ gm. } As^2O^3.$$

In cases where the direct titration of the hydrochloric acid solution cannot be accomplished, the arsenious acid is precipitated with $H^2S$ (with arsenates at 70°C.), the precipitate well washed, the filter and the precipitate placed in a stoppered flask, together with a saturated solution of mercuric chloride in hydrochloric acid of 1·12 sp. gr., and digested at a gentle heat until the precipitate is white, then water added in such proportion that not less than $\frac{1}{6}$ of the volume of liquid consists of concentrated HCl; $\frac{N}{10}$ bichromate is then added, and the titration with standard ferrous solution completed as usual.

### 3. Indirect Estimation by Distilling with Chromic and Hydrochloric Acids (Bunsen).

The principle of this very exact method depends upon the fact, that when potassic bichromate is boiled with concentrated hydrochloric acid, chlorine is liberated in the proportion of 3 eq. to 1 eq. chromic acid (see § 52.2).

If, however, arsenious acid is present, but not in excess, the chlorine evolved is not in the proportion mentioned above, but so much less as is necessary to convert the arsenious into arsenic acid.

$$As^2O^3 + 4Cl + 2H^2O = As^2O^5 + 4HCl.$$

Therefore every 4 eq. of chlorine, short of the quantity yielded when bichromate and hydrochloric acid are distilled alone, represent 1 eq. arsenious acid. The operation is conducted in the apparatus fig. 26 or 27.

### 4. By Precipitation as Uranic Arsenate (Bödeker).

The arsenic must exist in the state of arsenic acid ($As^2O^5$), and the process is in all respects the same as for the estimation of phosphoric acid, devised by Neubauer, Pincus, and myself (§ 69). The strength of the uranium solution may be ascertained and fixed by pure sodic or potassic arsenate, or by means of a weighed quantity of pure arsenious acid converted into arsenic acid by boiling with strong nitric acid. The method of testing is precisely the same as with phosphoric acid; that is to say, the solution of uranium used for $P^2O^5$ will suffice, and if its exact strength as regards that body be known, a slight calculation will show the quantity to be used for arsenic acid; but it is, nevertheless, preferable to titrate it upon a weighed amount of arsenical compound, bearing in mind here, as in the case of $P^2O^5$, that the titration must take place under precisely similar conditions as to quantity of liquid, the amount of sodic acetate and acetic acid added, and the depth of colour obtained by contact of the fluid under titration with the yellow prussiate solution (see § 69).

The precipitate of uranic arsenate possesses the composition—

$$2[Ur^2O^3]As^2O^5 = 566.$$

The solution of arsenic acid must of course be free from metals liable to give a colour with the indicator. Alkalies, alkaline earths, and zinc are of no consequence, but it is advisable to add nearly the required volume of uranium to the liquid before heating.

The arsenic acid must be separated from all bases which would yield compounds insoluble in weak acetic acid.

The arsenetted hydrogen evolved from Marsh's apparatus may be passed into fuming $HNO^3$, evaporated to dryness, the arsenic acid dissolved in water (antimony if present is insoluble), then titrated cautiously with uranium in presence of free acetic acid and sodic acetate as above described.

### 5. By Standard Silver as Arsenate.

The principle of this method has been adopted by Pearce of the Colorado Smelting Company, and also by McCay (*C. N.* xlviii. 7). The authors, however, differ in the details of the process.

The former prefers to separate the arsenic as silver arsenate, and, estimating the silver so combined, thence calculate the arsenic. The latter uses a known excess of standard silver, and estimates the combined silver residually.

**Pearce's Process.**—The finely-powdered substance for analysis is mixed in a large porcelain crucible with from six to ten times its weight of a mixture of equal parts of sodic carbonate and potassic nitrate. The mass is then heated with a gradually increasing temperature to fusion for a few minutes, allowed to cool, and the soluble portion extracted by warming with water in the crucible, and filtering from the insoluble residue. The arsenic is in the filtrate as alkaline arsenate. The solution is acidified with nitric acid and boiled to expel $CO^2$ and nitrous fumes. It is then cooled to the ordinary temperature, and almost exactly neutralized as follows:—Place a small piece of litmus paper in the liquid: it should show an acid reaction. Now gradually add strong ammonia till the litmus turns blue, avoiding a great excess. Again make slightly acid with a drop or two of strong nitric acid; and then, by means of very dilute ammonia and nitric acid, added drop by drop, bring the solution to such a condition that the litmus paper, after having previously been reddened, will, in the course of half a minute, begin to show signs of alkalinity. The litmus paper may now be removed and washed, and the solution, if tolerably clear, is ready for the addition of silver nitrate. If the neutralization has caused much of a precipitate (alumina, etc.), it is best to filter it off at once, to render the subsequent filtration and washing of the arsenate of silver easier.

A solution of silver nitrate (neutral) is now added in slight excess; and after stirring a moment, to partially coagulate the precipitated arsenate, which is of a brick-red colour, the liquid is filtered, and the precipitate washed with cold water. The filtrate is then tested with silver and dilute ammonia, to see that the precipitation is complete.

The object is now to determine the amount of silver in the precipitate, and from this to calculate the arsenic. The arsenate of silver is dissolved on the filter with dilute nitric acid (which leaves undissolved any chloride of silver), and the filtrate titrated, after the addition of ferric sulphate, with ammonic thiocyanate (§ 39).

From the formula $3Ag^2O.As^2O^5$, 648 parts $Ag=150$ parts As, or $Ag : As=108 : 25$.

**McCay's Process.**—The preliminary fusion is the same as in the former method, but after acidulating with nitric acid and boiling off $CO^2$, the liquid is evaporated to dryness and heated till no more acid fumes are given off. The residue is taken up with water, filtered, made up to a definite volume, and the arsenic determined in the following manner:—

The solution of arsenic acid or arsenate is heated to boiling, and excess of standard silver nitrate run in; the liquid is then stirred briskly until the precipitate begins to settle and the liquid becomes clear, when the beaker is to be removed from the flame and left to cool to about 37°. Dilute ammonia is now carefully added until a cloudiness ceases to form. The solution should be well stirred before each successive addition, so as to obtain a clear liquid in order to observe the cloud formation more distinctly. The silver arsenate is finally filtered off and well washed; the filtrate is acidulated with nitric acid; ferric sulphate added; and the silver titrated with ammonic thiocyanate according to Volhard's method (§ 39). The amount of silver thus found deducted from the quantity taken gives the amount combined with the arsenic; and from this datum the quantity of arsenic present is calculated.

Of these two methods the preference must be given to the first on the score of accuracy, there being less probability of error from contaminating substances; both, however, are available for technical purposes.

Owing to the large amount of arsenate of silver formed from a small quantity of arsenic (nearly six times by weight), it is not at all necessary or even desirable to work with large amounts of substance. 0·5 gm. is usually sufficient for the determination of the smallest quantity of arsenic; and where the percentage is high, as little as 0·1 gm. may be taken with advantage. The method has been used with very satisfactory results on the sulphide of arsenic obtained in the ordinary course of analysis.

Substances such as molybdic and phosphoric acids, which may behave similarly to arsenic under this treatment, interfere, of course, with the method. Antimony, by forming antimoniate of sodium, remains practically insoluble and without effect.

The method has been used by McCay for the estimation of arsenic in the presence of alkaline earths, as occurring in some minerals, with success.

## BARIUM.

Ba=136·8.

§ 44. In a great number of instances the estimation of barium is simply the converse of the process for sulphuric acid (§ 73), using either a standard solution of sulphuric acid or a neutral sulphate, in a known excess, and finding the amount by residual titration.

When barium can be separated as carbonate, the estimation is made as in § 17.

### Precipitation as Baric Chromate.

*Direct Titration with Potassic Bichromate.*—A decinormal solution of bichromate for precipitation purposes must differ from that used for oxidation purposes. In the present case the solution is made by dissolving 7·37 gm. of pure potassic bichromate, and diluting to 1 liter.

The barium compound, which may contain alkalies, magnesia, strontia, and lime, is dissolved in a good quantity of water, ammonia free from carbonate added, heated to 60° or 70° C., and the standard bichromate added cautiously, with shaking, so long as the yellow precipitate of baric chromate is formed, and until the clear supernatant liquid possesses a faint yellow colour.

1 c.c. $\frac{N}{10}$ solution = 0·00684 gm. Ba.

*Titration of the Precipitate with Permanganate:* In this case the precipitate of baric chromate is well washed, transferred to a flask, and mixed with an excess of double iron salt; the amount of iron oxidized by the chromic acid is then estimated by titration with permanganate; the quantity of iron changed to the ferric state multiplied by the factor 0·8187=Ba.

## BISMUTH.

### Bi=210.

§ 45. The estimation of this metal or its compounds volumetrically has occupied the attention of Pattinson Muir, to whom we are indebted for several methods of gaining this end. Two of the best are given here, namely, (1) precipitation of the metal as basic oxalate, and titration with permanganate; (2) precipitation as phosphate with excess of standard sodic phosphate, and titration of that excess by standard uranic acetate.

### 1. Titration as Oxalate.

Normal bismuth oxalate, produced by adding excess of oxalic acid to a nitric solution of the metal, possesses the formula $Bi^2O^33C^2O^4+aq$. This precipitate, when separated by filtration, and boiled with successive quantities of water for three or four times, is transformed into basic oxalate, $Bi^2O^32C^2O^3+aq$. The method of titration is as follows:—

The solution containing bismuth must be free from hydrochloric acid, as the basic oxalate is readily soluble in that acid. A large excess of nitric acid must also be avoided. Oxalic acid must be added in considerable excess. If the precipitate be thoroughly shaken up with the liquid, and the vessel be then set aside, the precipitate quickly settles, and the supernatant liquid may be poured off through a filter in a very short time. If the precipitate be boiled for five or ten minutes with successive quantities of about 50 c.c. of water, it is quickly transformed into the basic salt. So soon as the supernatant liquid ceases to show an acid reaction, the transformation is complete. It is well to employ a solution of permanganate so dilute, that at least 50 c.c. are required for the titration ($\frac{N}{20}$ strength suffices). The basic oxalate may be dissolved in dilute sulphuric acid in place of hydrochloric; it is more soluble, however, in the latter acid. If the solution contains but little hydrochloric acid, there is no danger of chlorine being evolved during the process of titration.

In applying this process to the estimation of bismuth in a solution containing other metals, it is necessary, if the solution contain substances capable of acting upon, or of being acted on by permanganate, to separate the bismuth from the other metals present. This is easily done by precipitating in a partially neutralized solution with much warm water and a little ammonic chloride. The precipitate must be dissolved in nitric acid, and the liquid boiled down once or twice with addition of the same acid in order to expel all hydrochloric acid, before precipitating as oxalate. The liquid should contain just sufficient nitric acid to prevent precipitation of the basic nitrate before oxalic acid is added. 1 molecule oxalic acid corresponds to 1 atom bismuth, or 126=210.

A shorter method, based on the same reactions, has been arranged by Muir and Robbs (*J. C. S. I.* xli. 1). In this case, however, the double oxalate of potassium and bismuth is the compound obtained, the excess of oxalate of potash being determined residually. Reis (*Berichte*, xiv. 1172) has shown that when normal potassic oxalate is added to a solution of bismuth nearly free from mineral acid, but containing acetic acid, a double salt of the formula $Bi^2 (C^2O^4)^3, K^2C^2O^4$ is precipitated. In applying this process for the estimation of bismuth in mixtures, it is necessary to separate the metal as oxychloride, and that it should be obtained in solution as nitrate with a small excess of nitric acid. This is done by evaporating off the greater part of the free acid, allowing just sufficient to remain that the bismuth may remain in solution while hot. A large excess of acetic acid is then added, it is made up to a definite measure, and an aliquot portion taken for titration.

The solution of normal potassic oxalate standardized by permanganate must not be added in great excess. It is well, therefore, to deliver it into the bismuth liquid from a burette until the precipitation is apparently complete, then add a few extra c.c., and allow to remain for some time with shaking. It is then filtered through a dry filter, a measured portion taken, and the residual oxalic acid found by permanganate.

### 2. Precipitation as Phosphate.

The necessary standard solutions are—

(*a*) *Standard sodic phosphate* containing 35·8 gm. per liter, 1 c.c.=0·0071 gm. $P^2O^5$.

(*b*) *Standard uranic acetate*, corresponding volume for volume with the above, when titrated with an approximately equal amount of sodic acetate and free acetic acid.

Success depends very much upon identity of conditions, as is explained in § 69.

The bismuth to be estimated must be dissolved in nitric acid; bases other than the alkalies and alkaline earths must be absent. The absence of those acids which interfere with the determination of phosphoric acid by the uranium process (non-volatile, and reducing organic acids, sulphuretted hydrogen, hydriodic acid, etc.) must be assured. As bismuth is readily separated from other metals, with the exception of antimony and tin, by addition of much warm water and a little ammonic chloride to feebly acid solutions, a separation of the bismuth from those other metals which are present should precede the process of estimation. If alkalies or alkaline earths be alone present, the separation may be dispensed with. The precipitated bismuth salt is to be washed, dissolved in a little strong nitric acid, and the solution boiled down twice with addition of a little more nitric acid, in order to remove the whole of the hydrochloric acid present.

Such a quantity of a tolerably concentrated solution of sodic acetate is added as shall insure the neutralization of the nitric acid, and therefore the presence in the liquid of free acetic acid. If a precipitate form, a further addition of sodic acetate must be made. The liquid is heated to boiling; a measured volume of the sodic phosphate solution is run in; the boiling is continued for a few minutes; the liquid is passed through a ribbed filter, the precipitate being washed repeatedly with hot water; and the excess of phosphoric acid is determined in the filtrate by titration with uranium. If the filtered liquid be received in a measuring flask, which is subsequently filled to the mark with water, and if the inverted uranium method be then employed, the results are exceedingly accurate. This method is especially to be recommended in the estimation of somewhat large quantities of bismuth, since it is possible that in such cases a large amount of sodic acetate will have been used, which, as is well known, has a considerable disturbing effect on the reaction of the indicator.

If the bismuth solution contain a large excess of nitric acid, it is better to neutralize nearly with sodic carbonate before adding sodic acetate and titrating.

Fuller details of both the above processes are contained in *J. C. S.* 1877 (p. 674) and 1878 (p. 70).

## BROMINE.

### Br=80.

§ 46. This element, or its unoxidized compounds, can be estimated precisely in the same way as chlorine by $\frac{N}{10}$ silver solution (§ 37), or alkalimetrically as in § 28, or by sulphocyanate (§ 39), but these methods are seldom of any avail, since the absence of chlorine or its combinations is a necessary condition of accuracy.

Bromine in aqueous solution, or as gas, may be estimated by absorption with solution of potassic iodide, in many cases by mere digestion, and in other cases by distillation, in any of the forms of apparatus given in § 35, and the operation is carried out precisely as for chlorine (§ 50). 1 eq. I=1 eq. Br. or I found × 0·63 = Br.

A process for the estimation of bromine in presence of chlorine is still much wanted in the case of examining kelp liquors, etc. Heine (*Journ. f. pract. Chem.* xxxvi. 184) uses a colour method in which the bromine is liberated by free chlorine, absorbed by ether, and the colour compared with an ethereal solution of bromine of known strength. Fehling states that with care the process gives fairly accurate results. It is of course necessary to have an approximate knowledge of the amount of bromine present in any given solution.

Reimann (*Annal. d. Chem. u. Pharm.* cxv. 140) adopts the following method, which gives tolerably accurate results, but requires skill and practice.

The neutral bromine solution is placed in a stoppered vessel, together with a globule of chloroform about the size of a hazel nut. Chlorine water of known strength is then added cautiously from a burette, protected from bright light, in such a way as to insure first the liberation of the bromine, which colours the chloroform orange yellow; then more chlorine water, until the yellowish white colour of chloride of bromine occurs ($KBr+2Cl=KCl+BrCl$).

The operation may be assisted by making a weak solution of potassic chromate, of the same colour as a solution of chloride of bromine in chloroform, to serve as a standard of comparison.

The strength of the chlorine water is ascertained by potassic iodide and $\frac{N}{10}$ hyposulphite. 2 eq. Cl=1 eq. Br.

In examining mother-liquors containing organic matter, they must be evaporated to dryness in presence of free alkali, ignited, extracted with water; then neutralized with hydrochloric acid before titrating as above.

## CADMIUM

Cd=111·6

§ 47. This metal may be estimated, as is the case with many others, by precipitation as sulphide, and decomposing the sulphide with a ferric salt, the iron being reduced to the ferrous state in proportion to the amount of sulphide present.

Follenius has found that when cadmium is precipitated as sulphide in acid liquids, the precipitate is apt to be contaminated with salts other than sulphide to a small extent. The separation as sulphide is best made by passing $H^2S$ into the hot liquid which contains the cadmium, and which should be acidified with 10 per cent. of concentrated sulphuric acid by volume. From hydrochloric acid solutions the metal is only completely separated by $H^2S$ when the hot solution contains not more than 5 per cent of acid of sp. gr. 1·11, or 14 per cent. if the liquid is cold.

Ferric chloride is to be preferred for the decomposition of the cadmium sulphide, and the titration is carried out precisely as in the case of zinc (§ 78.2).

Cadmium may also be estimated, when existing as sulphate or nitrate, by precipitation as oxalate, and titration of the washed precipitate by permanganate. The details are carried out precisely as in the case of estimating zinc as oxalate (§ 78).

## CALCIUM.

Ca=40.

1 c.c. $\frac{N}{10}$ permanganate =0·0028 gm. CaO
,, ,, =0·0050 gm. $CaCO^3$
,, ,, =0·0086 gm. $CaSO^4 + 2H^2O$
,, normal oxalic acid =0·0280 gm. CaO
Cryst. oxalic acid × 0·444 =CaO
Double iron salt × 0·07143 =CaO

§ 48. The estimation of calcium alkalimetrically has already been given (§ 17), but that method is of limited application, unless calcic oxalate, in which form Ca is generally separated from other bases, be converted into carbonate or oxide by ignition, and thus determined with normal nitric acid and alkali. This and the following method by Hempel, are as exact in their results as the determination by weight; and where a series of estimations have to be made, the method is very convenient.

### Titration with Permanganate.

The readiness with which calcium can be separated as oxalate facilitates the use of this method, so that it can be applied successfully in a great variety of instances. It is not necessary here to enter into detail as to the method of precipitation; except to say, that it may occur in either ammoniacal or weak acetic acid solution; and that it is absolutely necessary to remove all excess of ammonic oxalate from the precipitate, by washing with warm water previous to titration.

When the clean precipitate is obtained, a hole is made in the filter, and the bulk of the precipitate is washed through the funnel into a flask; the filter is then treated with small quantities of hot dilute hydrochloric acid, and again washed into the flask. Hydrochloric acid in moderate quantity may be safely used for the solution of the oxalate, since there is not the danger of liberating free chlorine which exists in the case of iron (Fleischer, *Titrirmethode*, p. 76).

When the precipitate is completely dissolved, the solution is freely diluted with water, and further acidified with sulphuric acid, warmed to 70° or 80°, and the standard permanganate cautiously delivered into the liquid with constant agitation until a faint permanent pink tinge occurs, precisely as in the case of standardizing permanganate with oxalic acid (§ 30.2*c*).

In all cases where a clean oxalate precipitate can be obtained, such as mineral waters, manures, etc., very exact results are obtainable; in fact, quite as accurate as by the gravimetric method. Ample testimony on this point is given by Fresenius, Mohr, Hempel, and others.

Tucker (*Iron*, Nov. 16, 1878) has given the results of many experiments made by him upon mixtures of Ca with abnormal proportions of iron, magnesia, alumina, etc.; and even here the numbers obtained did not vary more than 2 to 3 per cent. from the truth. In the case of large proportions of these substances it will be preferable to re-precipitate the oxalate, so as to free it from adhering contaminations previous to titration.

Tucker recommends the method for the rapid estimation of Ca in furnace slags, etc., by dissolving in *aqua regia*, without filtering, precipitating with ammonic oxalate, and then filtering, washing well, and titrating as usual. If the slag contain much manganese or iron they should first be removed.

*Indirect Titration.*—In the case of calcic salts soluble in water and of tolerably pure nature, the estimation by permanganate can be made by adding to the solution a measured excess of normal oxalic acid, neutralizing with ammonia in slight excess, and heating to boiling, so as to rapidly separate the precipitate. The mixture is then cooled, diluted to a measured volume, filtered through a dry filter, and an aliquot portion titrated with permanganate after acidifying with sulphuric acid as usual. A great variety of calcium salts may be converted into oxalate by short or long treatment with oxalic acid or ammonic oxalate, including calcic sulphate, phosphate, tartrate, citrate, etc.

## CERIUM.

$Ce=141{\cdot}2$.

§ 49. The most exact method of estimating this metal is by precipitating as cerous oxalate, then drying the precipitate, and strongly igniting in an open crucible, so as to convert it into ceric oxide.

Stolba (*Z. a C.* xix. 194) states that the moist oxalate may be titrated precisely as in the case of calcic oxalate with permanganate, and with accurate results. No examples or details, however, are given.

## CHLORINE.

$Cl=35{\cdot}37$.

1 c.c. or 1 dm. $\frac{N}{10}$ silver solution $=0{\cdot}003537$ gm. or $0{\cdot}03537$ grn. Cl.

" " " $=0{\cdot}005837$ gm. or $0{\cdot}05837$ grn. NaCl.

§ 50. The powerful affinity existing between chlorine and silver in solution, and the ready precipitation of the resulting chloride, seem to have led to the earliest important volumetric process in existence, viz., the assay of silver by the wet method of Gay Lussac. The details of the process are more particularly described under the article relating to the assay of silver (§ 70); the determination of chlorine is just the converse of the process there described, and the same precautions, and to a certain extent the same apparatus, are required.

The solutions required, however, are systematic, and for exactness and convenient dilution are of decinormal strength, as described in § 37. In many cases it is advisable to possess also centinormal solutions, made by diluting 100 c.c. of $\frac{N}{10}$ solution to 1 liter.

### 1. Direct Precipitation with $\frac{N}{10}$ Silver.

Very weak solutions of chlorides, such as drinking waters, are not easily examined for chlorine by direct precipitation, unless they are considerably concentrated by evaporation previous to treatment, owing to the fact that, unless a tolerable quantity of chloride can be formed, it will not collect together and separate so as to leave the liquid clear enough to tell on the addition of fresh silver whether a distinct formation of chloride occurs. The best effects are produced when the mixture contains chlorine equal to from 1½ to 2 gm. of salt per 100 c.c. Should the proportion be much less than this, the difficulty of precipitation may be overcome by adding a quantity of freshly precipitated chloride, made by mixing equal volumes of $\frac{N}{10}$ salt and silver solution, shaking vigorously, pouring off the clear liquid, and adding the chloride to the mixture under titration. The best vessel to use for the trial is a well-stoppered round white bottle, holding 100 to 150 c.c. and fitting into a paper case, so as to prevent access of strong light during the analysis. Supposing, for instance, a neutral solution of potassic chloride requires titration, 20 or 30 c.c. are measured into the shaking bottle, a few drops of strong nitric acid added (free acid must always be present in direct precipitation), and a round number of c.c. of silver solution added from the burette. The bottle is placed in its case, or may be enveloped in a dark cloth and vigorously shaken for half a minute, then uncovered, and gently tapped upon a table or book, so as to start the chloride downward from the surface of the liquid where it often swims. A quick clarification indicates excess of silver. The nearer the point of exact counterbalance the more difficult to obtain a clear solution by shaking, but a little practice soon accustoms the eye to distinguish the faintest precipitate.

In case of overstepping the balance in any trial, it is only necessary to add to the liquid under titration a definite volume of $\frac{N}{10}$ salt solution, and finish the titration in the same liquid, deducting, of course, the same number of c.c. of silver as has been added of salt solution.

Fuller details and precautions are given in § 70.

### 2. Precipitation by $\frac{N}{10}$ Silver in Neutral Solution with Chromate Indicator (see § 37, 2 b).

### 3. Titration with $\frac{N}{10}$ Sulphocyanate (see § 39).

This method requires some little practice to ensure accurate results, owing to the fact that silver chloride slowly decomposes silver sulphocyanate.

In cases where the amount of chlorine is approximately known, the material is dissolved in 300 c.c. or so of water; 5 c.c. of ferric indicator (§ 39. 3) and 10 c.c. of nitric acid (§ 39. 4) are added; then $\frac{N}{10}$ silver in moderate excess delivered in from the burette with constant agitation. The flask is then brought under the sulphocyanate burette, and the solution delivered in with a constant gentle movement of the liquid until a permanent light-brown colour appears. The immediate mixing of the solutions is necessary in order to prevent the solvent effect of the concentrated sulphocyanate.

If the amount of chlorine is totally unknown, the method of procedure is as follows:—

Dilute the solution and add the indicator and acid as above; but during the addition of the silver solution, add from a burette, ready filled with sulphocyanate, a drop or two from time to time. So long as there is chlorine present the dark red colour disappears slowly and gradually; but when the colour produced by a fresh drop goes off at once on agitation, and the liquid appears of a pure milk white, the silver will be in excess. The titration is then completed as above. The volume of sulphocyanate used, including the amount used during the addition of the silver, deducted from the $\frac{N}{10}$ silver, will show the volume of the latter necessary for precipitating the chlorine present.

### 4. By Distillation and Titration with Thiosulphate or Arsenite.

In cases where chlorine is evolved direct in the gaseous form or as the representative of some other body (see § 35), a very useful absorption apparatus is shown in fig. 26. The little flask *a* is used as a distilling vessel, connected with the bulb tubes by an india-rubber joint; the stoppers for the tubes are also of the same material, the whole of which should be cleansed from sulphur by boiling in weak alkali. A fragment of solid magnesite may with advantage be added to the acid liquid in the distilling flask; in all other respects the process is conducted exactly as is described in § 35.

This apparatus is equally well adapted to the absorption of ammonia or other gases, and possesses the great recommendation that there is scarcely a possibility of regurgitation.

Mohr's apparatus (fig. 27) is also equally serviceable for this method.

Bohlig (*Z. a. C.* xxiv. 408) estimates chlorine by boiling the substance with magnesic carbonate and filtering. An aliquot part is shaken up with dry silver oxalate and filtered, then acidified with $H^2SO^4$, and titrated with $\frac{N}{10}$ permanganate for oxalic acid set free. I cannot recommend the process.

## CHLORINE GAS AND BLEACHING COMPOUNDS.

1 c.c. $\frac{N}{10}$ arsenious or thiosulphate solution = 0·003537 gm. Cl.

1 liter of chlorine at 0°C., and 0·76 m.m., weighs 3·17 gm.

§ 51. CHLORINE water may be titrated with thiosulphate by adding a measured quantity of it to a solution of potassic iodide, then delivering the thiosulphate from a burette till the colour of the free iodine has disappeared; or by using an excess of the reducing agent, then starch, and titrating residually with $\frac{N}{10}$ iodine. When arsenious solution is used for titration, the chlorine water is delivered into a solution of sodic carbonate, excess of arsenic added, then starch and $\frac{N}{10}$ iodine till the colour appears, or the iodized starch-paper may be used (§ 36).

**Bleaching Powder.**—The chief substance of importance among the compounds of hypochlorous acid is the so-called chloride of lime. The estimation of the free chlorine contained in it presents no difficulty when arsenious solution is used for titration.

Commercial bleaching powder consists of a mixture in variable proportions of calcic hypochlorite (the true bleaching agent), calcic chloride, and hydrate; and in some cases the preparation contains considerable quantities of chlorate, due to imperfect manufacture. In such cases Bunsen's method of analysis gives inaccurate results, the chlorate being recorded as a bleaching agent, whereas it is not so. It is generally valued and sold in this country by its percentage of chlorine. In France it is sold by degrees calculated from the volume of gaseous chlorine: 100° French = 31·78 per cent. English.

### 1. Titration by Arsenious Solution.

The first thing to be done in determining the value of a sample of bleaching powder is to bring it into solution, which is best managed as follows :—

The sample is well and quickly mixed, and 7·17 gm. weighed, put into a mortar, a little water added, and the mixture rubbed to a smooth cream; more water is then stirred in with the pestle, allowed to settle a little while, then poured off into a liter flask; the sediment again rubbed with water, poured off, and so on repeatedly, until the whole of the chloride has been conveyed into the flask without loss, and the mortar washed quite clean. The flask is then filled to the mark with water, well shaken, and 50 c.c. of the milky liquid taken out with a pipette, emptied into a beaker, and the $\frac{N}{10}$ arsenious solution delivered in from a burette until a drop of the mixture taken out with a glass rod, and brought in contact with the prepared starch-paper (§ 36) gives no blue stain.

The starch paper may be dispensed with by adding arsenious solution in excess, then starch liquor, and titrating residually with $\frac{N}{10}$ iodine till the blue colour appears. The number of c.c. of arsenic used shows direct percentage of available chlorine.

A more rapid method can be adopted in cases where a series of samples has to be tested, as follows;—4·95 gm. of pure arsenious acid are finely powdered and dissolved by the aid of a gentle heat in about 15 c.c. of glycerine, then diluted with water to 1 liter; 25 c.c. are measured into a flask and 1 c.c. of indigo solution added. The turbid solution of bleaching powder is poured into a suitable burette, and before it has time to settle is delivered with constant shaking into the blue arsenious solution until the colour is just discharged; the percentage of chlorine is then found by a slight calculation.

### 2. Bunsen's Method.

10 or 20 c.c. of the chloride of lime solution, prepared as above, are measured into a beaker, and an excess of solution of potassic iodide added; the mixture is then diluted somewhat, acidified with hydrochloric acid, and the liberated iodine titrated with $\frac{N}{10}$ thiosulphate and starch: 1 eq. iodine so found represents 1 eq. chlorine.

This is an exceedingly ready method of estimating chlorine, but in cases were calcic chlorate is present, it records the chlorine in it, as well as that existing as hypochlorite; but as the chlorate is of no value in bleaching, it is always preferable to analyze bleaching powder by means of arsenious solution. The amount of chlorate can always be found by taking the difference between the two methods.

### 3. Gasometric Process.

This method has been devised by Lunge (*Berichte* xix. 868) and is both accurate and rapid.

5 c.c. of a turbid solution of bleach (10 gm. in 250 c.c. water) are placed in the decomposing flask of the nitrometer (see Part VII.), an excess of hydrogen peroxide (about 2 c.c. of the commercial solution) is put into the inner tube, the flask is then fitted to the rubber stopper, and the tap turned so that the flask communicates with the measuring tube, the mercury being at zero. The liquids are mixed by inclining the flask, and in one or two minutes the reaction is complete, the oxygen given off is measured, and represents its own volume of chlorine gas.

## CHLORATES, IODATES, AND BROMATES.

Chloric anhydride, $Cl^2O^5$=150·74. Iodic anhydride, $I^2O^5$=333.
Bromic anhydride, $Br^2O^5$=239·5.

The compounds of chloric, iodic, and bromic anhydrides may all be determined by distillation or digestion with excess of hydrochloric acid; with chlorates the quantity of acid must be considerably in excess.

In each case 1 eq. of the respective anhydrides taken as monobasic, or their compounds, liberates 6 eq. of chlorine, and consequently 6 eq. of iodine when decomposed in the digestion flask. In the case of distillation, however, iodic and bromic acids only set free 4 eq. iodine, while iodous and bromous chlorides remain in the retort. In both these cases digestion is preferable to distillation.

*Example:* 0·2043 gm. pure potassic chlorate, equal to the sixth part of $\frac{1}{10000}$ eq., was decomposed by digestion with potassic iodide and strong hydrochloric acid in the bottle shown in fig. 28. After the reaction was complete, and the bottle cold, the stopper was removed, and the contents washed out into a beaker, starch added, and 103 c.c. $\frac{N}{10}$ thiosulphate delivered in from the burette; then again 23·2 c.c. of $\frac{N}{100}$ iodine solution, to reproduce the blue colour; this latter was therefore equal to 2·32 c.c. $\frac{N}{10}$ iodine, which deducted from the 103 c.c. thiosulphate gave 100·68 c.c., which multiplied by the factor 0·002043, gave 0·2056 gm. instead of 0·2043 gm.

## CHROMIUM.

Cr=52·4.

### Factors.

| | | | | |
|---|---|---|---|---|
| Metallic iron | × | 0·3123 | = | Chromium |
| ,, | × | 0·5981 | = | Chromic acid |
| ,, | × | 0·8784 | = | Potassic bichromate |
| ,, | × | 1·926 | = | Lead chromate |
| Double iron salt | × | 0·0446 | = | Chromium |
| ,, | × | 0·0854 | = | Chromic acid |
| ,, | × | 0·1255 | = | Potassic bichromate |
| ,, | × | 0·275 | = | Lead chromate |
| 1 c.c. $\frac{N}{10}$ solution | = | 0·003349 gm. $CrO^3$ | | |
| ,, | = | 0·00492 gm. $K^2Cr^2O^7$ | | |

### 1. Reduction by Iron.

§ 52. The estimation of chromates is very simply and successfully performed by the aid of ferrous sulphate, being the converse of the process devised by Penny for the estimation of iron (see § 33).

The best plan of procedure is as follows :—

A very small beaker or other convenient vessel is partly or wholly filled, as may be requisite, with perfectly dry and granular double sulphate of iron and ammonia; the exact weight then taken and noted. The chromium compound is brought into solution, not too dilute, acidified with sulphuric acid, and small quantities of the iron salt added from time to time with a dry spoon taking care that none is spilled, until the mixture becomes green, and the iron is in excess, best known by a small drop being brought in contact with a drop of red prussiate of potash on a white plate; if a blue colour appears at the point of contact, the iron is in excess. It is necessary to estimate this excess, which is most conveniently done by $\frac{N}{10}$ bichromate being added until the blue colour produced by contact with the red prussiate disappears. The vessel containing the iron salt is again weighed, the loss noted; the quantity of the salt represented by the $\frac{N}{10}$ bichromate deducted from it, and the remainder multiplied by the factor required by the substance sought. A freshly made standard solution of iron salt may be used in place of the dry salt.

*Example:* 0·5 gm. pure potassic bichromate was taken for analysis, and to its acid solution 4·15 gm. double iron salt added. 3·3 c.c. of $\frac{N}{10}$ bichromate were required to oxidize the excess of iron salt; it was found that 0·7 gm. of the salt = 17·85 c.c. bichromate, consequently 3·3 c.c. of the latter were equal to 0·12985 gm. iron salt; this deducted from the quantity originally used left 4·02015 gm., which multiplied by 0·1255 gave 0·504 gm. instead of 0·5 gm.

In the case of lead chromate being estimated in this way, it is best to mix both the chromate and the iron salt together in a mortar, rubbing them to powder, adding hydrochloric acid, stirring well together, then diluting with water and titrating as before. Where pure double iron salt is not at hand, a solution of iron wire in sulphuric acid, freshly made, and of ascertained strength, can of course be used.

### 2. Estimation of Chromates by Distillation with Hydrochloric Acid.

When chromates are boiled with an excess of strong hydrochloric acid in one of the apparatus (fig. 26 or 27), every 1 eq. of chromic acid liberates 3 eq. chlorine. For instance, with potassic bichromate the reaction may be expressed as follows—

$$K^2Cr^2O^7 + 14HCl = 2KCl + Cr^2Cl^6 + 7H^2O + 6Cl.$$

If the liberated chlorine is conducted into a solution of potassic iodide, 3 eq. of iodine are set free, and can be estimated by $\frac{N}{10}$ arsenite or thiosulphate. 3 eq. of iodine so obtained = 379·5 represent 1 eq. chromic acid = 100·40. The same decomposition takes place by mere digestion, as described in § 35.

### 3. Chrome Iron Ore.

The ore varies in quality, some samples being very rich, while others are very poor, in chromium. In all cases the sample is to be first of all brought into *very fine* powder. About a gram is rubbed tolerably fine in a steel mortar, then finished fractionally in an agate mortar.

Christomanos recommends that the coarse powder should be ignited for a short time on platinum previous to powdering with the agate mortar; after that it should be sifted through the finest material that can be used, and the coarser particles returned to the mortar for regrinding.

Previous to analysis it should be again ignited, and the analysis made on the dry sample.

(*a*) **O'Neill's Process.**—The very finely powdered ore is fused with ten times its weight of potassic bisulphate for twenty minutes, taking care that it does not rise over the edge of the platinum crucible; when the fusion is complete, the molten mass is caused to flow over the sides of the crucible, so as to prevent the formation of a solid lump, and the crucible set aside to cool. The mass is transferred to a porcelain dish, and lixiviated with warm water until entirely dissolved (no black residue must occur, otherwise the ore is not completely decomposed); sodic carbonate is then added to the liquid until it is strongly alkaline; it is then brought on a filter, washed slightly, and the filter dried. When perfectly dry, the precipitate is detached from the filter as much as possible; the filter burned separately; the ashes and precipitate mixed with about twelve times the weight of the original ore, of a mixture of two parts potassic chlorate and three parts sodic carbonate, and fused in a platinum crucible for twenty minutes or so; the resulting mass is then treated with boiling water, filtered, and the filtrate titrated for chromic acid as in § 52.1.

The ferric oxide remaining on the filter is titrated, if required, by any of the methods described in §§ 59 and 60.

(*b*) **Britton's Process.**—Reduce the mineral to the finest state of division possible in an agate mortar. Weigh off 0·5 gm., and add to it 4 gm. of flux, previously prepared, composed of one part potassic chlorate and three parts soda-lime; thoroughly mix the mass by triturating in a porcelain mortar, and then ignite in a covered platinum crucible at a bright-red heat for an hour and a half or more. 20 minutes is sufficient with the gas blowpipe. The mass will not fuse, but when cold can be turned out of the crucible by a few gentle taps, leaving the interior of the vessel clean and bright. Triturate in the mortar again and turn the powder into a tall 4-oz. beaker, and add about 20 c.c of hot water, and boil for two or three minutes; when cold, add 15 c.c. of HCl, and stir with a glass rod, till the solid matter, with the exception probably of a little silica in flakes, becomes dissolved. Both the iron and chromium will then be in the highest state of oxidation—$Fe^2O^3$ and $Cr^2O^3$. Pour the fluid into a white porcelain dish of about 20-oz. capacity, and dilute with washings of the beaker to about 3 oz. Immediately after, also, add cautiously 1 gm. of metallic iron of known purity, or an equivalent quantity of double iron salt, previously dissolved in dilute sulphuric acid, and further dilute with cold water to about 5 oz., to make up the volume in the dish to about 8 oz., then titrate with $\frac{N}{10}$ permanganate the amount of ferrous oxide remaining. The difference between the amount of iron found and of the iron weighed will be the amount oxidized to sesquioxide by the chromic acid. Every one part so oxidized will represent 0·320 of Cr or 0·4663 of sesquioxide, $Cr^2O^3$, in which last condition the substance usually exists in the ore.

If the amount of iron only in the ore is to be determined, the process is still shorter. After the fluxed mineral has been ignited and reduced to powder, as already directed, dissolve it by adding first, 10 c.c. of hot water and applying a gentle heat, and then 15 c.c. of HCl, continuing the heat to incipient boiling till complete decomposition has been effected; cool by immersing the tube in a bath of cold water, add pieces of pure metallic zinc sufficient to bring the iron to the condition of protoxide and the chromium to sesquioxide, and apply heat till small bubbles of hydrogen cease, and the zinc has become quite dissolved; then nearly fill the tube with *cold* water, acidulated with one-tenth of sulphuric acid, and pour the contents into the porcelain dish, add *cold* water to make up the volume to about 8 oz., and complete the operation with standard permanganate or bichromate.

(*c*) **Sell's Process.**—This method is described in *J. C. S.* 1879 (p. 292), and is carried out by first fusing the finely ground ore with a mixture of sodic bisulphate and fluoride in the proportion of 1 mol. bisulphate, and 2 mol. fluoride, and subsequent titration of the chromic acid by standard thiosulphate and iodine.

From 0·1 to 0·5 gm. of the ore is placed on the top of ten times its weight of the above-mentioned mixture in a large platinum crucible, and ignited for fifteen minutes; an equal weight of sodic bisulphate is then added and well incorporated by fusion, and stirring with a platinum wire; then a further like quantity of bisulphate added in the same way. When complete decomposition has occurred, the mass is boiled with water acidulated with sulphuric acid, and the solution diluted to a definite volume according to the quantity of ore originally taken.

To insure the oxidation of all the chromium and iron previous to titration, a portion, or the whole, of the solution is heated to boiling, and permanganate added until a permanent red colour occurs. Sodic carbonate is then added in slight excess, and sufficient alcohol to destroy the excess of permanganate; the manganese precipitate is then filtered off, and the clear solution titrated with $\frac{N}{10}$ thiosulphate and iodine.

The author states that the analysis of an ore by this method may be accomplished in one hour and a half.

For the preliminary fusion and oxidation of chrome iron ore, Dittmar recommends a mixture of two parts borax glass, and one and a half part each of sodic and potassic carbonate. These are fused together in a platinum crucible until all effervescence ceases, then poured out into a large platinum basin or upon a clean iron plate to cool, broken up, and preserved for use.

Ten parts of this mixture is used for one part of chrome ore, and the fusion made in a platinum crucible, closed for the first five minutes, then opened for about forty minutes, frequently stirring with a platinum wire, and using a powerful Bunsen flame.

The gas blowpipe hastens this method considerably.

## COBALT.

$Co = 59$.

### Estimation by Mercuric Oxide and Permanganate (Winkler).

§ 53. If an aqueous solution of cobaltous chloride or sulphate be treated with moist finely divided mercuric oxide, no decomposition ensues, but on the addition of permanganate to the mixture, hydrated cobaltic and manganic oxides are precipitated. It is probable that no definite formula can be given for the reaction, and therefore practically the working effect of the permanganate is best established by a standard solution of cobalt of known strength, say metallic cobalt dissolved as chloride, or neutral cobaltous sulphate.

*The Analysis:* The solution, free from any great excess of acid, is placed in a flask, diluted to about 200 c.c., and a tolerable quantity of moist mercuric oxide (precipitated from the nitrate or perchloride by alkali and washed) added. Permanganate from a burette is then slowly added to the cold solution with constant shaking until the rose colour appears in the clear liquid above the bulky brownish precipitate.

The appearance of the mixture is somewhat puzzling at the beginning, but as more permanganate is added the precipitate settles more freely, and the end as it approaches is very easily distinguished. The final ending is when the rose colour is persistent for a minute or two; subsequent bleaching must not be regarded.

The actual decomposition as between cobaltous sulphate and permanganate may be formulated thus—

$$6CoSO^4 + 5H^2O + 2MnKO^4 = K^2SO^4 + 5H^2SO^4 + 3Co^2O^3 + 2MnO^2$$

but as this exact decomposition cannot be depended upon in all the mixtures occurring, it is not possible to accept systematic numbers calculated from normal solutions.

Solutions containing manganese, phosphorus, arsenic, active chlorine or oxygen compounds, or organic matter, cannot be used in this estimation; moderate quantities of nickel are of no consequence.

Cobalt and nickel may be separated as sesquioxides from zinc, iron, chromium, cadmium, tin, alumina, and the alkalies and earths by sodic hypochlorite or bromine water, in the presence of much caustic soda. The mixture must be boiled till the precipitate becomes granular, and of dark brown or black colour.

This precipitate when boiled with weak ammonia will contain the whole of the cobalt as $Co^2O^3$ with some $NiO$. The cobalt may now be estimated by addition of standard ferrous solution, and titration with permanganate. In a separate portion of the original solution, the two oxides may be precipitated as before and without treatment by warm ammonia; both are titrated with ferrous solution and permanganate. In this way the nickel is estimated by difference (Fleischer).

## COPPER.

$Cu = 63$.

### Factors.

1 c.c. $\frac{N}{10}$ solution = 0·0063 gm. Cu.
Iron × 1·125 = Cu.
Double Iron Salt × 0·1607 = Cu.

### 1. Reduction by Grape Sugar and subsequent titration with Ferric Chloride and Permanganate (Schwarz).

§ 54. This process is based upon the fact that grape sugar precipitates cuprous oxide from an alkaline solution of the metal containing tartaric acid; the oxide so obtained is collected and mixed with ferric chloride and hydrochloric acid. The result is the following decomposition:—

$$Cu^2O + Fe^2Cl^6 + 2HCl = 2CuCl^2 + 2FeCl^2 + H^2O.$$

Each equivalent of copper reduces one equivalent of ferric to ferrous chloride, which is estimated by permanganate with due precaution. The iron so obtained is calculated into copper by the requisite factor.

*The Analysis:* The weighed substance is brought into solution by nitric or sulphuric acid or water, in a porcelain dish or flask, and most of the acid in excess saturated with sodic carbonate; neutral potassic tartrate is then added in not too large quantity, and the precipitate so produced dissolved to a clear blue fluid by adding caustic potash or soda in excess; the vessel is next heated cautiously to about 50° C., in the water bath, and sufficient grape sugar added to precipitate the copper present; the heating is continued until the precipitate is of a bright red colour, and the upper liquid is brownish at the edges from the action of the alkali on the sugar; the heat must never exceed 90° C. When the mixture has somewhat cleared, the upper fluid is poured through a moistened filter, and afterwards the precipitate brought on the same, and washed with hot water till thoroughly clean; the precipitate which may adhere to the dish or flask is well washed, and the filter containing the bulk of the protoxide put with it, and an excess of solution of ferric chloride (free from nitric acid or free chlorine) added, together with a little sulphuric acid; the whole is then warmed and stirred until the cuprous chloride is all dissolved. It is then filtered into a good-sized flask, the old and new filters being both well washed with hot water, to which at first a little free sulphuric acid should be added, in order to be certain of dissolving all the oxide in the folds of the paper. The entire solution is then titrated with permanganate in the usual way. Bichromate may also be used, but the end of the reaction is not so distinct as usual, from the turbidity produced by the presence of copper.

### 2. Reduction by Zinc and subsequent titration with Ferric Chloride and Permanganate (Fleitmann).

The metallic solution, free from nitric acid, bismuth, or lead, is precipitated with clean sticks of pure zinc; the copper collected, washed, and dissolved in a mixture of ferric chloride and hydrochloric acid: a little sodic carbonate may be added to expel the atmospheric air. The reaction is—

$$Cu + Fe^2Cl^6 = CuCl^2 + 2FeCl^2.$$

When the copper is all dissolved, the solution is diluted and titrated with permanganate; 56 Fe= 31·5 Cu.

If the original solution contains nitric acid, bismuth, or lead, the decomposition by zinc must take place in an ammoniacal solution, from which the precipitates of either of the above metals have been removed by filtration; the zinc must in this case be finely divided and the mixture warmed. The copper is all precipitated when the colour of the solution has disappeared. It is washed first with hot water, then with weak HCl and water to remove the zinc, again with water, and then dissolved in the acid and ferric chloride as before.

### 3. Estimation as Cuprous Iodide (E. O. Brown).

This process is based on the fact that when potassic iodide is mixed with a salt of copper in acid solution, cuprous iodide is precipitated as a dirty white powder, and iodine set free. If the latter is then immediately titrated with thiosulphate and starch, the corresponding quantity of copper is found.

The solution of the metal, if it contain nitric acid, is evaporated with sulphuric acid till the former is expelled, or the nitric acid is neutralized with sodic carbonate, and acetic acid added; the sulphate solution must be neutral, or only faintly acid; excess of acetic acid is of no consequence.

It is always preferable to get rid of all free mineral acids and work only with free acetic acid.

Westmorland (*J. S. C. I.* v. 51) strongly recommends this process for the estimation of copper in its various ores. The metal may very conveniently be separated from a hot sulphuric acid solution by sodic thiosulphate: this gives a flocculent precipitate of subsulphide mixed with sulphur, which filters readily, and can be washed with hot water. Arsenic and antimony, if present, are also precipitated; tin, zinc, iron, nickel, cobalt, and manganese are not precipitated. On igniting the precipitate most of the arsenic and the excess of sulphur is expelled, an impure subsulphide of copper being left. Sulphuretted hydrogen may of course be used instead of the thiosulphate, but its use is objectionable to many operators. Rich copper ores, matts, or precipitates, are dissolved in appropriate solvents, and a quantity representing about 0·5 gm. Cu taken for analysis. The metal is separated either with thiosulphate or $H^2S$, the sulphide dissolved in nitric acid, evaporated with sulphuric acid to separate lead, diluted, filtered, sodic carbonate added in excess, and then acetic acid to acid reaction. Cupreous pyrites, burnt ores, etc., are taken in larger quantity, according to their contents of copper, and treated in the same way; or they may be calcined, dissolved in HCl, the ferric salt reduced by boiling with sodic sulphide, and $H^2S$ passed through the cold solution: the precipitated sulphides are then treated as before.

*Standardizing the Thiosulphate Solution.*—This is best done on pure electrotype copper, dissolved first in nitric acid, boiling to expel nitrous fumes, diluting, neutralizing with sodic carbonate till a precipitate occurs, then adding acetic acid till clear. The liquid is then made up to a definite volume, and a quantity equal to about 0·5 gm. Cu taken in a flask or beaker, a few crystals of potassic iodide added, and when dissolved the thiosulphate is run in from a burette until the free iodine is nearly removed, add then some starch liquor, and finish the titration in the usual way. The thiosulphate will of course need to be checked occasionally, as it is not permanent.

If strictly $\frac{N}{10}$ thiosulphate is used, each c.c. = 0·0063 gm. Cu.

### 4. Estimation by Potassic Cyanide (Parkes and C. Mohr).

This well-known and much-used process for estimating copper depends upon the decoloration of an ammoniacal solution of copper by potassic cyanide. The reaction (which is not absolutely uniform with variable quantities of ammonia) is such that a double cyanide of copper and ammonia is formed; cyanogen is also liberated, which reacts on the free ammonia, producing urea, oxalate of urea, ammonic cyanide and formate (Liebig). Owing to the influence exercised by variable quantities of ammonia, or its neutral salts, upon the decoloration of a copper solution by the cyanide, it is necessary that the solution analyzed should contain pretty nearly the same proportion of ammonia as that upon which the cyanide has been originally titrated, and no heat should be used (see also § 54.8).

It has generally been thought that where copper and iron occur together, it is necessary to separate the latter before using the cyanide. F. Field, however, has stated that this is not necessary (*C. N.* i. 25); and I can fully endorse his statement that the presence of the suspended ferric oxide is no hindrance to the estimation of the copper; in fact, it is rather an advantage, as it acts as an indicator to the end of the process.

While the copper is in excess, the oxide possesses a purplish-brown colour, but as this excess lessens, the colour becomes gradually lighter, until it is orange brown. If it be now allowed to settle, which it does very rapidly, the clear liquid above will be found nearly colourless. A little practice is of course necessary to enable the operator to hit the exact point.

The solution of potassic cyanide should be titrated afresh at intervals of a few days. Further details of this process are given in § 54.8.

### 5. Estimation as Sulphide (Pelouze).

It is first necessary to have a solution of pure copper of known strength, which is best made by dissolving 39·334 gm. of pure cupric sulphate in 1 liter of water; each c.c. will contain 0·01 gm. Cu.

*Precipitation in Alkaline Solution.*—This process is based on the fact that if an ammoniacal solution of copper is heated to from 40° to 80° C., and a solution of sodic sulphide added, the whole of the copper is precipitated as oxysulphide, leaving the liquid colourless. The loss of colour indicates, therefore, the end of the process, and this is its weak point. Special practice, however, will enable the operator to hit the exact point closely.

*Example:* A measured quantity (say 50 c.c.) of standard solution of copper is freely supersaturated with caustic ammonia, and heated till it begins to boil. The temperature will not be higher than 80° C. in consequence of the presence of the ammonia; it is always well, however, to use a thermometer. The sodic sulphide is delivered cautiously from a Mohr's burette, until the last traces of blue colour have disappeared from the clear liquid above the precipitate. The experiment is repeated, and if the same result is obtained, the number of c.c. or dm. required to precipitate the amount of copper contained in 50 c.c. or dm. = 0·5 gm. or 5 grn. respectively, is marked upon the alkaline sulphide bottle. As the strength of the solution gradually deteriorates, it must be titrated afresh every day or two. Special regard must be had to the temperature of the precipitation, otherwise the accuracy of the process is seriously interfered with.

Casamajor (*C. N.* xlv. 167) uses instead of ammonia the alkaline tartrate solution same as for Fehling, adding a slight excess so as to make a clear blue solution. The addition of the sulphide gives an intense black brown precipitate, which is stirred vigorously till clear. The copper sulphide agglomerates into curds, and the re-agent is added until no further action occurs with a drop of the sodic sulphide. This modification can also be used for lead. $PbSO^4$ is easily soluble in the tartrate solution, and can be estimated by the sodic sulphide in the same way as copper.

Copper can also be first separated by glucose, or as sulphocyanate (Rivot), then dissolved in $HNO^3$, and treated with the tartrate. The colour of the solution is not regarded, but the clotty precipitate of sulphide, which is easily cleared by vigorous stirring. Very good results may be gained by this modification.

*Precipitation in Acid Solution.*—The copper solution is placed in a tall stoppered flask of tolerable size (400 or 500 c.c.), freely acidified with hydrochloric acid, then diluted with about 200 c.c. of hot water.

The alkaline sulphide is then delivered in from a burette, the stopper replaced, and the mixture well shaken; the precipitate of copper sulphide settles readily, leaving the supernatant liquid clear; fresh sulphide solution is then at intervals added until no more precipitate occurs. The calculation is the same as in the case of alkaline precipitation, but the copper is precipitated as pure sulphide instead of oxysulphide.

### 6. Estimation by Stannous Chloride (Weil).

This process is based on the fact, that a solution of a cupric salt in large excess of hydrochloric acid at a boiling heat shows, even when the smallest trace is present, a greenish-yellow colour. If to such a solution stannous chloride is added in minute excess, a colourless cuprous chloride is produced, and the loss of colour indicates the end of the process.

$$2CuCl^2 + SnCl^2 = Cu^2Cl^2 + SnCl^4.$$

The change is easily distinguishable to the eye, but should any doubt exist as to whether stannous chloride is in excess, a small portion of the solution may be tested with mercuric chloride. Any precipitate of calomel indicates the presence of stannous chloride.

The tin solution is prepared as described in § 33.2.

A standard copper solution is made by dissolving pure cupric sulphate in distilled water, in the proportion of 39·334 gm. per liter=10 gm. of Cu.

*Process for Copper alone:* 10 c.c. of the copper solution=0·1 gm. of Cu are put into a white-glass flask, 25 c.c. of pure strong hydrochloric acid added, placed on a sand-bath and brought to boiling heat; the tin solution is then quickly delivered in from a burette until the colour is nearly destroyed, finally a drop at a time till the liquid is as colourless as distilled water. No oxidation will take place during the boiling owing to the flask being filled with acid vapours.

A sample of copper ore is prepared in the usual way by treatment with nitric acid, and afterwards evaporating with sulphuric acid to remove the nitric. Silica, lead, tin, silver, or arsenic, are of no consequence, as when the solution is diluted with water to a definite volume, the precipitates of these substances settle to the bottom of the measuring flask, and the clear liquid may be taken out for titration. In case antimonic acid is present it will be reduced with the copper, but on exposing the liquid for a night in an open basin, the copper will be completely re-oxidized but not the antimony; a second titration will then show the amount of copper.

*Process for Ores containing Copper and Iron:* In the case of copper ores where iron is also present, the quantity of tin solution required will of course represent both the iron and the copper. In this case a second titration of the original solution is made with zinc and permanganate, and the quantity so found is deducted from the total quantity; the amount of tin solution corresponding to copper is thus found.

*Example:* A solution was prepared from 10 gm. of ore and diluted to 250 c.c.: 10 c.c. required 26·75 c.c. of tin solution whose strength was 16·2 c.c. for 0·1 gm. of Cu.

10 c.c. of ore solution were diluted, warmed, zinc and platinum added till reduction was complete, and the solution titrated with permanganate whose quantity = 0·0809 gm. of Fe.

The relative strength of the tin solution to iron is 18·34 c.c. = 0·1 gm. of Fe: thus—

63 : 56 = 0·1 : 0·0888

therefore 0·1 gm. of Cu = 0·0888 gm. of Fe = 16·2 c.c. of $SnCl^2$
whence 0·0888 : 0·1 = 16·2 : 18·34
thus 0·0809 Fe (found above) = 14·837 of c.c. $SnCl^2$
0·1 : 0·0809 = 18·34 : 14·837 hence
Iron and copper = 26·750 c.c. $SnCl^2$
Subtract for iron = 14·837

Leaving for copper 11·913

10 c.c. of ore solution therefore contained 16·2 : 0·1 : : 11·913 = 0·0735 gm. of Cu, and as 10 gm. of ore = 250 c.c. contained of course 1·837 gm. of Cu = 18·37 per cent. Cu. Analysis by weight as a control gave 18·34 per cent. Cu.

Fe volumetrically 20·25 per cent., by weight 20·10 per cent.

The method is specially adapted to the analysis of fahl-ores.

*Process for Ores containing Nickel or Cobalt*: The ore is dissolved in nitric or nitro-hydrochloric acid, then nearly neutralized with sodic carbonate, diluted with cold water, and freshly precipitated baric carbonate and some ammonic chloride added; the whole is well mixed together, producing a precipitate containing all the copper and iron, while the nickel or cobalt remains in solution; the precipitate is first washed by decantation, collected on a filter, well washed, then dissolved in hydrochloric acid, and titrated with stannous chloride as before described.

*Further method for Copper, Iron, and Antimony by Weil* (*C. N.* xlvi. 284).—The necessary solutions are:—(1) *Standard copper*. 19·667 gm. of copper sulphate are dissolved in water to 500 c.c. (2) A similar solution containing 7·867 gm. of copper sulphate. (3) *Standard tin solution*. 4·5 to 5 gm. of stannous chloride, and 230 gm. of HCl, are made up to 500 c.c. with water. This solution is standardized with No. 1, 10 c.c. of which solution should be mixed with 25 c.c. hydrochloric acid, boiled, and the tin solution to be standardized, run in until the green colour disappears.

*Estimation of Copper.*—5 grams of substance are dissolved in HCl or $H^2SO^4$, and made up to 250 c.c. 10 c.c. of this solution are taken, 25 c.c. HCl added, and then titrated as above.

*Estimation of Iron.*—When there are 2½ vols. of free HCl to 1 vol. of the ferric solution, no indicator is necessary, and the standard tin solution is run in until the iron solution is colourless; in this way the quantity of iron is obtained in terms of copper. Of solutions containing 2 gm. of the sample in 250 c.c., 10 c.c. are evaporated in a porcelain capsule, with 10 c.c. of the copper solution (No. 2); to the concentrated mixed solution large excess (about 75 c.c.) of HCl is added, and this is titrated with the tin solution as before; of course the tin required for the copper used must be deducted. The copper is used as an indicator, and is not required with substances containing more than 2 per cent. of iron.

*Estimation of Iron and Copper.*—5 grams of ore in 250 c.c. Titrate as above. In another, 10 c.c. of solution, precipitate the copper with zinc, filter, reconvert the ferrous into ferric salt by means of permanganate, and titrate the iron again.

*Estimation of Antimony.*—In making up the 250 c.c. in this case, it is necessary to use aqueous solution of tartaric acid to prevent precipitation of antimony. The solution of antimonic chloride is mixed with No. 1 copper solution, and a large excess of HCl, then titrated; the c.c. standard tin solution used indicates the sum of the Cu and Sb. If the mixed solution of cuprous and antimonious chloride is allowed to remain some hours the Cu becomes re-oxidized, but the Sb does not, therefore a second titration gives the quantity of Cu only; this is scarcely required when strength and quantity of copper solution added is known.

*Antimony, Copper, and Iron,* when together in same sample, are thus determined. 5 gm. substance is dissolved in nitric acid, evaporated down, and filtered. The filtrate contains iron and copper, which are determined as above directed. The precipitate contains all the antimony; it is dissolved in HCl, treated with permanganate, and the antimonic chloride determined as directed.

This process depends on the reducing action of stannous chloride. It is therefore necessary to get rid of extraneous oxidizing influences, such as free chlorine, nitric acid, or excess of permanganate, etc., before titration; this is effected by evaporating to dryness, taking up with hydrochloric acid, and repeating, until the solution or vapour evolved on boiling ceases to turn iodized starch-paper blue.

### 7. Volhard's method.

The necessary standard solutions are described in § 39. Each c.c. of $\frac{N}{10}$ thiocyanate represents 0·0063 gm. Cu.

*The Analysis:* The copper in sulphuric or nitric acid solution is evaporated to remove excess of acid, or if the acid is small in quantity neutralized with sodic carbonate, washed into a 300 c.c. flask, and enough aqueous solution of $SO^2$ added to dissolve the traces of basic carbonate and leave a distinct smell of $SO^2$. Heat to boiling, and run in from a burette the thiocyanate until the addition produces no change of colour, add 3 or 4 c.c., and note the entire quantity, allow to cool, fill to mark, and shake well. 100 c.c. are then filtered through a dry filter, 10 c.c. of ferric indicator with some nitric acid added, then titrated with $\frac{N}{10}$ silver till colourless; then again thiocyanate till the reddish colour occurs. The volume of silver solution, less the final correction with thiocyanate, deducted from the original thiocyanate, will give the volume of the latter required to precipitate the copper.

The process is not accurate in presence of Fe, Ag, Hg, Cl, I or Br.

### 8. Technical Examination of Copper Ores (Steinbeck's Process).

In 1867 the Directors of the Mansfield Copper Mines offered a premium for the best method of examining these ores, the chief conditions being tolerable accuracy, simplicity of working, and the possibility of one operator making at least eighteen assays in the day.

The fortunate competitor was Dr. Steinbeck, whose process satisfied completely the requirements. The whole report is contained in *Z. a. C.* 1869, p. 1, and is also translated in *C. N.*, April 16, 1869. The following is a condensed *résumé* of the process, the final titration of the copper being accomplished by potassic cyanide as in § 54.4. A very convenient arrangement for filling the burette with standard solution where a series of analyses has to be made, and the burette continually emptied, is shown in fig. 30: it may be refilled by simply blowing upon the surface of the liquid.

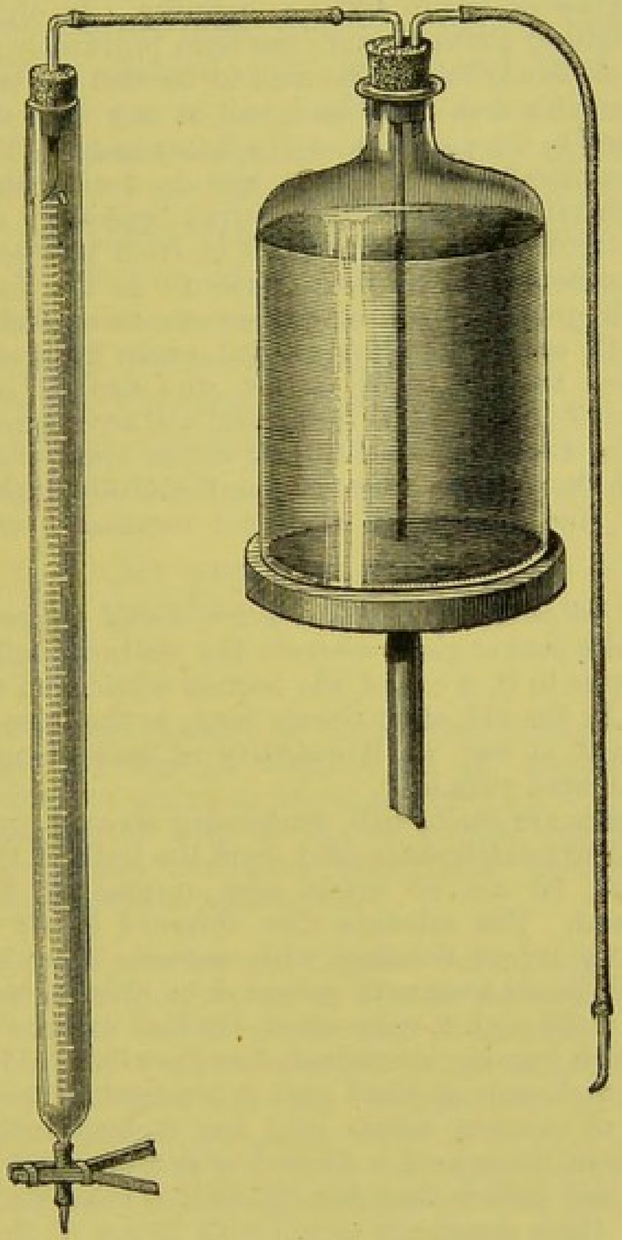

Fig. 30.

*(a) The extraction of the Copper from the Ore.*—5 gm. of pulverized ore are put into a flask with from 40 to 50 c.c. of crude hydrochloric acid (specific gravity 1·16), whereby all carbonates are converted into chlorides, while carbonic acid is expelled. After a while there is added to the fluid in the flask 6 c.c. of a normal nitric acid, prepared by mixing equal bulks of water and pure nitric acid of 1·2 sp. gr. As regards certain ores, however, specially met with in the district of Mansfield, some, having a very high percentage of sulphur and bitumen, have to be roasted previous to being subjected to this process; and others, again, require only 1 c.c. of nitric acid instead of 6. The flask containing the assay is digested on a sand-bath for half an hour, and the contents boiled for about fifteen minutes; after which

the whole of the copper occurring in the ore, and all other metals, are in solution as chlorides. The blackish residue, consisting of sand and schist, has been proved by numerous experiments to be either entirely free from copper, or to contain at the most only 0·01 to 0·03 per cent.

*(b) Separation of the Copper.*—The solution of metallic and earthy chlorides, and some free hydrochloric acid, obtained as just described, is separated by filtration from the insoluble residue, and the fluid run into a covered beaker glass of about 400 c.c. capacity. In this beaker a rod of metallic zinc, weighing about 50 gm., has been previously placed, fastened to a piece of stout platinum foil. The zinc to be used for this purpose should be as much as possible free from lead, and at any rate should not contain more than from 0·1 to 0·3 per cent. of the latter metal. The precipitation of the copper in the metallic state sets in already during the filtration of the warm and concentrated fluid, and is, owing especially also to the entire absence of nitric acid, completely finished in from half to three quarters of an hour after the beginning of the filtration. If the fluid be tested with sulphuretted hydrogen, no trace of copper can or should be detected; the spongy metal partly covers the platinum foil, partly floats about in the liquid, and in case either the ore itself or the zinc applied in the experiment contained lead, small quantities of that metal will accompany the precipitate l copper. After the excess of zinc (for an excess must always be employed) has been removed, the metal is repeatedly and carefully washed by decantation with fresh water, and care taken to collect together every particle of the spongy mass.

*(c) Quantitative estimation of the precipitated Copper.*—To the spongy metallic mass in the beaker glass, wherein the platinum foil is left, since some of the metal adheres to it, 8 c.c. of the normal nitric acid are added, and the copper dissolved by the aid of moderate heat, in the form of cupric nitrate which, in the event of any small quantity of lead being present, will of course be contaminated with lead.

When copper ores are dealt with, containing above 6 per cent. of copper, which may be approximately estimated from the bulk of the spongy mass of precipitated metal, 16 c.c. of nitric acid, instead of 8, are applied for dissolving the metal. The solution thus obtained is left to cool, and next mixed, immediately before titration with potassic cyanide, with 10 c.c. of normal solution of liquid ammonia, prepared by diluting 1 volume of liquid ammonia (sp. gr. 0·93) with 2 volumes of distilled water.

The titration with cyanide is conducted as described in § 54.4.

In the case of such ores as yield over 6 per cent. of copper, and when a double quantity of normal nitric acid has consequently been used, the solution of copper in nitric acid is diluted with water, and made to occupy a bulk of 100 c.c.; this bulk is then exactly divided into two portions of 50 c.c. each, and each of these separately mixed with 10 c.c. of the liquid ammonia solution just alluded to, and the copper therein volumetrically determined. The deep blue coloured solution only contains, in addition to the copper compound, ammonic nitrate; any lead which might have been dissolved having been precipitated as hydrated oxide, which does not interfere with the titration with cyanide. The solution of the last-named salt is so arranged, that 1 c.c. thereof exactly indicates 0·005 gm. of copper. Since, for every assay, 5 gm. of ore have been taken, 1 c.c. of the titration fluid is equal to 0·1 per cent. of copper, according to the following proportion:—

$$5 : 0{\cdot}005 :: 100 : x = 0{\cdot}1$$

it hence follows that, by multiplying the number of c.c. of cyanide solution used to make the blue colour of the copper solution disappear by 0·1, the percentage of copper contained in the ore is immediately ascertained.

Steinbeck tested this method specially, in order to see what influence is exercised thereupon by (1) ammonic nitrate, (2) caustic ammonia, (3) lead. The copper used for the experiments for this purpose was pure metal, obtained by galvanic action, and was ignited to destroy any organic matter which might accidentally adhere to it, and, next, cleaned by placing it in dilute nitric acid. 5 gm. of this metal were placed in a liter flask, and dissolved in 266·6 c.c. of normal nitric acid, the flask gently heated, and, after cooling, the contents diluted with water, and thus brought to a bulk of 1000 c.c. 30 c.c. of this solution were always applied to titrate one and the same solution of potassic cyanide under all circumstances. When 5 gm. of ore, containing on an average 3 per cent. of copper, are taken for assay, that quantity of copper is exactly equal to 0·150 gm. of the chemically pure copper. The quantity of normal nitric acid taken to dissolve 5 gm. of pure copper (266·6 c.c.) was purposely taken, so as to correspond with the quantity of 8 c.c. of normal nitric acid which is applied in the assay of the copper obtained from the ore, and this quantity of acid is exactly met with in 30 c.c. of the solution of pure copper.

The influence of double quantities of ammonic nitrate and free caustic ammonia (the quantity of copper remaining the same) is shown as follows:—

(*a*) 30 c.c. of the normal solution of copper, containing exactly 0·150 gm. of copper, were rendered alkaline with 10 c.c. of normal ammonia, and were found to require, for entire decoloration, 29·8 c.c. of cyanide solution. A second experiment, again with 30 c.c. of normal copper solution, and otherwise under identically the same conditions, required 29·9 c.c. of cyanide solution. The average is 29·85 c.c.

(*b*) When to 30 c.c. of the normal copper solution first 8 c.c. of normal nitric acid are added, and then 20 c.c. of normal ammonia instead of only 8, whereby the quantity of free ammonia and of ammonic nitrate is made double what it was in the case of *a*, there is required of the same cyanide solution 30·3 c.c. to produce decoloration. A repetition of the experiment, exactly under the same conditions, gave 30·4 c.c. of the cyanide solution employed; the average is, therefore, 30·35 c.c. The difference amounts to only 0·05 per cent. of copper, which may be allowed for in the final calculation.

When, however, larger quantities of ammoniacal salts are present in the fluid to be assayed for copper, by means of cyanide, and especially when ammonic carbonate, sulphate, and, worse still, chloride are simultaneously present, these salts exert a very disturbing influence. The presence of lead in the copper solution to be assayed has the effect of producing, on the addition of 10 c.c. of normal ammonia, a milkiness with the blue tint; but this does not at all interfere with the estimation of the copper by means of the cyanide, provided the lead be not in great excess; and a slight milkiness of the solution even promotes the visibility of the approaching end of the operation.

Steinbeck purposely made some experiments to test this point, and his results show that a moderate quantity of lead has no influence.

Experiments were also carefully made to ascertain the influence of zinc, the result of which showed that up to 5 per cent. of the copper present, the zinc had no disturbing action; but a considerable variation occurred as the percentage increased above that proportion. Care must therefore always be taken in washing the spongy copper precipitated from the ore solution by means of zinc.

The titration must always take place at ordinary temperatures, since heating the ammoniacal solution while under titration to 40° or 45° C. considerably reduces the quantity of cyanide required.

J. J. and C. Beringer (*C. N.* xlix. 111) report a series of experiments upon this cyanide process, showing that serious variations occur from varying quantities of ammonia or its salts, and the state of dilution. The results end in the recommendation that uniformity in the standardizing and the analysis should be practised, and that good proportional results may be obtained by using to 300 c.c. of the copper solution, rendered faintly alkaline with caustic soda, 15 c.c. of ammonia 88°.

### 9. Estimation of Copper by Colour Titration.

This method can be adopted with very accurate results, as in the case of iron, and is available for slags, poor cupreous pyrites, waters, etc. (see Carnelly, *C. N.* Dec. 31, 1875).

The re-agent used is the same as in the case of iron, viz., potassic ferrocyanide, which gives a purple-brown colour with very dilute solutions of copper. This reaction, however, is not so delicate as it is with iron, for 1 part of the latter in 13,000,000 parts of water can be detected by means of potassic ferrocyanide; while 1 part of copper in a neutral solution, containing ammonic nitrate, can only be detected in 2,500,000 parts of water. Of the coloured reactions which copper gives with different re-agents, those with sulphuretted hydrogen and potassic ferrocyanide are by far the most delicate, both showing their respective colours in 2,500,000 parts of water.

Of the two reagents sulphuretted hydrogen is the more delicate; but potassic ferrocyanide has a decided advantage over sulphuretted hydrogen in the fact that lead, when not present in too large quantity, does not interfere with the depth of colour obtained, whereas to sulphuretted hydrogen it is, as is well known, very sensitive.

And though iron if present would, without special precaution being taken, prevent the determination of copper by means of ferrocyanide; yet, by the method as described below, the amounts of these metals contained together in a solution can be estimated by this re-agent.

Ammonic nitrate renders the reaction much more delicate; other salts, as ammonic chloride and potassic nitrate, have likewise the same effect.

The method of analysis consists in the comparison of the purple-brown colours produced by adding to a solution of potassic ferrocyanide—first, a solution of copper of known strength; and, secondly, the solution in which the copper is to be determined.

The solutions and materials required are as follows:—

(1) *Standard copper solution.*—Prepared by dissolving 0·393 gm. of pure $CuSO^4, 5H^2O$ in one liter of water. 1 c.c. = 0·1 m.gm. Cu.

(2) *Solution of ammonic nitrate.*—Made by dissolving 100 gm. of the salt in one liter of water.

(3) *Potassic ferrocyanide solution.*—1 : 25.

(4) Two glass cylinders holding rather more than 150 c.c. each, the point equivalent to that volume being marked on the glass. They must both be of the same tint, and as colourless as possible. Instead of these the colorimeter may be used.

A burette, graduated to $\frac{1}{10}$ c.c. for the copper solution; a 5 c.c. pipette for the ammonic nitrate; and a small tube to deliver the ferrocyanide in drops.

*The Analysis:* Five drops of the potassic ferrocyanide are placed in each cylinder, and then a measured quantity of the neutral solution in which the copper is to be determined is placed into one of them, and both filled up to the mark with distilled water, 5 c.c. of the ammonic nitrate solution added to each, and then the standard copper solution ran gradually into the other till the colours in both cylinders are of the same depth, the liquid being well stirred after each addition. The number of c.c. used are then read off. Each c.c. corresponds to 0·1 m.gm. of copper, from which the amount of copper in the solution in question can be calculated.

The solution in which the copper is to be estimated must be neutral; for if it contain free acid the latter lessens the depth of colour, and changes it from a purple-brown to an earthy brown. If it should be acid, it is rendered slightly alkaline with ammonia, and the excess of the latter got rid of by boiling. The solution must not be alkaline, as the brown coloration is soluble in ammonia and decomposed by potash or soda; if it be alkaline from ammonia, this is remedied as before by boiling it off; while free potash or soda, should they be present, are neutralized by an acid, and the latter by ammonia.

Lead, when present in not too large quantity, has little or no effect on the accuracy of the method. The precipitate obtained on adding potassic ferrocyanide to a lead salt is white; and this, except when present in comparatively large quantity with respect to the copper, does not interfere with the comparison of the colours.

When copper is to be estimated in a solution containing iron, the following method is adopted:—

A few drops of nitric acid are added to the solution in order to oxidize the iron, the liquid evaporated to a small bulk, and the iron precipitated by ammonia. Even when very small quantities of iron are present, this can be done easily and completely if there be only a very small quantity of fluid. The precipitate of ferric oxide is then filtered off, washed once, dissolved in nitric acid, and re-precipitated by ammonia, filtered and washed. The iron precipitate is now free from copper, and in it the iron can be estimated by dissolving in nitric acid, making the solution nearly neutral with ammonia, and determining the iron by the method in § 60.4. The filtrate from the iron precipitate is boiled till all the ammonia is completely driven off, and the copper estimated in the solution so obtained as already described.

When the solution containing copper is too dilute to give any coloration directly with ferrocyanide, a measured quantity of it must be evaporated to a small bulk, and filtered if necessary; and if it contain iron, also treated as already described.

In the determination of copper and iron in water, for which the method is specially applicable, a measured quantity is evaporated to dryness with a few drops of nitric acid, ignited to get rid of any organic matter that might colour the liquid, dissolved in a little boiling water and a drop or two of nitric acid; if it is not all soluble it does not matter. Ammonia is next added to precipitate the iron, the latter filtered off, washed, re-dissolved in nitric acid, and again precipitated by ammonia, filtered off, and washed. The filtrate is added to the one previously obtained, the iron estimated in the precipitate, and the copper in the united filtrates.

## CYANOGEN.

$CN=26$.

1 c.c. $\frac{N}{10}$ silver solution = 0·0052 gm. Cyanogen.
,, ,, = 0·0054 gm. Hydrocyanic acid.
,, ,, = 0·01302 gm. Potassic cyanide.
,, iodine = 0·003255 gm. Potassic cyanide.

### 1. By Standard Silver Solution (Liebig).

§ 55. This ready and accurate method of estimating cyanogen in prussic acid, alkaline cyanides, etc., was discovered by Liebig, and is fully described in *Ann. der Chem. und Pharm.* lxxvii. 102. It is based on the fact, that when a solution of silver nitrate is added to an alkaline solution, containing cyanogen, with constant stirring, no permanent precipitate of silver cyanide occurs until all the cyanogen has combined with the alkali and the silver, to form a soluble double salt (in the presence of potash, for example, KCy, AgCy). If the slightest excess of silver, over and above the quantity required to form this combination, be added, a permanent precipitate of silver cyanide occurs, the double compound being destroyed. If, therefore, the silver solution be of known strength, the quantity of cyanogen present is easily found; 1 eq. of silver in this case being equal to 2 eq. cyanogen.

So fast is this double combination, that, when sodic chloride is present, no permanent precipitate of silver chloride occurs, until the quantity of silver necessary to form the compound is slightly overstepped.

Siebold, however, has pointed out that this process, in the case of free hydrocyanic acid, is liable to serious errors unless the following precautions are observed :—

(*a*) The solution of sodic or potassic hydrate should be placed in the beaker first, and the hydrocyanic acid added to it from a burette dipping into the alkali. If, instead of this, the acid is placed in the beaker first, and the alkaline hydrate added afterwards, there may be a slight loss by evaporation, which becomes appreciable whenever there is any delay in the addition of the alkali.

(*b*) The mixture of hydrocyanic acid and alkali should be largely diluted with water before the silver nitrate is added. The most suitable proportion of water is from ten to twenty times the volume of the officinal or of Scheele's acid. With such a degree of dilution, the final point of the reaction can be observed with greater precision.

(*c*) The amount of alkali used should be as exactly as possible that required for the conversion of the hydrocyanic acid into alkaline cyanide, as an insufficiency or an excess both affect the accuracy of the result. It is advisable to make first a rough estimation with excess of soda as a guide, then finish with a solution as neutral as possible.

*Caution.*—In using the pipette for measuring hydrocyanic acid, it is advisable to insert a plug of cotton wool, slightly moistened with silver nitrate, into the upper end, so as to avoid the danger of inhaling any of the acid; otherwise it is decidedly preferable to weigh it.

*Example with Potassic Cyanide:* The quantity of this substance necessary to be taken for analysis, so that each c.c. or dm. shall be equal to 1 per cent. of the pure cyanide, is 1·30 gm. or 13·0 grn. 13 grains, therefore, of the commercial article were dissolved in water, no further alkali being necessary, and 54 dm. $\frac{N}{10}$ silver required to produce the permanent turbidity. The sample therefore contained 54 per cent. of real cyanide.

### 2. By Standard Mercuric Chloride (Hannay).

This convenient method is fully described by the author (*J. C. S.* 1878, 245), and is well adapted for the technical examination of commercial cyanides, etc., giving good results in the presence of cyanates, sulphocyanates, alkaline salts, and compounds of ammonia and silver.

*The standard solution of mercury* is made by dissolving 13·537 gm. $HgCl^2$ in water, and diluting to a liter. Each c.c. = 0·00651 gm. of potassic cyanide or 0·0026 gm. Cy.

*The Analysis:* The cyanide is dissolved in water, and the beaker placed upon black paper or velvet; ammonia is then added in moderate quantity, and the mercuric solution cautiously added with constant stirring until a bluish-white opalescence is permanently produced. With pure substances the reaction is very delicate, but not so accurate with impure mixtures occurring in commerce.

### 3. By Iodine (Fordos and Gelis).

This process, which is principally applicable to alkaline cyanides, depends on the fact, that when a solution of iodine is added to one of potassic cyanide, the iodine loses its colour so long as any undecomposed cyanide remains. The reaction may be expressed by the following formula:—

$$CyK + 2I = IK + ICy.$$

Therefore, 2 eq. iodine represent 1 eq. cyanogen in combination; so that 1 c.c. of $\frac{N}{10}$ iodine expresses the half of $\frac{1}{10000}$ eq. cyanogen or its compounds. The end of the reaction is known by the yellow colour of the iodine solution becoming permanent.

Commercial cyanides are, however, generally contaminated with caustic or monocarbonate alkalies, which would equally destroy the colour of the iodine as the cyanide; consequently these must be converted into bicarbonates, best done by adding carbonic acid water (ordinary soda water).

*Example:* 5 gm. of potassic cyanide were weighed and dissolved in 500 c.c. water; then 10 c.c. (=0·1 gm. cyanide) taken with a pipette, diluted with about ¼ liter of water, 100 c.c. of soda water added, then $\frac{N}{10}$ iodine delivered from the burette until the solution possessed a slight but permanent yellow colour; 25·5 c.c. were required, which multiplied by 0·003255 gave 0·08300 gm., instead of 0·1 gm. or 83 per cent. real cyanide. Sulphides must of course be absent.

### 4. By $\frac{N}{10}$ Silver and Chromate Indicator.

Vielhaber (*Arch. Pharm.* [3] xiii. 408) has shown that weak solutions of prussic acid, such as bitter-almond water, etc., may be readily titrated by adding magnesic hydrate suspended in water until alkaline, adding a drop or two of chromate indicator, and delivering in $\frac{N}{10}$ silver until the red colour appears, as in the case of titrating chlorides. 1 c.c. silver solution=0·0027 gm. HCy.

This method may be found serviceable in the examination of opaque solutions of hydrocyanic acid, such as solutions of bitter-almond oil, etc.; but of course the absence of chlorine must be insured, or, if present, the amount must be allowed for.

It is preferable to add the HCy to a mixture of magnesia and chromate, then immediately titrate with silver.

## FERRO- AND FERRI-CYANIDES.

### Potassic Ferrocyanide.

$K^4Cy^6Fe+3H^2O=422.$

| | | | | |
|---|---|---|---|---|
| Metallic iron | × | 7·541 | = | Crystallized Potassic ferrocyanide. |
| Double iron salt | × | 1·077 | = | ,, ,, ,, |

### 1. Oxidation to Ferricyanide by Permanganate (De Haen).

§ 56. This substance may be estimated by potassic permanganate, which acts by converting it into red prussiate. The process is easy of application, and the results accurate. A standard solution of pure ferrocyanide should be used as the basis upon which to work, but can, however, be dispensed with, if the operator chose to calculate the strength of his permanganate upon iron or its compounds. If the permanganate is decinormal, there is of course very little need for calculation (1 eq.=422 must be used as the systematic number, and therefore 1 c.c. of $\frac{N}{10}$ permanganate is equal to 0·0422 gm. of yellow prussiate). The standard solution of pure ferrocyanide contains 20 gm. in the liter: each c.c. will contain 0·020 gm.

*The Analysis*: 10 c.c. of the standard prussiate solution are put into a white porcelain dish or beaker standing on white paper, and 250 c.c. or so of water added; it is then acidified pretty strongly with sulphuric acid, and the permanganate delivered from the burette until a pure uranium yellow colour appears; it is then cautiously added until the faintest pink tinge occurs.

*Ferrocyanides in Alkali waste.*—Acidulate the solution with HCl, and add strong bleaching powder solution with agitation until a drop of the liquid gives no blue colour with ferric indicator. The liquid is then titrated with a solution of cupric sulphate, standardized on pure potassic ferrocyanide, using dilute ferrous sulphate as indicator; as soon as no more blue or grey colour occurs, but a faint reddening, the process is ended.

*Ferrocyanides in Gas Liquor.*—250 c.c. are evaporated to dryness, dissolved in water, the solution filtered, and prussian blue precipitated by ferric chloride. The blue is filtered off, washed, and decomposed with caustic soda. The ferric hydroxide so obtained is, after filtering, washing, and dissolving in dilute $H^2SO^4$ reduced with zinc, and titrated with permanganate. $Fe \times 5{\cdot}07=(NH^4)^4FeCy^6$.

## POTASSIC FERRICYANIDE.

$K^6Cy^{12}Fe^2=658.$

| | | | | |
|---|---|---|---|---|
| Metallic iron | × | 5·88 | = | Potassic ferricyanide. |
| Double iron salt | × | 1·68 | = | ,, ,, |
| $\frac{N}{10}$ Thiosulphate | × | 0·0329 | = | ,, ,, |

### 2. By Iodine and Thiosulphate.

This salt can be estimated either by reduction to ferrocyanide and titration with permanganate or bichromate as above, or by Lenssen's method, which is based upon the fact, that when potassic iodide and ferricyanide are mixed with tolerably concentrated hydrochloric acid, iodine is set free

$$K^6Fe^2Cy^{12} + 2KI = 2K^4Cy^6Fe + I^2$$

the quantity of which can be estimated by $\frac{N}{10}$ thiosulphate and starch liquor. This method does not, however, give the most satisfactory results, owing to the variation produced by working with dilute or concentrated solutions. C. Mohr's modification (see Zinc, § 78.1) is, however, more accurate, and is as follows:—The ferricyanide is dissolved in a convenient quantity of water, potassic iodide in crystals added, together with hydrochloric acid in tolerable quantity, then a solution of pure zinc sulphate in excess; after standing a few minutes to allow the decomposition to perfect itself, the excess of acid is neutralized by sodic carbonate, so that the latter slightly predominates.

At this stage all the zinc ferricyanide first formed is converted into the ferrocyanide of that metal, and an equivalent quantity of iodine set free, which can at once be titrated with $\frac{N}{10}$ thiosulphate and starch, and with very great exactness. 1 c.c. $\frac{N}{10}$ thiosulphate =0·0329 gm. potassic ferricyanide.

The mean of five determinations made by Mohr gave 100·21 instead of 100.

### 3. Reduction of Ferri- to Ferro-cyanide.

This process is, of course, necessary when the determination by permanganate has to be made, and is best effected by boiling the weighed ferricyanide with an excess of potash or soda, and adding small quantities of concentrated solution of ferrous sulphate until the precipitate which occurs possesses a blackish colour (signifying that the magnetic oxide is formed). The solution is then diluted to a convenient quantity, say 300 c.c., well mixed and filtered through a dry filter; 50 or 100 c.c. may then be taken, sulphuric acid added, and titrated with permanganate as before described.

Other soluble ferro- or ferri-cyanides may be examined in the same way as the potassium salts, and if insoluble, they may generally be converted into the latter by boiling with strong caustic potash.

## SULPHOCYANIDES.

For the estimation of sulphocyanic acid in combination with the alkaline or earthy bases, Barnes and Liddle (*J. S. C. I.* ii. 122) have devised a method which is easy of application, and gives good technical results. It is not, however, available for gas liquors.

The method depends upon the fact that when a solution of a cupric salt is added to a solution of a sulphocyanide in presence of a reducing agent, as sodic bisulphite, the insoluble cuprous salt of sulphocyanic acid is precipitated, the end of the reaction being ascertained by a drop of the solution in the flask giving a brown colouration when brought in contact with a drop of ferrocyanide. The following reactions take place—

$$2CuSO^4 + 2KSCN + Na^2SO^3 + H^2O = Cu^2S^2C^2N^2 + K^2SO^4 + 2NaHSO^4$$

and

$$2CuSO^4 + Ba(SCN)^2 + Na^2SO^3 + H^2O = Cu^2S^2C^2N^2 + BaSO^4 + 2NaHSO^4$$

The following solutions are required :—

1. *A Standard Solution of Cupric Sulphate* containing 6·2375 gm. per liter, 1 c.c. of which is equivalent to 0·00145 gm. SCN.
2. *A Solution of Sodic Bisulphite* of specific gravity 1·3.
3. *A Solution of Potassic Ferrocyanide* (1 : 20).

*The Analysis:* About 3 gm. of the sample are weighed from a stoppered tube into a liter flask, dissolved in water, and made up to the mark. After well mixing, 25 c.c. are measured into a flask, about 3 c.c. of the bisulphite added, and the whole boiled. Whilst this is heating a burette is filled with the copper solution, and a white porcelain slab is dotted over with the ferrocyanide. When the liquid in the flask has reached the boiling point, 20 c.c. of the copper solution are run in, well shaken, the precipitate allowed to settle for about a minute, a drop is taken out by means of a glass rod, and brought in contact with a drop of ferrocyanide, and should no brown colouration appear, more of the copper solution is run in, say 1 c.c. at a time, and again tested. This is continued until a drop gives an immediate colour. By this means an approximation to the truth is obtained. It will be observed, during a titration, that the mixed drops, after standing for a minute, or even less, produce a brown tint. It is of the utmost importance that the colouration be immediate.

A second 25 c.c. of the sulphocyanide solution are run into a clean flask, the bisulphite added, and boiled as before.

Suppose that in the first experiment, after an addition of 27 c.c. of copper solution, no colour was formed with ferrocyanide, but that 28 c.c. gave an immediate colour; then in the second experiment 27 c.c. are run in at once, and the liquid is again tested, when no colour should appear. The copper solution is then run in drop by drop until there is a slight excess of copper, as proved by the delicate reaction with the ferrocyanide. The second experiment is thus rendered more exact by the experience gained in the first.

## GOLD.

$$Au = 196·5.$$

1 c.c. or 1 dm. normal oxalic acid = 0·0655 gm. or 0·655 grn. Gold.

§ 57. The technical assay of gold for coining purposes is invariably performed by cupellation. Terchloride of gold is, however, largely used in photography and electro-gilding, and therefore it may be necessary sometimes to ascertain the strength of a solution of the chloride or its value as it occurs in commerce.

If to a solution of gold in the form of chloride (free from nitric acid) an excess of oxalic acid be added, in the course of from eighteen to twenty-four hours all the gold will be precipitated in the metallic form, while the corresponding quantity of oxalic acid has been dissipated in the form of carbonic acid; if, therefore, the quantity of oxalic acid originally added be known, and the excess, after complete precipitation of the gold, be found by permanganate, the amount of gold will be obtained.

*Example:* A 15-grain tube of the chloride of gold of commerce was dissolved in water, and the solution made up to 300 decems. 20 dm. of normal oxalic acid were then added, and the flask set aside for twenty-four hours in a warm, dark place; at the end of that time the gold had settled, and the supernatant liquid was clear and colourless. 100 dm. were taken out with a pipette, and titrated with $\frac{N}{10}$ permanganate, of which 25 dm. were required; this multiplied by 3 gives 75 dm.=7·5 dm. normal oxalic acid, which deducted from the 20 dm. originally added, left 12·5 dm.; this multiplied by $\frac{1}{3}$ the equivalent of gold (1 eq. of gold chloride decomposing 3 eq. oxalic acid) =0·655 gave 8·195 grn. metallic gold, or multiplied by 101 ($=\frac{1}{3}$ eq. $AuCl^3$) gave 12·625 grn.; the result was 84 per cent. of chloride of gold instead of 100.

## IODINE.

### I = 126·5.

### 1. By Distillation.

§ 58. Free iodine is of course very readily estimated by solution in potassic iodide, and titration with starch and $\frac{N}{10}$ thiosulphate, as described in § 34.*

Combined iodine in haloid salts, such as the alkaline iodides, must be subjected to distillation with hydrochloric acid, and some other substance capable of assisting in the liberation of free iodine, which is received into a solution of potassic iodide, and then titrated with $\frac{N}{10}$ thiosulphate in the ordinary way. Such a substance presents itself best in the form of ferric oxide, or some of its combinations; if, therefore, hydriodic acid, or what amounts to the same thing, an alkaline iodide, be mixed with an excess of ferric oxide, and distilled in the apparatus shown in fig. 26 or 27, the following reaction occurs:—

$$Fe^2O^3 + 2IH = 2FeO + H^2O + I^2.$$

The best form in which to use the ferric oxide is iron alum.

---

* I would here again impress upon the operator's notice that it is of great importance to ascertain the exact strength of the standard solutions of iodine and thiosulphate as compared with each other. Both solutions constantly undergo an amount of change depending upon the temperature at which they are kept, their exposure to light, etc., and therefore it is absolutely necessary to ensure exactness in the multifarious analyses which can be made by the aid of these two re-agents, to verify their agreement by weighing a small portion of pure dry iodine at intervals, and titrating it with the standard thiosulphate or arsenite.

The iodide and iron alum being brought into the little flask, fig. 27, sulphuric acid, of about 1·3 sp. gr. or so, is added, and the cork carrying the still tube inserted. This tube is not carried into the solution of potassic iodide in this special case, but within a short distance of it; and the end must not be drawn out to a fine point, as there represented, but cut off straight. The reason for this arrangement is, that it is not a chlorine distillation for the purpose of setting iodine free from the iodide solution, as is usually the case, but an actual distillation of iodine, which would speedily choke up the narrow point of the tube, and so prevent the further progress of the operation.

As the distillation goes on, the steam washes the condensed iodine out of the tube into the solution of iodide, which must be present in sufficient quantity to absorb it all. When no more violet vapours are to be seen in the flask, the operation is ended; but to make sure, it is well to empty the solution of iodine out of the condensing tube into a beaker, and put a little fresh iodide solution with starch in, then heat the flask again; the slightest traces of iodine may then be discovered by the occurrence of the blue colour when cooled. In case this occurs, the distillation is continued a little while, then both liquids mixed, and titrated with $\frac{N}{10}$ thiosulphate as usual.

Ferric chloride may be used instead of the iron alum, but it must be free from nitric acid or active chlorine (best prepared from dry $Fe^2O^3$ and HCl).

The analysis may be checked by titrating the ferrous oxide in the retort with $\frac{N}{10}$ permanganate or bichromate.

### 2. Mixtures of Iodides, Bromides, and Chlorides.

Donath (*Z. a. C.* xix. 19) has shown that iodine may be accurately estimated by distillation in the presence of other halogen salts, by means of a solution containing about 2 to 3 per cent. of chromic acid, free from sulphuric acid.

In the case of iodides and chlorides together the action is perfectly regular, and the whole of the iodine may be received into potassic iodide without any interference from the chlorine.

In the case of bromides being present, the chromic solution must be rather more dilute, and the distillation must not be continued more than two or three minutes after ebullition has commenced, otherwise a small amount of bromide is decomposed.

The reaction in the case of potassic iodide may be expressed thus:—

$$6KI + 8CrO^3 = I^6 + Cr^2O^3 + 3K^2Cr^2O^7.$$

The distillation may be made in Mohr's apparatus (fig. 27), using about 50 c.c. of chromic solution for about 0·3 gm. I.

The titration is made with thiosulphate in the usual way.

A much less troublesome method of estimating iodine in the presence of bromides or chlorides has been worked out by Cook (*J. C. S.* 1885, 471), and depends on the fact that hydrogen peroxide liberates iodine completely from an alkaline base in the presence of excess of acetic acid, while neither bromine nor chlorine are affected.

Hydrogen peroxide alone will only partially liberate iodine from potassic iodide, but with excess of a weak organic acid to combine with the alkaline hydroxide, the liberation is complete. Strong mineral acids must not be used, or bromine and chlorine, if present, would also be set free.

*The Analysis:* The solution is strongly acidified with acetic acid, and sufficient hydrogen peroxide added to liberate the iodine (5 c.c. will suffice for 1 gm. KI). The mixture is allowed to stand from half an hour to an hour; the whole of the iodine separates, some being in the solid state if the quantity is considerable. Chloroform is now added in sufficient volume to dissolve the iodine, the solution syphoned off, and the globule repeatedly washed with small quantities of water to remove excess of peroxide, then titrated with thiosulphate, with or without starch, in the usual way. If the peroxide is not completely removed by washing, it will decompose the sodic iodide produced in the titration, and so liberate traces of iodine.

The results obtained by Cook in mixtures of bromides, iodides, and chlorides, were about 99 per cent. of the iodine present.

### 3. Titration with $\frac{N}{10}$ Silver and Sulphocyanate.

The sulphocyanate and silver solutions are described in § 39.

The iodide is dissolved in 300 or 400 times its weight of water in a well-stoppered flask, and $\frac{N}{10}$ silver delivered in from the burette with constant shaking until the precipitate coagulates, showing that silver is in excess. Ferric indicator and nitric acid are then added in proper proportion, and the excess of silver estimated by sulphocyanate as described in § 39.

### 4. Oxidation of combined Iodine by Chlorine (Golfier Besseyre and Dupré).

This wonderfully sharp method of estimating iodine depends upon its conversion into iodic acid by free chlorine. When a solution of potassic iodide is treated with successive quantities of chlorine water, first iodine is liberated, then chloride of iodine (ICl) formed. If starch, chloroform, benzole, or bisulphide of carbon be added, the first will be turned blue, while any of the others will be coloured intense violet. A further addition of chlorine, in sufficient quantity, produces pentachloride of iodine ($ICl^5$), or rather, as water is present, iodic acid ($IO^3H$). No coloration of the above substances is produced by these compounds, and the accuracy with which the reaction takes place has been made use of by Golfier Besseyre and Dupré, independently of each other, for the purpose of estimating iodine. The former suggested the use of starch, the latter chloroform or benzole, with very dilute chlorine water. Dupré's method is preferable on many accounts.

*Example:* 30 c.c. of weak chlorine water were put into a beaker with potassic iodide and starch, and then titrated with $\frac{N}{10}$ thiosulphate, of which 17 c.c. were required.

10 c.c. of solution of potassic iodide containing 0·010 gm. of iodine were put into a stoppered bottle, chloroform added, and the same chlorine water as above delivered in from the burette, with constant shaking, until the red colour of the chloroform had disappeared; the quantity used was 85·8 c.c. The excess of chlorine was then ascertained by adding sodic bicarbonate, potassic iodide, and starch. A slight blue colour occurred; this was removed by $\frac{N}{10}$ thiosulphate, of which 1·2 c.c. was used. Now, as 30 c.c. of the chlorine solution required 17 c.c., the 85·8 c.c. required 48·62 c.c. of thiosulphate. From this, however, must be deducted the 1·2 c.c. in excess, leaving 47·42 c.c. $\frac{N}{100}$=4·742 c.c. of $\frac{N}{10}$ solution, which multiplied by 0·00211, the one-sixth of $\frac{1}{10000}$ eq. (1 eq. of iodic acid liberating 6 eq. iodine), gave 0·010056 gm. iodine instead of 0·01 gm.

Mohr suggests a modification of this method, which dispenses with the use of chloroform, or other similar agent.

The weighed iodine compound is brought into a stoppered flask, and chlorine water delivered from a large burette until all yellow colour has disappeared. A drop of the mixture brought in contact with a drop of starch liquor must produce no blue colour; sodic bicarbonate is then added till the mixture is neutral or slightly alkaline, together with potassic iodide and starch; the blue colour is then removed by $\frac{N}{10}$ thiosulphate. The strength of the chlorine water being known, the calculation presents no difficulty.

Mohr obtained by this means 0·010108 gm. iodine, instead of 1·01 gm.

### 5. Oxidation by Permanganate (**Reinige**).

This process for estimating iodine in presence of bromides and chlorides gives satisfactory results.

When potassic iodide and permanganate are mixed, the rose colour of the latter disappears, a brown precipitate of manganic peroxide results, and free potash with potassic iodate remain in solution. 1 eq. $I = 126·5$ reacts on 1 eq. $K^2Mn^2O^8 = 316$, thus—

$$KI + K^2Mn^2O^8 = KIO^3 + K^2O + 2MnO^2.$$

Heat accelerates the reaction, and it is advisable, especially with weak solutions, to add a small quantity of potassic carbonate to increase the alkalinity. No organic matter must be present.

The permanganate and thiosulphate solutions required in the process may conveniently be of $\frac{N}{10}$ strength, but their reaction upon each other must be definitely fixed by experiment as follows:—2 c.c. of permanganate solution are freely diluted with water, a few drops of sodic carbonate added, and the thiosulphate added in very small portions until the rose colour is just discharged. The slight turbidity produced by the precipitation of hydrated manganic oxide need not interfere with the observation of the exact point.

*The Analysis:* The iodine compound being dissolved in water, and always existing only in combination with alkaline or earthy bases, is heated to gentle boiling, rendered alkaline with sodic or potassic carbonate, and permanganate added till in distinct excess, best known by removing the liquid from the fire for a minute, when the precipitate will subside, leaving the upper liquid rose-coloured; the whole may then be poured into a 500-c.c. flask, cooled, diluted to the mark, and 100 c.c. taken out for titration with thiosulphate. The amount so used, being multiplied by 5, will give the proportion required for the whole liquid, whence can be calculated the amount of iodine. To prove the accuracy of the process in a mixture of iodides, bromides, and chlorides, with excess of alkali, the following experiment was made. 7 gm. commercial potassic bromide, the same of sodic chloride, with 1 gm. each of potassic hydrate and carbonate, were dissolved in a convenient quantity of water, and heated to boiling; permanganate was then added cautiously to destroy the traces of iodine and other impurities affecting the permanganate so long as decoloration took place; the slightest excess showed a green colour (manganate). To the mixture was then added 0·1246 gm. pure iodine, and the titration continued as described; the result was 0·125 gm. I.

With systematic solutions of permanganate and thiosulphate the calculation is as follows:—

$$1 \text{ c.c. } \tfrac{N}{10} \text{ solution} = 0{\cdot}01265 \text{ gm. I.}$$

### 6. By Nitrous Acid and Carbon Bisulphide (Fresenius).

This process requires the following standard solutions:—

(*a*) *Potassic iodide*, about 5 gm. per liter.

(*b*) *Sodic thiosulphate*, $\frac{1}{20}$ normal, 12·4 gm. per liter, or thereabout.

(*c*) *Nitrous acid*, prepared by passing the gas into tolerably strong sulphuric acid until saturated.

(*d*) *Pure carbon bisulphide.*

(*e*) *Solution of sodic bicarbonate*, made by dissolving 5 gm. of the salt in 1 liter of water, and adding 1 c.c. of hydrochloric acid.

The strength of the sodic thiosulphate in relation to iodine is first ascertained by placing 50 c.c. of the iodide solution into a 500 c.c. stoppered flask, then about 150 c.c. water, 20 c.c. carbon bisulphide, then dilute sulphuric acid, and lastly, 10 drops of the nitrous solution. The stopper is then replaced, and the whole well shaken, set aside to allow the carbon liquid to settle, and the supernatant liquid poured into another clean flask. The carbon bisulphide is then treated three or four times successively with water in the same way till the free acid is mostly removed, the washings being all mixed in one flask; 10 c.c. of bisulphide are then added to the washings, well shaken, and if at all coloured, the same process of washing is carried on. Finally, the two quantities of bisulphide are brought upon a moistened filter, washed till free from acid, a hole made in the filter, and the bisulphide which now contains all the iodine in solution allowed to run into a clean small flask, 30 c.c. of the sodic bicarbonate solution added, then brought under the thiosulphate burette, and the solution allowed to flow into the mixture while shaking until the violet colour is entirely discharged. The quantity so used represents the weight of iodine contained in 50 c.c. of the standard potassic iodide, and may be used on that basis to ascertain any unknown weight contained in a similar solution.

When very small quantities of iodine are to be titrated, weaker solutions and smaller vessels may be used.

### 7. By $\frac{N}{10}$ Silver Solution and Starch Iodide (Pisani).

The details of this process are given under the head of silver assay (§ 70.2), and are of course simply a reversal of the method there given. This method is exceedingly serviceable for estimating small quantities of combined iodine in the presence of chlorides and bromides, inasmuch as the silver solution does not react upon these bodies until the blue colour is destroyed.

## IRON.

Fe=56.

### Factors.

1 c.c. $\frac{N}{10}$ permanganate, bichromate, or thiosulphate =0·0056 Fe
" " " =0·0072 FeO
" " " =0·0080 $Fe^2O^3$

## ESTIMATION IN THE FERROUS STATE.

### 1. Verification of the standard solutions of Permanganate or Bichromate.

§ 59. The estimation of iron in the ferrous state has already been incidentally described in §§ 31, 32, and 33. The present section is an amplification of the methods there given, as applied more distinctly to ores and products of iron manufacture; but before applying the permanganate or bichromate process to these substances, and since many operators prefer, with reason, to standardize such solutions upon metallic iron, especially for use in iron analysis, the following method is given as the best :—

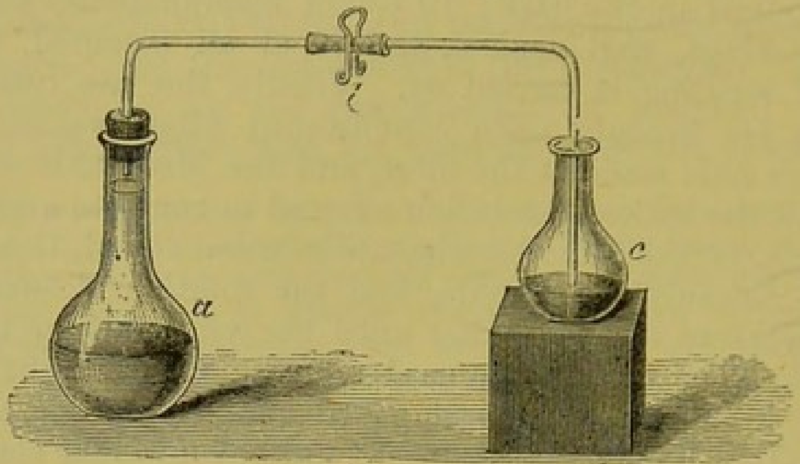

Fig. 31.

A piece of soft iron wire, known as "flower" wire, is well cleaned with scouring paper, and about 1 gram accurately weighed; this is placed into a 250 c.c. boiling flask *a*, and 100 c.c. of dilute pure sulphuric acid (1 part concentrated acid to 5 of water) poured over it ; about a gram of sodic bicarbonate is then added, and the apparatus fixed together as in fig. 31, the pinch-cock remaining open. The flask *a* is closed by a tight-fitting india-rubber stopper, through which is passed the bent tube. The flask *c* contains 20 or 30 c.c. of pure distilled water ; the flask *a* being supported over a lamp is gently heated to boiling, and kept at this temperature until all the iron is dissolved ; meanwhile about 300 c.c. of distilled water are boiled in a separate vessel to remove all air, and allowed to cool. As soon as the iron is dissolved, the lamp is removed, and the pinch-cock closed; when cooled somewhat, the pinch-cock is opened, and the wash water suffered to flow back together with the boiled water, which is added to it until the flask is filled nearly to the mark. The apparatus is then disconnected, and the flask *a* securely corked with a solid rubber cork, and suffered to cool to the temperature of the room. Finally, the flask is filled exactly to the mark with the boiled water, and the whole well shaken and mixed. When the small portion of undissolved carbon has subsided, 50 c.c., equal to $\frac{1}{5}$ the weight of iron taken, may be removed with the pipette for titration with the permanganate or bichromate.

In the case of permanganate the 50 c.c. are freely diluted with freshly boiled and cooled distilled water, and the standard solution cautiously added from a tap burette, divided into $\frac{1}{10}$ c.c., until the rose colour is faintly perceived.

In the case of bichromate the solution should be less diluted, and the titration conducted precisely as in § 33.

Instead of the two flasks, many operators use a single flask, fitted with caoutchouc stopper, through which a straight glass tube is passed, fitted with an india-rubber slit valve (known as Bunsen's valve), which allows gas or vapour to pass out, but closes by atmospheric pressure when the evolution ceases.

If the solution of permanganate or bichromate have been carefully prepared by weighing the purest re-agents, the probability is that they will be found exact in the titration when conducted as just described, allowing for the known average impurity in metallic iron, which may be taken at 0·4 per cent.; but in order to be absolutely secure in the working power of the solution, it is well to prove them thoroughly, and in case non-systematic solutions are used, it is of course absolutely necessary to do so. Therefore, supposing that 1·050 gm. of iron has been dissolved as above described, and the mean of three separate titrations has shown that 21·3 c.c. of permanganate or bichromate have been required, the amount of pure iron converted by 100 c.c. of standard solution is found as follows:—$\frac{1{\cdot}05}{5}=0{\cdot}210$ gm. of iron wire, but as this is not pure iron, the following correction is necessary—$0{\cdot}210 \times 0{\cdot}996 = 0{\cdot}20915$ gm., which is the actual weight of pure iron—hence by the equation 21·3 c.c. : 0·20915 gm. : : 100 c.c. : $x$ gm. = 0·98197 gm., therefore 100 c.c. of such permanganate represent 0·98197 gm. pure metallic iron.

The double iron salt is a most convenient material for adjusting standard solutions, but it must be most carefully made from pure materials, dried perfectly in the granular form, and kept from the light in small dry bottles, well closed. In this state it will keep for years unchanged, and only needs immediate solution in water for use. Even in the case of the salt not being strictly free from ferric oxide, due to faulty preparation, if it be once thoroughly dried, and kept as above described, its actual ferrous strength may be found by comparison with metallic iron, and a factor found for weighing it in system.

One cardinal point must never be forgotten; namely, that ferrous compounds are much more stable in sulphuric than in hydrochloric acid solution, and whenever possible, sulphuric acid should be used as the solvent. When hydrochloric acid must be used, manganous or magnesic sulphate should invariably be added.

### 2. Direct Estimation of the Percentage of Pure Iron in Steel, Cast and Wrought Iron, Spiegeleisen, Ores, etc. (Mohr's Method).

Instead of the hitherto common method of separately estimating the impurities in samples of manufactured iron and steel, this process is adapted to the delicate estimation of the iron itself, and is similar in principle to the assay of silver by Gay Lussac's method; that is to say, the analysis is so arranged that the greatest accuracy shall be secured.

The standard solutions of potassic bichromate, of which there are two, are so prepared that 100 c.c. or dm. of the first will exactly convert respectively 1 gm. or 10 grains of iron into ferric oxide; the second, or decimal solution, is one-tenth the strength of the first.

The solution of bichromate No. 1 is prepared by dissolving 8·772 gm. of the pure salt in 1 liter, or 87·72 grn. in 10,000 grains of distilled water at 16° C. The decimal solution No. 2 is made by taking 100 c.c. of No. 1 and diluting it to 1 liter, or 100 decems to 10,000 grains; therefore—

1 c.c. or dm. of No. 1 = 0·01 gm. or 0·1 grn. iron.
1 c.c. or dm. of No. 2 = 0·001 gm. or 0·01 grn. ditto.

*The Analysis:* The sample of iron to be examined is reduced to powder in a hardened steel mortar, or if in the form of wire, or in a soft state, cut into small pieces, and exactly 1·050 gm. or 10·50 grn. weighed off; this is brought into the apparatus fig. 31, or some similar arrangement, and dissolved in pure hydrochloric or sulphuric acid. When the solution is accomplished, 100 c.c. or dm. of bichromate solution No. 1 (containing 0·8785 gm. or 8·758 grn. of bichromate, which is exactly sufficient to peroxide respectively 1 gm. or 10 grn. of pure iron) are added; the decimal solution is then added from a small burette, until a drop of the mixture brought in contact with red potassic prussiate, no longer produces a blue colour. The analysis is then calculated in the usual way.

*Example:* 1·05 gm. of Bessemer steel was dissolved in pure sulphuric acid, 100 c.c. of bichromate No. 1 added, and afterwards 39 c.c. of No. 2 required for complete oxidation; consequently there was 1·039 gm. of pure iron contained in the 1·050 gm. taken for analysis. This is equal to 989·4 parts per thousand, or 98·94 per cent.

Instead of the empirical solutions here described, the ordinary decinormal and centinormal solutions of bichromate, or permanganate may be employed with equal accuracy. As 100 c.c. of decinormal solution are equal to 0·56 gm. of pure iron, it is necessary that somewhat more than this quantity of the sample should be weighed, say 0·58 or 0·60 gm. 100 c.c. of decinormal solution are then added, and the analysis completed with the centinormal solution.

### 3. Reduction of Ferric Compounds to the Ferrous State.

This may be accomplished by metallic zinc, for use with permanganate, or by stannous chloride, for bichromate solution. Some operators use other reducing agents, such as sodic sulphite or thiosulphate, hydric sulphide or ammonic sulphide, etc., but the zinc or tin methods are simpler and better. In the case of zinc being used, the metal must either be free from iron, or if it contain any, the exact quantity must be known and allowed for; and further, the pieces of zinc used must be entirely dissolved before the solution is titrated.* In the case of stannous chloride the solution must be clear, and is best made to contain 10 to 15 gm. per liter, as directed in § 33·2. The point of exact reduction in the boiling hot liquid may be known very closely by the discharge of colour in the ferric solution; but may be made sure by the use of a freshly made solution of potassic sulphocyanide spread in drops on a white plate, care being taken to lose no time in bringing the drop of iron solution in contact with the test, in order to avoid re-oxidation from the air. The occurrence of a faint pink tinge may be accepted as an evidence of the proper point. When this occurs, two or three drops of the standard

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* Many operators now use amalgamated zinc in conjunction with platinum foil for the reduction, but a practical difficulty occurs from the platinum becoming also amalgamated through contact with the zinc and stopping the action. Beebe (*C.N.* liii. 269) suggests the following convenient arrangement:—A strip of thin platinum foil, 1 in. square, is perforated with pin holes all over, then bent into a U form, and the ends connected with platinum wire so as to form a basket. In this is placed a piece of amalgamated zinc, and the whole suspended by a stout platinum wire in the reducing flask. When lowered into the solution, another strip of platinum foil, 2 in. square, is dropped in and leaned against the wire carrying the basket: a very free evolution of hydrogen is then obtained from the foil. When the reduction is complete, the basket is lifted out and well washed into the beaker containing the liquid to be titrated.

bichromate may be added to the solution, and another test made; if this shows a slight, but nevertheless distinct accession of colour with the sulphocyanide, the absence of stannous salt in excess is proved, and the titration should be commenced at once.

When bichromate is used, Atkinson (*C.N.* xlvi. 217) strongly recommends the use of ammonic bisulphite as the reducing agent, and discourages the use of stannous chloride, owing to the liability to error from excess or deficiency of the re-agent. He also points out that zinc is less recommendable, owing to its interference with the colour produced with the indicator. The bisulphite is used as follows:—To the acid solution of the ore or metal, diluted and filtered, ammonia is added until a faint precipitate of ferric oxide occurs. This is re-dissolved with a few drops of HCl, and some strong solution of bisulphite added, in the proportion of about 1 c.c. for each 0·1 gm. of ore, or 0·05 gm. Fe. The mixture is well stirred, boiling water added, then acidified with dilute sulphuric acid, and boiled for half an hour: it is then ready for titration.

## ESTIMATION OF IRON IN THE FERRIC STATE.

### 1. Direct Titration of Iron by Stannous Chloride.

§ 60. The reduction of iron from the ferric to the ferrous state by this re-agent has been previously referred to; and it will be readily seen that the principle involved in the reaction can be made available for a direct estimation of iron, being, in fact, simply a reversion of the ordinary process by permanganate and bichromate.

Fresenius has recorded a series of experiments made on the weak points of this process, and gives it as his opinion that, with proper care, the results are quite accurate. The summary of his process is as follows:—

(*a*) A solution of ferric oxide of known strength is first prepared by dissolving 10·04 gm. of soft iron wire (=10 gm. of pure iron) in pure hydrochloric acid, adding potassic chlorate to complete oxidation, boiling till the excess of chlorine is removed, and diluting the solution to 1 liter.

(*b*) A clear solution of stannous chloride, of such strength that about one volume of it and two of the iron solution are required for the complete reaction (see § 33.2).

(*c*) A solution of iodine in potassic iodide, containing about 0·010 gm. of iodine in 1 c.c. (if the operator has the ordinary decinormal iodine solution at hand, it is equally applicable). The operations are as follows:—

(1) 1 or 2 c.c. of the tin solution are put into a beaker with a little starch liquor, and the iodine solution added from a burette till the blue colour occurs; the quantity is recorded.

(2) 50 c.c. of the iron solution (=0·5 gm. of iron) are put into a small flask with a little hydrochloric acid, and heated to gentle boiling (preferably on a hot plate); the tin solution is then allowed to flow in from a burette until the yellow colour of the solution is nearly destroyed; it is then added drop by drop, waiting after each addition until the colour is completely gone, and the reduction ended. If this is carefully managed, there need be

no more tin solution added than is actually required; however, to guard against any error in this respect, the solution is cooled, a little starch liquor added, and the iodine solution added by drops until a permanent blue colour is obtained. As the strength of the iodine solution compared with the tin has been found in 1, the excess of tin solution corresponding to the iodine used is deducted from the original quantity, so that by this means the volume of tin solution corresponding to 0·5 gm. of iron is found.

The operator is therefore now in a position to estimate any unknown quantity of iron which may exist, in a given solution, in the ferric state, by means of the solution of tin.

If the iron should exist partly or wholly in the state of ferrous oxide, it must be oxidized by the addition of potassic chlorate, and boiling to dissipate the excess of chlorine, as described in *a*.

*Example:* 50 c.c. of iron solution, containing 0·5 gm. of iron, required 25 c.c. of tin solution.

A solution containing an unknown quantity of iron was then taken for analysis, which required 20 c.c., consequently a rule-of-three sum gave the proportion of iron as follows :—

25 : 0·50 gm. : : 20 : 0·40 gm.

It must be remembered that the solution of tin is not permanent, consequently it must be tested every day afresh. Two conditions are necessary in order to ensure accurate results.

(1) The iron solution must be tolerably concentrated, since the end of the reduction by loss of colour is more distinct; and further, the dilution of the liquid to any extent interferes with the quantity of tin solution necessary to effect the reduction. Fresenius found that by diluting the 10 c.c. of iron solution with 30 c.c. of distilled water, 0·1 c.c. more was required than in the concentrated state. This is, however, always the case with stannous chloride in acid solution, and constitutes the weak point in Streng's method of analysis by its means.

(2) The addition of the tin solution to the iron must be so regulated, that only a very small quantity of iodine is necessary to estimate the excess; if this is not done another source of error steps in, namely, the influence which dilution, on the one hand, or the presence of great or small quantities of hydrochloric acid on the other, are known to exercise over this reaction. Practically, it was found that where the addition of tin to the somewhat concentrated iron solution was cautiously made, so that the colour was just discharged, the mixture then rapidly cooled, starch added, and then iodine till it became blue, the estimation was extremely accurate.

### 2. Titration by Sodic Thiosulphate.

Scherer first suggested the direct titration of iron by thiosulphate, which latter was added to a solution of ferric chloride until no further violet colour was produced. This was found by many to be inexact, but Kremer (*Journ. f. Pract. Chem.* lxxxiv. 339) has made a series of practical experiments, the result of which is that the following modified method can be recommended.

The reaction which takes place is such as to produce ferrous chloride, sodic tetrathionate, and sodic chloride. $2S^2O^3Na^2 +$

$Fe^2Cl^6 + 2HCl = S^4O^6H^2 + 4NaCl + 2FeCl^2$. The thiosulphate, which may conveniently be of $\frac{N}{10}$ strength, is added in excess, and the excess determined by iodine and starch.

*The Analysis:* The iron solution, containing not more than 1 per cent. of metal, which must exist in the ferric state without any excess of oxidizing material (best obtained by adding concentrated potassic permanganate until the red colour is produced, then boiling till both that and any free chlorine is expelled), is moderately acidified with hydrochloric acid, sodic acetate added till the mixture is red, then dilute hydrochloric acid until the red colour disappears; then diluted till the iron amounts to ¼ or ½ per cent., and $\frac{N}{10}$ thiosulphate added in excess, best known by throwing in a particle of potassic sulphocyanide after the violet colour produced has disappeared; if any red colour occurs, more thiosulphate must be added. Starch liquor and $\frac{N}{10}$ iodine are then used to ascertain the excess. A mean of several experiments gave 100·06 Fe, instead of 100.

**Oudemanns' Method.**—A simpler process for the direct titration of iron by thiosulphate has been devised by Oudemanns (*Z. a. C.* vi. 129 and ix. 342), which gives very good results.

*The Analysis:* To the dilute ferric solution, which should not contain more than 0·1 to 0·2 gm. Fe in 100 c.c., nor much free HCl, 3 c.c. of 1 per cent. solution of cupric sulphate are added, 2 c.c. of concentrated hydrochloric acid, and to about every 100 c.c. of fluid, 1 c.c. of a 1 per cent. solution of potassic sulphocyanide.

The mixture may with advantage be very slightly warmed, and the thiosulphate delivered in from the burette at first pretty freely. The red colour produced by the sulphocyanide gradually fades away; as this occurs, the thiosulphate must be added in smaller quantities, constantly agitating the liquid until it becomes as colourless as pure water. If any doubt exists as to the exact ending, a slight excess of thiosulphate may be added, and the quantity found by $\frac{N}{10}$ iodine and starch. Greater accuracy will always be insured by this latter method.

The accuracy of the process is not interfered with by the presence of salts of the alkalies, strontia, lime, magnesia, alumina, or manganous oxide; neither do salts of nickel, cobalt, or copper, unless their quantity is such as to give colour to the solution.

The process is a rapid one, and with care gives very satisfactory results.

An improvement on this process has been adopted by Haswell, who mixes the moderately acid solution of the ferric chloride in the presence of a cupric salt, with a few drops of sodic salicylate, and then reduces with thiosulphate previously standardized upon a known quantity of iron by the same method, and estimates the excess by bichromate.

The solutions required are:

*Standard ferric chloride.*
*Standard sodic thiosulphate.*
*Standard potassic bichromate, dilute.*
*Ammonio-cupric chloride*, 2 per cent. solution.
*Sodic salicylate*, ½ per cent. solution.

*The Analysis:* 10 c.c. of iron solution are mixed in a flask with a few drops of HCl and 2 c.c. of cupric solution, then a few drops of the salicylate: the colour should be pure violet on dilution with water. Thiosulphate is then added until perfectly colourless. The mixture is then titrated back with bichromate till a faint violet colour appears.

If $\frac{N}{10}$ thiosulphate and bichromate are used, the calculation is easy; but if otherwise, the relative strength must be found by experiment.

Bruel (*Compt. rend.* xcvii. 954) modifies this process by operating without the copper solution, relying merely on the discharge of the violet colour in a boiling solution by thiosulphate standardized on a ferric solution of known strength.

### 3. Estimation by Potassic Iodide and Sodic Thiosulphate.

When ferric chloride is digested with potassic iodide in excess, iodine is liberated, which dissolves in the free potassic iodide—

$$FeCl^3 + KI = FeCl^2 + KCl + I.$$

*The Analysis:* The hydrochloric acid solution, which must contain no free chlorine or nitric acid, and all the iron in the ferric state, is nearly neutralized with caustic potash or soda, transferred to a well-stoppered flask, and an excess of strong solution of potassic iodide added; it is then heated to 50° or 60° C. on the water bath, closely stoppered, for about twenty minutes; the flask is then cooled, starch liquor added, and titrated with thiosulphate till the blue colour disappears. This process gives very satisfactory results in the absence of all substances liable to affect the potassic iodide, such as free chlorine or nitric acid, and is particularly serviceable for estimating small quantities of iron.

### 4. Estimation of Iron by Colour Titration.

These methods, which approach in delicacy the **Nessler** test for ammonia, are applicable for very minute quantities of iron, such as may occur in the ash of bread when testing for alum, water residues, alloys, and similar cases.

It is first necessary to have a standard solution of iron in the ferric state, which can be made by dissolving 1·004 gm. of iron wire in nitro-hydrochloric acid, precipitating with ammonia, washing and re-dissolving the ferric oxide in a little hydrochloric acid, then diluting to 1 liter. 1 c.c. of this solution contains 1 milligram of pure iron in the form of ferric chloride. It may be further diluted, when required, so as to contain $\frac{1}{100}$ milligram in a c.c., as in the case of ammonia solution for Nesslerizing.* The solution used for striking the colour is either potassic ferrocyanide or thiocyanate dissolved in water (1 : 20).

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* A solution of this strength can also be made by weighing 0·07 gm. of pure ammonio-ferrous sulphate (§ 31.2*b*), dissolving in water, acidifying with sulphuric acid, adding sufficient permanganate solution to convert the iron exactly into ferric salt, then diluting to 1 liter.

*Example with Ferrocyanide:* The material containing a minute unknown quantity of iron, say a water residue, is dissolved in hydrochloric acid, and diluted to 100 c.c., or any other convenient measure. 10 c.c. are placed into a white glass cylinder marked at 100 c.c., 1 c.c. of concentrated nitric acid added (the presence of free acid is always necessary in this process), then diluted to the mark with distilled water, and well stirred.

1 c.c. of ferrocyanide solution is then added, well mixed, and allowed to stand at rest a few minutes to develop the colour.

A similar cylinder is then filled with a mixture of, say 1 c.c. of standard iron solution, 1 c.c. nitric acid and distilled water, and 1 c.c. ferrocyanide added; if this does not approach the colour of the first mixture, other quantities of iron are tried until an exact similarity of colour occurs. The exact strength of the iron solution being known, it is easy to arrive at the quantity of pure iron present in the substance examined, and to convert it into its state of combination by calculation. The colorimeter may of course be here used with advantage.

*With Thiocyanate.*—Thompson (*J. C. S.* 1885, 493) recommends this method as being specially available in the presence of other ordinary metals and organic matters, silver, copper, and cobalt being the only interfering substances. The delicacy is said to be such, that 1 part of iron can be recognized in 50 million parts of water. The presence of free mineral acids greatly adds to the sensitiveness. The standard ferric solution may be the same as for ferrocyanide; and in preparing the material for titration, the weighed quantity is dissolved in an appropriate acid, evaporated nearly to dryness, taken up with water, converted into the ferric state by cautious addition of permanganate, then diluted with water to a measured volume, and an aliquot portion taken for titration.

The standard iron used by Thompson $= \frac{1}{10}$ m.gm. per c.c. (0·7 gm. double iron salt [oxidized] per liter).

*Example:* Into two glass cylinders marked at 100 c.c. pour 1 c.c. of concentrated nitric or hydrochloric acid, or better, 5 c.c. of either acid (1 : 5), 15 c.c. of thiocyanate, and to one glass a measured volume of the solution to be tested: fill up both glasses to the mark. If iron be present, a blood red colour more or less intense will be produced. Standard iron is then cautiously added from a burette to the other glass till the colour agrees. The quantity of Fe taken should not require more than 2 or 3 c.c. of the standard to equal it, or the colour will be too deep for comparison.

If other metals are present which form two sets of salts, they must be in the higher state of oxidation, or the colour is destroyed. Oxalic acid also destroys it. Examples in the presence of a great variety of metals show very good results.

## IRON ORES.

§ 61. In the analysis of iron ores it is very often necessary to determine not only the total amount of iron, but also the state in which it exists; for instance, magnetic iron ore consists of a mixture of the two oxides in tolerably definite proportions, and it is sometimes advisable to know the quantities of each.

In order to prevent, therefore, in such cases, the further oxidation of the ferrous oxide, the little flask apparatus (fig. 32) adopted by Mohr is highly recommended, or fig. 31 is equally serviceable.

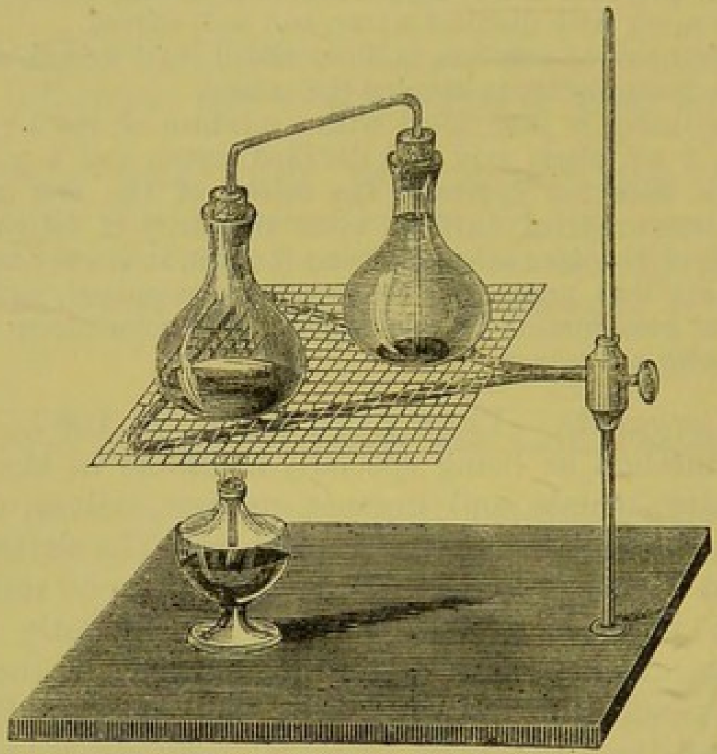

Fig. 32.

The left-hand flask contains the weighed ore in a finely powdered state, to which tolerably strong hydrochloric acid is added; the other flask contains distilled water only, the tube from the first flask entering to the bottom of the second. When the ore is ready in the flask and the tubes fitted, hydrochloric acid is poured in, and a few grains of sodic bicarbonate added to produce a flow of carbonic acid. The air of the flask is thus dispelled, and as the acid dissolves the ore, the gases evolved drive out in turn the carbonic acid, which is partly absorbed by the water in the second flask. When the ore is all dissolved and the lamp removed, the water immediately rushes out of the second flask into the first, diluting and cooling the solution of ore, so that, in the majority of cases, it is ready for immediate titration. If not sufficiently cool or dilute, a sufficient quantity of boiled and cooled distilled water is added.

When the total amount of iron present in any sample of ore has to be determined, it is necessary to reduce any peroxide present to the state of protoxide previous to titration.

(*a*) *Treatment of Ores to render them easily soluble in Acid.*—Hempel (*Berichte*, xviii. 1130) advocates the roasting of such ores as are naturally difficult of solution in a muffle for one hour, 1 part of ore to be mixed with 20 parts of calcic and 4 parts of sodic carbonate. By this means the formation of ferric silicate is avoided, organic matter is also destroyed, and an easily soluble ferric oxide is produced.

(*b*) *Reduction to the Ferrous state.*—When permanganate is to be used for titration the reduction is always best made with zinc. With bichromate, the best agent is either pure sodic sulphite, ammonic bisulphite, or stannous chloride.

It is often difficult to tell by mere colour whether the iron in any given solution is completely reduced to the ferrous state. In such cases it is well to spread a few drops of solution of potassic sulphocyanate on a white tile, and bring a drop of the iron solution in contact with it. A distinct red colour is a sure indication that reduction is not complete; a mere faint tinge is not an indication, because the reaction is so delicate that mere exposure to the air will produce an infinitesimal portion of $Fe^2O^3$, sufficient to give a faint colour.

*(c) Titration of the Iron Ore Solution.*—Owing to the fact that hydrochloric acid is in most instances the only solvent for some kinds of iron ore, technical operators often prefer bichromate to permanganate for titration. The reasons for this preference are twofold; namely, the irregularity which is liable to occur in the presence of hydrochloric acid, and the deep colour of the ferrous chloride. The first, however, may be set aside by proper precautions, and the second, by the use of lamp or gaslight instead of daylight. If the solution of the ore is well diluted and the liquid cold, the end of the reaction is very delicate; nevertheless, without special practice and judgment, the bichromate method will be found the best in all cases where hydrochloric acid has to be used.

Hart recommends permanganate as the best re-agent for titration. He heats the ore to redness in a porcelain tube, for three hours at least, in a stream of hydrogen; then cools, and adds it to boiling dilute sulphuric acid, at the same time passing a stream of hydrogen through the liquid, and titrates with permanganate in the ordinary way. Coal-gas is inapplicable, as some of its constituents absorbed by the acid act on the permanganate.

Some brown hæmatites, reduced by this method, yield an iron almost insoluble in the acid. Drown proposes to heat such ores in air or oxygen, to burn off carbonaceous matter before passing hydrogen over them; the iron then reduced dissolves easily. Most magnetic ores yield an insoluble portion containing iron; for such ores this method is no better than ordinary ones.

*(d) Direct Titration with Stannous Chloride.*—This method of estimating ferric iron in ores is extremely expeditious; and when the solution of iron is strongly acid and sufficiently hot, the results are very concordant, and especially adapted to the technical examination of mining samples.

Drown dissolves iron ore in hydrochloric acid, evaporates nearly to dryness, adds a little water, and then stannous chloride from a burette. The excess of stannous chloride is estimated by adding starch and standard iodine. The iron solution should be tolerably concentrated and warm; the tin solution is best freshly prepared: 1 c.c. = 0·012 gm. iron = 3 c.c. iodine or thereabout. Ten assays gave a mean of 38·235 per cent.; two assays with permanganate gave 38·17, and two gravimetric determinations gave 38·14 per cent. of iron. The author made four simultaneous assays in eighty minutes, the tin solution being prepared whilst the ores were dissolving. Metallic iron dissolved in hydrochloric acid with a little potassic chlorate, the solution being evaporated nearly to dryness, is used to standardize the tin solution.

### 1. Red and Brown Hæmatites.

Red hæmatite consists generally of ferric oxide accompanied with matters insoluble in acids. Sometimes, however, it contains phosphoric acid, manganese, and earthy carbonates.

Brown hæmatite contains hydrated ferric oxide, often accompanied by small quantities of ferrous oxide, manganese, and alumina; sometimes traces of copper, zinc, nickel, cobalt, with lime, magnesia and silica; occasionally also organic matters.

In cases where the total iron only has to be estimated, it is advisable to reduce the ore to fine powder; ignite gently to destroy organic matters, then treat with strong hydrochloric acid at near boiling heat till all iron is dissolved, and in case ferrous oxide is present add small quantities of potassic chlorate, afterwards evaporating to dryness to dissipate free chlorine; then dissolve the iron with hot dilute hydrochloric acid, filter, and make up to a given measure for titration.

In some instances the insoluble residue persistently retains some iron in an insoluble form; when this occurs, resort must be had to fluxing the residue with potassic bisulphate, followed by solution in hydrochloric acid, or to Hempel's method (§ 61 *a*).

### 2. Magnetic Iron Ore.

The ferrous oxide is determined first by means of the apparatus fig. 31 or 32. The ore is put into the vessel in a state of fine powder, strong hydrochloric acid added, together with a few grains of sodic bicarbonate, or still better, magnesite, and heat applied gently with the lamp until the ore is dissolved, then diluted if necessary, and titrated with bichromate or permanganate.

*Example:* 0·5 gm. of ore was treated as above, and required 19·5 c.c. of $\frac{N}{10}$ bichromate, which multiplied by 0·0056 gave 0·1092 gm. of iron = 0·1404 gm. of ferrous oxide = 28·08 per cent.

The ferric oxide was now found by reducing 0·5 gm. of the same ore, and estimating the total iron present: the quantity of bichromate required was—

59 c.c. $\frac{N}{10}$ = 0·3304 gm. total Fe
Deduct 0·1092 gm. as FeO

Leaving 0·2212 gm. as $Fe^2O^3$

The result of the analysis is therefore—

| | | |
|---|---|---|
| Ferrous oxide ... ... ... | 28·08 | per cent. |
| Ferric oxide ... ... ... | 63·20 | „ |
| Difference (Gangue, etc.) ... | 8·72 | „ |
| | 100·00 | |

### 3. Spathose Iron Ore.

The total amount of ferrous oxide in this carbonate is ascertained directly by solution in hydrochloric acid; as the carbonic acid evolved is generally sufficient to expel all air, the tube dipping under water may be dispensed with. Should the ore be very impure, zinc may have to be added in order to insure the reduction of all the iron present.

As the ore contains, in most cases, the carbonates of manganese, lime, and magnesia, these may all be determined, together with the iron, as follows :—

A weighed portion of ore is brought into solution in hydrochloric acid, and filtered, if necessary, to separate insoluble silicious matter.

The solution is then boiled, with a few drops of nitric acid to peroxidize the iron, diluted, and sodic carbonate added in sufficient quantity to precipitate the ferric oxide, then sodic acetate, and the whole boiled that the precipitate may become somewhat dense and separate from the liquid; filter, and if necessary, reduce the oxide of iron after careful washings, with zinc or stannous chloride, and determine with permanganate or bichromate.

The filtrate containing the other bases is treated with sodic hypochlorite, covered, and set aside for twenty-four hours in order to precipitate the manganese as hydrated oxide, which is collected and titrated as in § 64.

The filtrate from the last is mixed with ammonic oxalate to precipitate the lime, which is estimated by permanganate, as in § 48.

The filtrate from the lime contains the magnesia, which may be precipitated with sodic phosphate and ammonia, and the precipitate weighed as usual, or titrated with uranium solution.

### 4. Estimation of Iron in Silicates.

Wilbur and Whittlesey (*C. N.* xxii. 2) give a series of determinations of iron existing in various silicates, either as mixtures of ferric and ferrous salts or of either separately, which appear very satisfactory.

The very finely powdered silicate is mixed with rather more than its own weight of powdered fluor-spar or cryolite (free from iron) in a platinum crucible, covered with hydrochloric acid, and heated on the water-bath until the silicate is all dissolved. During the digestion either carbonic acid gas or coal gas free from $H^2S$ is supplied over the surface of the liquid, so as to prevent access of air. When decomposition is complete (the time varying with the nature of the material), the mixture is diluted and titrated with permanganate in the usual way for ferrous oxide; the ferric oxide can then be reduced by zinc and its proportion found.

*By Hydrofluoric Acid (Early's process)* : 2 gm. of the finely powdered silicate are placed in a deep platinum crucible, and 40 c.c. of hydrofluoric acid (containing about 20 per cent. HF) added. The mixture is heated to near the boiling point and occasionally stirred with a platinum wire until the decomposition of the silicate is complete, which occupies usually about ten minutes. 10 c.c. of pure $H^2SO^4$ diluted with an equal quantity of water are then added, and the heat continued for a few minutes. The crucible and its contents are then quickly cooled, diluted with fresh boiled water, and the ferrous salt estimated with permanganate or bichromate as usual.

Leeds (*Z. a. C.* xvi. 323) recommends that the finely powdered silicate be mixed with a suitable quantity of dilute sulphuric acid, and air excluded by $CO^2$ during the action of the hydrofluoric acid. The titration may then at once be proceeded with when the decomposition is complete.

If the hydrofluoric acid has been prepared in leaden vessels, it invariably contains $SO^2$; in such cases it is necessary to add to it, previous to use, some concentrated solution of permanganate, so as to oxidize the $SO^2$.

The process is a rapid and satisfactory one, yielding much more accurate results than the method of fusion with alkaline carbonates or acid potassic sulphate.

### 5. Estimation of Iron in Ores by comparison with the same weight of Pure Iron.

The principle of this method is fully explained in § 3, and is, of course, applicable to any substance which can be obtained tolerably pure, such as soft iron wire. The titrating solution may be either permanganate or bichromate of unknown strength.

### 6. Colorimetric estimation of Carbon in Steel and Iron.

The method devised by Eggertz, and largely adopted by chemists, for estimation of combined carbon, is well known, but is open to the objection that minute quantities of carbon cannot be discriminated by it, owing to the colour of the ferric nitrate present. Stead (*C. N.* xlvii. 285) in order to overcome this difficulty has devised a method described as follows :—

In some careful investigations on the nature of the colouring matter which is produced by the action of dilute nitric acid upon white iron and steel, it was found it had the property of being soluble in potash and soda solutions, and that the alkaline solution had about two and a half times the depth of colour possessed by the acid solution. This being so, it was clear that the colour matter might readily be separated from the iron, and be obtained in an alkaline solution, by simply adding an excess of sodium hydrate to the nitric acid solution of iron, and that the colour solution thus obtained might be used as a means of determining the amount of carbon present. Upon trial this was found to be the case, and that as small a quantity as 0·03 per cent. carbon could be readily determined.

The method is conducted as follows :—

*Standard solution of nitric acid*, 1·20 sp. gr.
*Standard solution of sodic hydrate*, 1·27 sp. gr.

One gram of the steel or iron to be tested is weighed off and placed in a 200 c.c. beaker, and, after covering with a watch-glass, 12 c.c. of standard nitric acid are added. The beaker and contents are then placed on a warm plate, heated to about 90° to 100° C., and there allowed to remain until dissolved, which does not usually take more than ten minutes. At the same time a standard iron containing a known quantity of carbon is treated in exactly the same way, and when both are dissolved 30 c.c. of hot water are added to each, and 13 c.c. soda solution.

The contents are now to be well shaken, and then poured into a glass measuring-jar and diluted till they occupy a bulk of 60 c.c. After again well mixing and allowing to stand for ten minutes in a warm place, they are filtered through dry filters, and the filtrates, only a portion of which is used, are compared. This may be done by pouring the two liquids into two separate measuring tubes in such quantity or proportion that upon looking down the tubes the colours appear to be equal.

Thus if 50 m.m. of the standard solution is poured into one tube, and if the steel to be tested contains say half as much as the standard, there will be 100 m.m. of its colour solution required to give the same tint. The carbon is therefore inversely proportional to the bulk compared with the standard, and in the above assumed case, if the standard steel contained 0·05 per cent. carbon, the following simple equation would give the carbon in the sample tested :—

$$\frac{0{\cdot}05 \times 50}{100} = 0{\cdot}025 \text{ per cent.}$$

The proportions here given must be strictly adhered to in order to insure exactness. The colours from low carbon irons differ in tint from those in high carbon steels, and therefore a low standard specimen must be used for comparison.

Stead has devised a special colorimeter for the process, but it is evident that any of the usual instruments may be used.

## LEAD.

$Pb = 206{\cdot}4.$

1 c.c. $\frac{N}{10}$ permanganate = 0·01032 gm. Lead.
1 c.c. normal oxalic acid = 0·1032 gm. „
Metallic iron × 1·842 = „
Double iron salt × 0·263 = „

§ 62. The accurate estimation of lead is in most cases better effected by weight than by measure; there are, however, instances in which the latter may be used with advantage.

### 1. As Oxalate (Hempel).

The acetic lead solution, which must contain no other body precipitable by oxalic acid, is put into a 300 c.c. flask, and a measured quantity of normal oxalic acid added in excess, the flask filled to the mark with water, shaken, and put aside to settle; 100 c.c. of the clear liquid may then be taken, acidified with sulphuric acid, and titrated with permanganate for the excess of oxalic acid. The amount so found multiplied by 3, and deducted from that originally added, will give the quantity combined with the lead.

Where the nature of the filtrate is such that permanganate cannot be used for titration, the precipitate must be collected, well washed, dissolved in dilute nitric acid, with a considerable quantity of sodic acetate, sulphuric acid added, and titrated with permanganate.

In neither case are the results absolutely accurate, owing to the slight solubility of the precipitate, but with careful manipulation the error need not exceed 1 per cent. The error is much increased in the presence of ammoniacal salts.

The technical analysis of red lead is best made as follows:—

2·064 gm. ($\frac{1}{50}$ eq. of Pb) are placed in a 300 c.c. porcelain basin, and 20 or 30 c.c. nitric acid sp. gr. 1·2 poured over it, then warmed gently with stirring. In a few minutes the lead oxide is dissolved and the peroxide left insoluble. 50 c.c. of $\frac{N}{5}$ oxalic acid are added and the mixture boiled: this decomposes and dissolves the peroxide, leaving undissolved any adulterant such as baryta, lead sulphate, oxide of iron, gypsum, or sand. While still hot $\frac{N}{5}$ permanganate is added in moderate portions until the colour is permanent for a few seconds. The volume of permanganate deducted from 50 gives direct the percentage of lead existing as peroxide.

The total lead may be found in the same solution by removing the excess of permanganate with a drop or two of oxalic acid, neutralizing with ammonia, adding a good excess of ammonic or sodic acetate, and titrating with bichromate as described in this section.

Lead acetates in crystals or in solution may readily and with tolerable accuracy be titrated direct with normal oxalic acid. The best effects are obtained however by adding the lead solution (diluted and rendered clear by a little acetic acid) from a burette into the oxalic acid contained in a flask or beaker, warmed by a water-bath. The addition of the lead solution is continued with shaking and warming until no further precipitation takes place.

Another method for acetates is to precipitate the lead with a slight excess of normal sulphuric acid in a 300 c.c. flask, fill to the mark, estimate the excess of $H^2SO^4$ in 100 c.c. by weight, then calculate the combined acid into lead; then by titrating another portion for acidity with phenolphthalein, the proportion of acetic acid can be obtained by deducting the free $H^2SO^4$ from the total acid found.

### 2. As Chromate.

The lead is precipitated as chromate, well washed and digested with a weighed excess of double iron salt and hydrochloric acid; the resulting solution contains ferric and chromic chlorides, together with lead chloride, and undecomposed iron salt. The quantity of the last is found by permanganate, and deducted from the original weight; the remainder, multiplied by the factor 0·263, will give the weight of lead.

Diehl (*Z. a. C.* 1880, 306) modifies the method originally devised by Schwarz by precipitating the lead with standard potassic bichromate in excess, and titrating the amount of excess with sodic thiosulphate.

The necessary solutions are—

*Standard potassic bichromate* containing 7·37 gm. per liter.

*Standard sodic thiosulphate* containing about 5 gm. per liter.

The relation of these solutions to each other is first found by blank experiment.

20 or 30 c.c. of the bichromate are placed in a boiling flask, with about 300 c.c. of water, and 20 or 30 c.c. of dilute $H^2SO^4$ (1 to 2). The liquid is then heated to boiling, and the thiosulphate cautiously dropped in until a point occurs at which the yellow colour just disappears, and which may be known by holding the flask over white paper or porcelain.

Lead ores and residues are treated with *aqua regia* and dilute sulphuric acid, concentrated by evaporation until the sulphuric acid fumes begin to appear, then transferred to a flask with water, and boiled in order to bring the ferric sulphate, etc., into solution; the solution is then cooled, and the tolerably clear liquid passed through a thin close filter previously moistened with dilute sulphuric acid, and leaving the bulk of lead sulphate in the flask. This latter is now boiled with some strong solution of neutral ammonic acetate (about 15 c.c. for 1 gm. of sulphate) and water, to bring it into solution, and passed through the same filter, the filtrate being received into a clean flask. The operation is repeated with a smaller quantity of acetate and water, and the filter finally washed with hot water containing some acetate. To make sure of dissolving all the lead out of the filter, it is well to make a final washing with hot dilute hydrochloric acid. The solution of lead is then acidified with a few drops of acetic acid, and precipitated in the cold with the bichromate in moderate excess (not less than 3—5 c.c.), which may be known by the colour. The mixture is well shaken, and set aside for half an hour to settle. The clear liquid is then passed through a double filter, the precipitate washed three or four times with cold water, and the mixed filtrate and washings titrated with thiosulphate for the excess of bichromate, as described in the blank experiment.

1 c.c. bichromate represents 0·01032 gm. of lead. The results obtained with known weights of pure lead salts were very exact.

Copper, cadmium, zinc, ferric salts, and cobalt, do not interfere with the reaction, but all metals precipitable by chromic acid should of course be removed.

Buisson again modifies this method as follows:—

The excess of bichromate is decomposed in the cold by potassic iodide in acid solution. The iodine set at liberty corresponds exactly with the amount of undecomposed bichromate.

Preference is given in titrating the iodine to the use of carbon disulphide as indicator, since the yellow colour of the chromate interferes with the blue colour of starch iodide.

*Standardizing the solutions.*—This will also show the method of analysis. 0·25 gm. pure lead is dissolved in about 5 c.c. of hot dilute nitric acid, boiled to expel nitrous vapours; the excess of acid neutralized with potash, and the precipitated lead oxide re-dissolved in acetic acid. It is then placed in a 250 c.c. flask with 50 c.c. of the bichromate and filled to the mark, let stand fifteen minutes, then a portion filtered through a dry filter, and 50 c.c. =0·5 gm. Pb taken for titration. It is acidified moderately with pure sulphuric acid, a few crystals of potassic iodide thrown in, and in a few moments about 5 c.c. of carbon disulphide, which assumes a rich rose colour. Thiosulphate solution is then run in from a burette until the colour is just destroyed.

Buisson uses a standard bichromate containing 14·218 gm. per liter, 5 c.c. of which represent 0·1 gm. lead, but the same solution as given for Diehl's process will suffice.

### 3. Alkalimetric Method (**Mohr**).

The lead is precipitated as carbonate by means of a slight excess of ammonic carbonate, together with free ammonia; the precipitate well washed, and dissolved in a measured excess of normal nitric acid; neutral solution of sodic sulphate is then added to precipitate the lead as sulphate. Without filtering, the excess of nitric acid is then estimated by normal alkali, each c.c. combined being equal to 0·1032 gm. of lead.

### 4. As Sulphide (**Casamajor**).

The lead, if not in a state convenient for titration, is separated as sulphate, well washed, and while still moist is dissolved in alkaline tartrate solution exactly as in the case of copper (see § 54.5); the precipitated sulphide separates very freely, and if the operation is performed in a white basin the end-point is easy of detection.

The chief drawback to the method is the instability of the sulphide solution, which necessitates a fresh standardizing with known quantities of metal for each day's work.

## MAGNESIA AND ALUMINA.

§ 63. The magnesia existing in the commercial Stassfurt salts used for manures, etc., and other soluble magnesia salts, may very readily be determined with accuracy by Stolba's method, as given for $P^2O^5$ in §§ 23.2 and 69, or in all cases where separation can be made as ammonio-magnesic phosphate. The precipitation may be hastened considerably by precipitating with microcosmic salt, in the presence of a tolerably large proportion of ammonic chloride, accompanied with vigorous stirring. Half an hour quite suffices to bring down the whole of the double phosphate, and its adherence to the sides of the beaker is of no consequence, if the titration is made in the same beaker, and with the same glass rod, using an excess of standard acid, and titrating back with weak standard ammonia and methyl orange.

The precipitate may also be titrated with standard uranium (§ 69). Precht (*Z. a. C.* 1879, 438) adopts the following method for soluble magnesia salts in kainit, kieserit, etc., depending upon the insolubility of magnesic hydrate in weak caustic potash:—

10 gm. of the substance are dissolved, filtered, and mixed with 25 c.c. of normal caustic potash, if it contains less than 50 per cent. of magnesic sulphate; or 50 c.c. if it contains more than 50 per cent. The mixture is warmed somewhat, transferred to a 500 c.c. flask, and the volume made up with water. After standing at rest for half an hour, 50 c.c. of the clear liquid are withdrawn, and the excess of normal alkali estimated in the usual way with normal acid. Ammonium and metallic salts must be absent.

1 c.c. normal potash = 0·02 gm. MgO.

Alumina salts (the alums and alumina sulphate used in dyeing and paper-making) may be titrated for alumina in the absence of iron (except in mere traces), by mixing the acid solutions with a tolerable quantity of sodic acetate, then a known volume in excess of $\frac{N}{10}$ phosphate solution (20·9 gm. of ammonio-sodic phosphate per liter), heating to boiling, without filtration; the excess of phosphate is found at once by titration with standard uranium. If iron in any quantity is present, it may be estimated in a separate portion of the substance, and its amount deducted before calculating the alumina. The latter is precipitated as $AlPO^4$, and any iron in like manner as $FePO^4$. Each c.c. of $\frac{N}{10}$ phosphate = 0·00513 gm. $Al^2O^3$. Only available for rough purposes.

*Bayer's method.*—As originally proposed, this process for estimating alumina in alums and aluminic sulphates was carried out by two titrations, a measured portion of the solution being first treated with an excess of normal soda in sufficient quantity to dissolve the precipitate of hydrate of alumina first formed. It was then diluted to a definite volume, half being titrated with litmus and other half with tropæolin.

A considerable improvement however has been made by using phenolphthalein as the indicator, one titration only being necessary. The method is based on the fact that, if to a solution of alumina, containing the indicator, standard soda is added in excess, or until the red colour is produced, standard acid be then added until the colour disappears, the volume of acid so required is less than the soda originally added in proportion to the quantity of alumina present.

The volume of acid which so disappears is in reality the quantity necessary to combine with the alumina set free by the alkali; and if this deficient measure of acid be multiplied by the factor 0·0171 ($\frac{1}{6}$ mol. wt. of $Al^2O^3$), the weight of alumina will be obtained.

The titration must take place in the cold and in dilute solutions. Very fair technical results have been obtained by me with potash and ammonia alums and the commercial sulphates of alumina.

The free sulphuric acid in alumina sulphates of commerce is best estimated by extraction with alcohol, diluting with water, and titrating with standard alkali and methyl orange.

## MANGANESE.

$Mn=55$, $MnO=71$, $MnO^2=87$.

### Factors.

| | | |
|---|---|---|
| Metallic iron | × | 0·63393 $=MnO$. |
| „ „ | × | 0·491 $=Mn$. |
| „ „ | × | 0·7768 $=MnO^2$. |
| Double iron salt | × | 0·0911 $=MnO$. |
| Cryst. oxalic acid | × | 0·6916 $=MnO^2$. |
| Double iron salt | × | 0·111 $=MnO^2$. |

1 c.c. $\frac{N}{10}$ solution$=$0·00355 gm. $MnO$ or$=$0·00435 gm. $MnO^2$.

§ 64. All the oxides of manganese, with the exception of the first or protoxide, when boiled with hydrochloric acid, yield chlorine in the following ratios :—

$Mn^2O^3=1$ eq. $O=$ 2 eq. Cl.
$Mn^3O^4=1$ eq. $O=$ 2 eq. Cl.
$Mn\,O^2=1$ eq. $O=$ 2 eq. Cl.
$Mn\,O^3=2$ eq. $O=$ 4 eq. Cl.
$Mn^2O^7=5$ eq. $O=10$ eq. Cl.

The chlorine so produced can be allowed to react upon a known weight of ferrous salt; and when the reaction is completed, the unchanged amount of iron salt is found by permanganate or bichromate.

Or, the chlorine may be led by a suitable arrangement into a solution of potassic iodide, there setting free an equivalent quantity of iodine, which is found by the aid of sodic thiosulphate.

Or, in the case of manganese ores, the reaction may take place with oxalic acid, resulting in the production of carbonic acid, which can be weighed as in Fresenius' and Wills' method, measured as in Parry's method, or the amount of unchanged acid remaining after the action can be found by permanganate.[*]

The largely increased use of manganese in the manufacture of steel has now rendered it imperative that some rapid and trustworthy method of estimation should be devised, and happily this has been done simultaneously by two chemists, Pattinson and Kessler; both have succeeded in finding a method of separating manganese as dioxide, of perfectly definite composition. Pattinson found that the regular precipitation was secured by ferric chloride,

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[*] The literature of manganese compounds and their estimation has now become very voluminous. The principal contributions to the subject are as follows :—

| | |
|---|---|
| Wright and Menke | *J. C. S.* 1880, 22—48. |
| Morawski and Stingl | *Jour. f. pract. Chem.* xviii. 96. |
| Volhard | *Annalen*, cxcviii. 318. |
| Guyard | *Bull. Soc. Chim.* [2] i. 88. |
| Kessler | *Z. a. C.* 1879, 1—14. |
| Pattinson | *J. C. S.* 1879, 365. |

and Kessler by zinc chloride. Wright and Menke have experimented on both processes with equally satisfactory results, but give a slight preference to zinc. Pattinson titrates the resulting $MnO^2$ with standard bichromate, and Kessler with permanganate.

Pattinson's method has been fully described (*J. C. S.* 1879, 365), and is essentially as follows :—

### 1. Precipitation as $MnO^2$ and Titration with Bichromate (Pattinson).

The necessary solutions and re-agents are :—

*Standard Potassic Bichromate.*—1 c.c. equal to 0·01 gm. Fe (1 dm.=0·1 grn. Fe).

*Standard Ferrous Sulphate.*—10 gm. of iron per liter, as near as may be, is a convenient strength, but as the strength alters from time to time, no exact quantity need be taken. 53 gm. of ferrous sulphate dissolved in a mixture of 250 c.c. of strong pure sulphuric acid, and 750 c.c. of water, will give a solution of about the proportion mentioned (or 530 grn. to 1000 dm.).

*Solution of Bleaching Powder.*—This re-agent is used to oxidize the manganese before precipitation (Kessler uses bromine water for the same purpose). 15 gm. per liter, or 150 grn. to 1000 dm. The clear solution is decanted, and preserved in well-stoppered bottles for use.

*Calcic Carbonate.*—Used for removing the free acid during precipitation. It should be in tolerably fine powder, and of granular texture.

The principle of the method is that the manganese compound being brought into solution in hydrochloric acid, ferric chloride (if iron is not already present) is added, or zinc chloride (zinc oxide or sulphate answers equally well), so that in either case there is not less than the same quantity of either of these metals present as there is of manganese; an excess of either of them is of no consequence. The oxidizing agent, followed by hot water, is then poured into the mixture so as to bring the temperature from about 60° to 70° (140°—160° F.), then a slight excess of calcic carbonate, and the whole well stirred till all $CO^2$ is evolved, and the precipitate of $MnO^2$ mixed with iron or zinc, or both, settles freely, leaving the supernatant liquid clear and colourless (in the case of using bromine water the colour should be amber, showing a decided excess of bromine). In examining manganiferous irons or steels, as also in many ores, there will always be plenty of iron present; if this, however, is not the case, it is always preferable to use zinc rather than iron for the necessary addition.

Wright and Menke obtained the best results when the solution was so diluted, that about 150 or 200 c.c. of total fluid (including the oxidizing solution) were present for every 0·1 gm. $MnO^2$ precipitated, using a quantity of zinc sulphate or ferric chloride containing from 1½ to 2 parts of metal for every 1 part of $MnO^2$.

*Titration of the precipitated* $MnO^2$.—The precipitate is collected on a large double filter, or on glass wool, and washed with warm water till the washings show no trace of chlorine or bromine when tested with iodized starch-paper.

Finally the precipitate, with its filter, is returned to the beaker in which it was originally thrown down, and which will contain traces adhering to its sides, a measured excess of ferrous solution added, which being freely acid speedily dissolves the $MnO^2$; cold water is then added, and the titration completed with bichromate in the usual way.

As some filtering paper has a slight reducing action upon the bichromate, it is well in standardizing the ferrous solution to add about the same amount of the paper as would be used in the actual analysis.

*Example* (Pattinson): The standard solution of ferrous sulphate was of such strength that 100 dm.=101·1 dm. of bichromate. The 100 dm. of iron solution, after addition of the precipitated $MnO^2$ (from 10 grn. of ore), required 57 dm. of bichromate. 101·1—57=44·1 dm.=4·41 grn. Fe; this multiplied by the factor for manganese in relation to iron (0·491) gave 2·165 grn. The percentage of manganese was therefore 21·65.

Should the ore or alloy be richer in manganese than iron, it is advisable to add zinc sulphate or chloride to make up the necessary quantity. The ferrous solution alters slightly from day to day, and therefore must be carefully standardized from time to time.

Kessler's process is more cumbrous than Pattinson's, and consists in reducing the $MnO^2$ by antimonious chloride, then titrating the manganous oxide with permanganate standardized upon manganous pyrophosphate.

**Ores and Alloys of Manganese.**—The following are practical examples, taken mainly from Pattinson's experience.

*Spiegeleisen.*—This alloy usually contains from 10 to 25 per cent. of manganese and, of course, a sufficient amount of iron for the dioxide precipitation. 10 grn. are taken for analysis. This amount is dissolved in about 12 dm. of hydrochloric acid with the aid of heat. About 5 dm. of nitric acid are then added for the purpose of converting the ferrous into ferric chloride (on the gram system the quantities would be 1 gm. of alloy, 12 c.c. of HCl, and 5 c.c. of $HNO^3$ respectively). After washing the cover and sides of the beaker with cold water, the excess of acid is neutralized by the addition of calcic carbonate until the solution has a reddish colour. 100 dm. of the bleaching-powder solution or about 50 dm. of bromine water are added, without previous addition of hydrochloric acid as in the case of ores. Hot water is then added to heat the solution to 140—160° F., and then about 25 grn. of calcic carbonate, and the solution well stirred. The rest of the process is conducted as before described.

*Ferro-Manganese.*—For the quantitative analysis of this alloy an amount which contains from two to four grains of manganese may be taken. The solution is made as in the case of spiegeleisen. If the alloy contains less iron than manganese, zinc chloride is added so as to make the amount of the iron and zinc fully equal to that of the manganese. The amount of bleaching-powder solution to be added must depend upon the amount of manganese in solution, taking care to add about 40 dm. of bleaching-powder solution of the strength above-named for every grain of manganese present.

As in the case of ores, instead of weighing off separately the amounts required for each test, a larger quantity may be dissolved and peroxidized, and, after making up the solution to a known bulk in a measuring flask, the necessary quantities for the test measured out.

*Steel.*—50 grn. of steel are dissolved, by the aid of heat, in about 35 dm. of hydrochloric acid of about 1·180 sp. gr. The ferrous chloride thus formed is then converted into ferric chloride by the addition of about 9 dm. of nitric acid of about 1·400 sp. gr. The solution is made in a beaker of about 35-oz. capacity. Calcic carbonate is then added until the solution is slightly red. 135 grn. of calcic carbonate are now weighed or measured, and about one-half of this added to the solution. After the effervescence caused by the escape of carbonic acid has ceased, about 40 dm. of the bleaching-powder solution are added, and then hot water to about 150° F., and then the remainder of the calcic carbonate. If the latter is added at once, the effervescence is so great that the substance is likely to froth over the edges of the vessel; and if the bleaching-powder solution is added before any calcic carbonate has been added, the chlorine is likely to be expelled by the evolution of the carbonic acid. The precipitate is then thrown on a sufficiently large filter, and washed until free from any trace of chlorine. Although the precipitate is bulky it is very readily washed.

About 20 dm. of the ferrous sulphate solution are standardized, and the same quantity used for decomposing the manganese dioxide in the case of steels; but it is sometimes found necessary to add a little additional sulphuric acid, in order to dissolve the ferric oxide precipitate and the excess of calcic carbonate it may contain.

*Manganese Slags, etc.*—These are treated similarly to the above, using for the analysis such a quantity as will not contain more than about 2·5 grn. of manganese for the above-named amounts of re-agents, and taking care to have a sufficient amount of ferric or zinc chloride in the solution when the manganese is precipitated.

Should lead, copper, nickel, or cobalt exist in the substance under examination, these must be separated before the manganese is precipitated, as they form higher oxides under the conditions of the precipitation, which oxides, like manganese dioxide, convert ferrous into ferric oxide. Fortunately, in most manganiferous iron ores and in spiegeleisen, ferro-manganese and steel, none of these metals occur in such quantity as to appreciably affect the correct estimation of the manganese.

The process as above described is undoubtedly by far the best volumetric one known for the estimation of manganese in steels and ores.

Atkinson (*J. S. C. I.* v. 365) gives the following short description of the method as practically in daily use in a large steel works.

Weigh out 0·5 gm. or 0·6 gm. of an ore containing about 20 per cent. manganese, dissolve in 7 or 8 c.c. of strong HCl, and, when dissolved, wash the whole, without filtering, into a large narrow-sided beaker. When cold it is neutralized with precipitated calcic carbonate, until the liquid assumes a reddish hue. 40 or 50 c.c. of saturated bromine water are added, and the mixture allowed to stand in the cold for half-an-hour. At the expiration of that time the beaker is nearly filled up with boiling water, and precipitated calcic carbonate added until there is no further effervescence, and part of the carbonate is evidently unacted upon. A small quantity of spirits of wine is then added, the whole well stirred, and the precipitate allowed to settle. The clear liquid is filtered off and fresh boiling water added to the residue in the beaker, a little spirits of wine being used to reduce any permanganate which is formed. The filtration and washing are repeated until the filtrate when cooled no longer turns iodized starch-paper blue. During the washing about 1·9 to 2·5 gm. of pure granular ferrous-ammonium sulphate are weighed out, washed into the beaker in which the precipitation took place, and about 30 to 50 c.c. of dilute sulphuric acid added. The filter containing the precipitated $MnO^2$ is then placed in the beaker, and the latter is quickly dissolved by the oxidation of a portion of the ferrous salt into ferric sulphate. The remaining ferrous iron is then titrated with potassic bichromate in the usual way. The difference in the number of c.c. of bichromate used from the number which the original weight of the ferrous-ammonium sulphate would have required if directly titrated, is a measure of the quantity of $MnO^2$ present. For rapidity and simplicity this volumetric process leaves nothing to be desired; duplicate experiments agree within very narrow limits; and if the assumption is accepted that the presence of ferric chloride enables the complete oxidation of the manganese to the state of peroxide, no other process can compete with it.

Pattinson prefers to use bleach solution to bromine, because the formation of permanganate is more easily seen. In any case there ought to be no quantity of permanganate formed, and if the first experiment shows this to be the case, another trial must be commenced with less oxidizing material.

### 2. By Precipitation with Potassic Permanganate (Guyard).

If a dilute neutral or faintly acid solution of manganese salt be heated to 80° C. and permanganate added, hydrated $MnO^2$ is precipitated, and the end of the reaction is known by the occurrence of the usual rose colour of permanganate in excess. The reaction is exact in neutral solutions. Any large excess of either HCl or $H^2SO^4$ causes irregularity, as also do ferric or chromic salts; nickel, cobalt, zinc, alumina, or lime, in moderate quantity are of no consequence.

This method is of easy execution, and gives good results in cases where it can be properly applied, but such instances are few.

*The Analysis:* 1 or 2 gm. of the manganese compound are dissolved in *aqua regia*, boiled a few minutes, the excess of acid neutralized with alkali, then diluted largely with boiling water (1 or 2 liters) kept at a temperature of 80°C., and standard permanganate added so long as a brownish precipitate forms, and until the clear supernatant liquid shows a distinct rose colour. 2 eq. of permanganate = 3 eq. of manganese, therefore 1 c.c. of $\frac{N}{10}$ solution = 0·0016542 gm. of Mn.

A modification of this process is strongly recommended by Wright and Menke (*J. C. S.* 1880, 42), and which combines the principle adopted by Kessler and Pattinson; viz., the addition of zinc sulphate to regulate the precipitation of $MnO^2$.

The neutral or only faintly acid solution is diluted, so that not more than 0·1 gm. $MnO^2$ is contained in 150 c.c. A solution of permanganate is prepared of about half-per-cent. strength, and in it are dissolved crystals of zinc sulphate in such proportion that about ten parts are present for every one part of $MnO^2$ to be precipitated.

The cold manganese solution is then poured into this mixture slowly, with gentle shaking or stirring. Of course there must be an excess of permanganate which is shown by the pink colour. In a few minutes the clear pink fluid may be poured off through a glass wool filter; the precipitate of $MnO^2$ (containing some zinc) is also brought on the same filter, washed well with cold water, and finally titrated with ferrous sulphate or double iron salt, and $\frac{N}{10}$ permanganate or bichromate.

The numbers obtained by Wright and Menke were extremely satisfactory with manganese solutions of known strength.

Volhard's method depends very much on the same principles as the foregoing, the details being as follows:—

A quantity of material is taken so as to contain from 0·3 to 0·5 gm. Mn, dissolved in nitric acid, evaporated in porcelain to dryness, first adding a little ammonic nitrate, then heated over the flame to destroy organic matter. The residue is digested with HCl, adding a little strong $H^2SO^4$, and again evaporated to dryness, first on the water bath, then with greater heat till vapours of $SO^3$ occur. It is then washed into a liter flask and neutralized with sodic hydrate or carbonate: sufficient pure zinc oxide, made into a cream, is added to precipitate all the iron. The flask is filled to the mark, shaken, and 200 c.c. filtered off into a boiling flask, acidified with 2 or 3 drops of nitric acid, heated to boiling, and titrated with $\frac{N}{10}$ permanganate whilst still hot.

A repetition should be made to verify the results.

*Indirect technical method.*—This is in use at several works as a rapid approximate estimation of the manganese in spiegels, ferromanganese, pig-iron, etc.

It consists in determining the iron by bichromate, the silicon by weight, adding 5 per cent. for samples containing less than 30 per cent. Mn., or 6 per cent. for richer samples, and calling the rest manganese. The results are said to be well within $\pm 0{\cdot}5$ per cent.

*The Analysis:* 0·5 gm. of the sample is dissolved in dilute $H^2SO^4$, and titrated in the usual way with bichromate. 2 gm. meantime is dissolved in either dilute $H^2SO^4$ or HCl, evaporated to dryness on a hot plate, residue treated again with acid, the silica filtered off, ignited, weighed, and calculated to Si. Then $Fe + Si + 5$ or 6 per cent. $= Mn$.

Experience seems to show that the accuracy of the method is greater with alloys containing only a moderate proportion of Mn. (Holditch, *C. N.* xlix. 9; Atkinson, *ibid.* p. 25).

There are many other volumetric methods in use for estimating manganese either as binoxide or metal, among which may be mentioned that of Chalmers Harvey (*C. N.* xlvii. 2) by stannous chloride, and that of Williams (*Trans. Amer. Inst. of Mining Engineers,* x. 100), which consists in separating $MnO^2$ from a nitric solution by potassic chlorate, dissolving in excess of standard oxalic acid, and estimating the excess by permanganate.

A critical paper on this process, accompanied with the results of experiment, is contributed by **Macintosh** (*C. N.* l. 75). Also another by **Hintz** (*Z. a C.* xxiv. 421—438) reviewing a large number of volumetric methods for manganese, but as none of them are more accurate or convenient than the methods here given, they are omitted.

### 3. Estimation of Manganese in small quantities (Chatard).

This method depends upon the production of permanganic acid by the action of nitric acid and lead peroxide; the accuracy of the process as a quantitative one can, however, only be depended on when the quantity of manganese is very small, such as exists in some minerals, soils, etc.

The material to be examined is dissolved in nitric acid and boiled with lead peroxide, by which means any manganese present is converted to permanganate; the quantity so produced is then ascertained by a weak freshly made standard solution of oxalic acid or ammonic oxalate.

The process gives good results in determining manganese in dolomites and limestones, where the proportions amount to from $\frac{1}{10}$ to 2 per cent. In larger quantities the total conversion of the manganese cannot be depended on.

**Peters** avails himself of this method for estimating manganese in pig iron or steel by weighing 0·1 gm. of the sample, and boiling in 3 or 4 c.c. of nitric acid until solution of the metal is complete, adding 0·2 or 0·3 gm. $PbO^2$, and again boiling for two or three minutes without filtering off the insoluble graphite, if such should be present. The solution is then cooled, filtered through asbestos into a suitable graduated tube, and the colour compared with a standard solution of permanganate contained in a similar tube.

The standard permanganate is best made by diluting 1 c.c. of $\frac{N}{10}$ solution with 109 c.c. of water; each c.c. will then represent 0·00001 gm. Mn. It has been previously mentioned that accurate results by this method can only be obtained by using very small quantities of material. **Peters** finds this to be the case, and hence recommends, that for irons containing from 0·10 to 0·35 per cent. of Mn. 0·1 gm. should be operated upon; when from 0·8 to 1 per cent. is present, 0·1 gm. of the sample is weighed and one-fourth of the solution only treated with $PbO^2$; in still richer samples proportionate quantities must be taken. As a guide, it is well to assume, that when the amount of iron taken yields a colour equal to 25—35 c.c. of the standard, the whole of the Mn is oxidized. The actual amount of manganese in any test should not exceed half a milligram (*C. N.* xxxiii. 35).

### 4. Estimation in Spiegeleisen, Steel, etc., by measurement of $CO^2$ (Parry).

Parry adopts the well-known reaction in Fresenius and Wills' process of decomposing $MnO^2$ with sulphuric or hydrochloric acid and sodic oxalate, by dissolving a known weight of spiegeleisen in strong nitric acid, in a small pear-shaped flask of hard glass; evaporating to dryness, igniting gently for ten minutes, and after cooling treating the residue with sodic oxalate and hydrochloric acid, connecting the flask immediately to the gas apparatus, and conveying the evolved $CO^2$ into it for measurement over mercury. Parry uses an apparatus devised by himself, and figured in his paper (*C. N.* xxix. 86); but any of the gas apparatus described in Part VII. will suffice. The number of c.c. of $CO^2$ at 760° m.m. pressure and 0° C. temperature being known, it is easy to calculate the corresponding quantity of manganese.

$$87 \text{ parts by weight of } MnO^2 = 88\ CO^2 = 55 \text{ Manganese.}$$

It was, however, found impossible to obtain a product containing $MnO^2$. Although many experiments were made with this object, heating over the Bunsen's burner as previously described, the manganese was always present as $Mn^2O^3$, and further heating for thirty minutes showed no loss of oxygen. Consequently, 88 parts of $CO^2$ represented 110 of metallic manganese.

*Example.*

| | |
|---|---|
| 0·5 gm. of Spiegeleisen gave $CO^2$ | 31·80 c.c. |
| Temperature ... ... ... | 19·00° |
| Barometer ... ... ... | 738·00 m.m. |
| Tension of aqueous vapour ... | 16·36 m.m. |

$$\frac{31{\cdot}8 \times 721{\cdot}64}{760 \times \{1+(0{\cdot}003665 \times 19)\}} = \frac{28{\cdot}22 \text{ c.c. } CO^2 \times 0{\cdot}1966 \times 110}{88} = 0{\cdot}06934 \text{ gm. Mn} = 13{\cdot}868 \text{ per cent.}$$

The calculation may be simplified by the use of a table, where the divisor for the formula—

$$\frac{V \times B}{760 \times (1 + \delta t)}$$

is given. Also the value of 1 c.c. of $CO^2$ shown by the instrument may be expressed in parts by weight of Mn. Thus, 28·22 c.c. of $CO^2 = 0{\cdot}06934$ gm. of $CO^2$; therefore 1 c.c. $= 0{\cdot}00245716$ gm. of Mn, which, multiplied by $x$ c.c. of $CO^2$ found, gives at once the corresponding amount of manganese.

This method has been applied to the determination of manganese in steel, treating not less than 4 gm. of steel, and measuring over mercury. The dry product requires a rather stronger heat, best obtained by heating over a small Bunsen's burner in an open platinum capsule. It is best to take 10 gm. of steel for solution, evaporate to dryness in a porcelain dish, and heat a weighed portion of the dry residue as above, reserving part for a second trial.

## 5. Technical Examination of Manganese Ores used for Bleaching Purposes, etc.

One of the most important things connected with the analysis of manganese ores is the determination of moisture. Fresenius has found by a most careful series of experiments that the temperature at which all hygroscopic moisture is expelled, without disturbing that which is chemically combined, is 120° C., and this temperature is now used by most chemists. The drying apparatus devised by Fresenius consists of a round cast-iron air chamber, about ten inches in diameter, and two inches deep, having six openings at the top, into which little brass pans, two and a half inches in diameter, are dropped, containing the very finely powdered ore; into one of the pans the bulb of a thermometer is placed, imbedded in iron filings, and the instrument kept upright by an iron rod and ring attached to the upper surface of the air chamber. The whole is supported by a tripod, and heated by a gas flame to the required temperature. The ore, when powdered and dried at this temperature, rapidly absorbs moisture on exposing it to the air, and consequently has to be weighed quickly; it is better to keep the powdered and dried sample in a small light stoppered bottle, the weight of which, with its contents and stopper, is accurately known. About 1 or 2 gm., or any other quantity within a trifle, can be emptied into the proper vessel for analysis, and the exact quantity found by reweighing the bottle.

A hardened steel or agate mortar must be used to reduce the mineral to the finest possible powder, so as to insure its complete and rapid decomposition by the hydrochloric acid.

Considerable discussion has occurred as to the best processes for estimating the available oxygen in manganese ores, arising from the fact that many of the ores now occurring in the market contain iron in the ferrous state; and if such ores be analyzed by the usual iron method with hydrochloric acid, a portion of the chlorine produced is employed in oxidizing the iron contained in the original ore. Such ores, if examined by Fresenius and Wills' method, show therefore a higher percentage than by the iron method, since no such consumption of chlorine occurs in the former process. Manufacturers have therefore refused to accept certificates of analysis of such ores when based on Fresenius and Wills' method. This renders the volumetric processes of more importance, and hence various experiments have been made to ascertain their possible sources of error.

The results show that the three following methods give very satisfactory results (see Scherer and Rumpf, *C. N.* xx. 302; also Pattinson, *ibid.* xxi. 266; and Paul, xxi. 16).

### 6. Direct Analysis by Distillation with Hydrochloric Acid.

This is the quickest and most accurate method of finding the quantity of available oxygen present in any of the ores of manganese or mixtures of them. It also possesses the recommendation that the quantity of chlorine which they liberate is directly expressed in the analysis itself; and, further, gives an estimate of the quantity of hydrochloric acid required for the decomposition of any particular sample of ore, which is a matter of some moment to the manufacturer of bleaching powder.

The best form of apparatus for the operation is shown in fig. 26. For precautions in conducting the distillation see § 35.

In order that the percentage of dioxide shall be directly expressed by the number of c.c. of $\frac{N}{10}$ thiosulphate solution used, 0·436 gm. of the properly dried and powdered sample is weighed and put into the little flask; solution of potassic iodide in sufficient quantity to absorb all the iodine set free is put into the large tube (if the solution containing $\frac{2}{10}$ eq. or 33·2 gm. in the liter be used, about 70 or 80 c.c. will in ordinary cases be sufficient); very strong hydrochloric acid is then poured into the distilling flask, and the operation conducted as in § 35. Each equivalent of iodine liberated represents 1 eq. Cl, also 1 eq. $MnO^2$.

Instead of using a definite weight, it is well to do as before proposed, namely, to pour about the quantity required out of the weighed sample-bottle into the flask, and find the exact weight afterwards.

Barlow (*C. N.* liii. 41) records a good method of separating Mn from the metals of its own group as well as from alkalies and alkaline earths.

For the quantitative estimation of Fe and Mn in the same solution as chlorides (other metals except Cr and Al may be present, but best absent), solution of $NH^4Cl$ is first added, then strong $NH^4HO$ in excess; boil, then hydrogen peroxide so long as a precipitate falls, boil for a few minutes, filter, wash with hot water, ignite, and weigh the mixed oxides together as $Fe^2O^3 + Mn^3O^4$.

The oxides are then distilled with HCl in Mohr's apparatus as above, and the amount of iodine found by thiosulphate.

The weight of mixed oxides, minus the $Mn^3O^4$, gives the weight of $Fe^2O^3$.

Pickering (*J. C. S.* 1880, 128) has pointed out that pure manganese oxides, freshly prepared, or the dry oxides in very fine powder, may be rapidly estimated without distillation by merely adding them to a large excess of potassic iodide solution in a beaker, running in 2 or 3 c.c. of hydrochloric acid, when the oxides are immediately attacked and decomposed; the liberated iodine is then at once titrated with thiosulphate. Impure oxides, containing especially ferric oxide, cannot, however, be estimated in this way, since the iron would have the same effect as manganic oxide; hence, distillation must be resorted to in the case of all such ores, and it is imperative that the strongest hydrochloric acid should be used.

Pickering's modified process is well adapted to the examination of the Weldon mud, for its available amount of manganese dioxide.

### 7. Estimation by Oxalic Acid.

The very finely powdered ore is mixed with a known volume of normal oxalic acid solution, sulphuric acid added, and the mixture heated and well shaken to bring the materials into intimate contact, and liberate the $CO^2$. When the whole of the ore is decomposed, which may be known by the absence of brown or black sediment, the contents of the vessel are made up to a definite volume, say 300 c.c., and 100 c.c. of the dirty milky fluid well acidified, diluted, and titrated for the excess of oxalic acid by permanganate. If, in consequence of the impurities of the ore, the mixture be brown or reddish coloured, this would of course interfere with the indication of the permanganate, and consequently the mixture in this case must be filtered; the 300 c.c. are therefore well shaken and poured upon a large filter. When about 100 c.c. have passed through, that quantity can be taken by the pipette and titrated as in the former case.

If the solution be not dilute and freely acid, it will be found that the permanganate produces a dirty brown colour instead of its well-known bright rose-red; if the first few drops of permanganate produce the proper colour immediately they are added, the solution is sufficiently acid and dilute.

If 4·357 gm. of the ore be weighed for analysis, the number of c.c. of normal oxalic acid will give the percentage of dioxide; but as that is rather a large quantity, and takes some time to dissolve and decompose, half the quantity may be taken, when the percentage is obtained by doubling the volume of oxalic acid.

*Example:* The permanganate was titrated with normal oxalic acid, and it was found that 1 c.c.=0·25 c.c. of normal oxalic acid. 2·178 gm. of a fine sample of commercial manganese (pyrolusite) were treated with 50 c.c. of normal oxalic, together with 5 c.c. of concentrated sulphuric acid until the decomposition was complete. The resulting solution was milky, but contained nothing to obscure the colour of the permanganate, and, therefore, needed no filtration. It was diluted to 300 c.c., and 100 c.c. taken for titration, which required 6·2 c.c. of permanganate. A second 100 c.c. required 6·3, mean 6·25, which multiplied by 3 gave 18·75 c.c.; this multiplied by the factor 0·25 to convert it into oxalic acid gave 4·68 c.c. normal oxalic, and this being deducted from the original 50 c.c. used, left 45·32 c.c.=90·64 per cent. of pure manganic dioxide.

This process possesses an advantage over the following, inasmuch as there is no fear of false results occurring from the presence of air. The analysis may be broken off at any stage, and resumed at the operator's convenience.

### 8. Estimation by Iron.

The most satisfactory form of iron is soft "flower" wire, which is readily soluble in sulphuric acid. If a perfectly dry and unoxidized double iron salt be at hand, its use saves time. 1 mol. of this salt = 392, representing 43 5 of $MnO^2$, consequently, 1 gm. of the latter requires 9 gm. of the double salt; or in order that the percentage shall be obtained without calculation, 1·111 gm. of ore may be weighed and digested in the presence of free sulphuric acid, with 10 gm. of double iron salt, the whole of which would be required supposing the sample were pure dioxide. The undecomposed iron salt remaining at the end of the reaction is estimated by permanganate or bichromate; the quantity so found is deducted from the original 10 gm., and if the remainder be multiplied by 10 the percentage of dioxide is gained.

Instead of this plan, which necessitates exact weighing, any convenient quantity may be taken from the tared bottle, as before described, and digested with an excess of double salt, the weight of which is known. After the undecomposed quantity is found by permanganate or bichromate, the remainder is multiplied by the factor 0·111, which gives the proportion of dioxide present, whence the percentage may be calculated.

The decomposition of the ore may very conveniently be made in the flask apparatus fig. 31. The ore is first put into the decomposing flask, then the iron salt and water, so as to dissolve the salt to some extent before the sulphuric acid is added. Sulphuric acid should be used in considerable excess, and the flask heated by the spirit lamp till all the ore is decomposed; the solution is then cooled, diluted, and the whole or part titrated with permanganate or bichromate. Instead of this apparatus, a single flask, with tube and indiarubber valve, will be equally convenient.

*Example:* 1 gm. of double iron salt was titrated with permanganate solution, of which 21·4 c.c. were required.

1·111 gm. of the sample of manganese was accurately weighed and digested with 8 gm. of iron salt, and sulphuric acid. After the decomposition 8·8 c.c. of permanganate were required to peroxidize the undecomposed iron salt (=0·42 gm.), which deducted from the 8 gm. originally used, left 7·58 gm.; or placing the decimal point one place to the right, 75·8 per cent. of pure dioxide.

In the case of using $\frac{N}{10}$ bichromate for the titration, the following plan is convenient:—100 c.c. of $\frac{N}{10}$ bichromate = 3·92 gm. of double iron salt (supposing it to be perfectly pure), therefore if 0·436 gm. of the sample of ore be boiled with 3·92 gm. of the double salt and excess of acid, the number of c.c. of bichromate required deducted from 100 will leave the number corresponding to the percentage.

*Example:* 0·436 gm. of the same sample as examined before, was boiled with 3·92 gm. of double salt, and afterwards required 24 c.c. of $\frac{N}{10}$ bichromate, which deducted from 100 leaves 76 per cent. of dioxide, agreeing very closely with the previous examination.

When using metallic iron for the titration (which in most cases is preferred) Pattinson proceeds as follows:—30 grn. of clean iron wire are placed in the apparatus fig. 31, with 3 oz. of dilute sulphuric acid, made by adding 3 parts of water to one of concentrated acid. When the iron is quite dissolved, 30 grn. of the finely powdered and dried sample of manganese ore to be tested are put into the flask, the cork replaced, and the contents again made to boil gently over a gas flame until it is seen that the whole of the black part of the manganese is dissolved. The water in the small flask is then allowed to recede through the bent tube into the larger flask, more distilled water is added to rinse out the small flask or beaker and bent tube, the cork well rinsed, and the contents of the flask made up to about 8 or 10 oz. with distilled water. The amount of iron remaining unoxidized in the solution is then ascertained by means of a standard solution of potassic bichromate. The amount indicated by the bichromate deducted from the total amount of iron used, gives the amount of iron which has been oxidized by the manganese ore, and from which the percentage of manganic dioxide contained in the ore can be calculated. Thus, supposing it were found that 4 grn. of iron remained unoxidized, then 30—4=26 grn. of iron which have been oxidized by the 30 grn. of ore. Then, as

$$56 : 43·5 : : 26 : 20·2$$

the amount of dioxide in the 30 grn. of ore. The percentage is, therefore, 67·33. Thus—

$$30 : 20·2 : : 100 : 67·33$$

Grain weights are given in this example, but those who use the gram system will have no difficulty in arranging the details accordingly.

The method generally adopted at alkali works is as follows :—

Weigh out 1·0875 gm. of the finely ground dried ore into a small flask, fitted with tube and elastic valve. Add to it 75 c.c. of a solution made by dissolving 100 gm. pure ferrous sulphate in water, adding 100 c.c. pure $H^2SO^4$, and diluting to a liter. Close the flask by its indiarubber stopper containing the valve, and heat till the ore is decomposed, leaving only a light coloured sediment. After complete cooling, add about 200 c.c. cold water, and immediately titrate with $\frac{N}{10}$ permanganate to a faint pink. While the ore is decomposing, titrate 25 c.c. of the iron solution to ascertain its exact strength, and calculate the volume for 75. c.c. Deduct the difference between the two titrations. Each c.c. of permanganate so found represents 0·02175 gm. $MnO^2$ or 2 per cent.

## MERCURY.

$Hg=200$.

1 c.c. $\frac{N}{10}$ solution = 0·0200 gm. Hg.
= 0·0208 gm. $Hg^2O$
= 0·0271 gm. $HgCl^2$
Double iron salt × 0·5104 = Hg
" " × 0·6914 = $HgCl^2$

### 1. Precipitation as Mercurous Chloride.

§ 65. THE solution to be titrated must not be warmed, and contain the metal only in the form of protosalt. $\frac{N}{10}$ sodic chloride is added in slight excess, the precipitate washed with the least possible quantity of water to ensure the removal of all the sodic chloride; to the filtrate a few drops of chromate indicator are added, then pure sodic carbonate till the liquid is of clear yellow colour, $\frac{N}{10}$ silver is then delivered in till the red colour occurs. The quantity of sodic chloride so found is deducted from that originally used, and the difference calculated in the usual way.

### 2. By Ferrous Oxide and Permanganate (Mohr).

This process is based on the fact that when mercuric chloride (corrosive sublimate) is brought in contact with an alkaline solution of ferrous oxide in excess, the latter is converted into ferric oxide, while the mercury is reduced to mercurous chloride (calomel). The excess of ferrous oxide is then found by permanganate or bichromate—

$$2HgCl^2 + 2FeCl^2 = Hg^2Cl^2 + Fe^2Cl^6.$$

It is therefore advisable in all cases to convert the mercury to be estimated into the form of sublimate, by evaporating it to dryness with nitro-hydrochloric acid; this must take place, however, below boiling heat, as vapours of chloride escape with steam at 100° C. (Fresenius).

Nitric acid or free chlorine must be altogether absent during the decomposition with the iron protosalt, otherwise the residual titration will be inexact, and the quantity of the iron salt must be more than sufficient to absorb half the chlorine in the sublimate.

*Example:* 1 gm. of pure sublimate was dissolved in warm water, and 3 gm. of double iron salt added, then solution of caustic soda till freely alkaline. The mixture became muddy and dark in colour, and was well shaken for a few minutes, then sodic chloride and sulphuric acid added, continuing the shaking till the colour disappeared and the precipitate of ferric oxide dissolved, leaving the calomel white; it was then diluted to 300 c.c. filtered through a dry filter, and 100 c.c. titrated with $\frac{N}{10}$ permanganate, of which 13·2 c.c. were required—$13·2 \times 3 = 39·6$, which deducted from 76·5 c.c., (the quantity required for 3 gm. double iron salt) left 36·9 c.c.=1·447 gm. of undecomposed iron salt, which multiplied by the factor 0·6914, gave 1·0005 gm. of sublimate, instead of 1 gm., or the 36·9 c.c. may be multiplied by the $\frac{N}{10}$ factor for mercuric chloride, which will give 1 gm. exactly.

### 3. By Iodine and Thiosulphate (Hempel).

If the mercury exist as a protosalt it is precipitated by sodic chloride, the precipitate well washed and together with its filter pushed through the funnel into a stoppered flask, a sufficient quantity of potassic iodide added, together with $\frac{N}{10}$ iodine solution (to 1 gm. of calomel about 2·5 gm. of iodide, and 100 c.c. of $\frac{N}{10}$ iodine), the flask closed, and shaken till the precipitate has dissolved—

$$Hg^2Cl^2 + 6KI + 2I = 2HgK^2I^4 + 2KCl.$$

The brown solution is then titrated with $\frac{N}{10}$ thiosulphate till colourless, diluted to a definite volume, and a measured portion titrated with $\frac{N}{10}$ iodine and starch for the excess of thiosulphate. 1 c.c. $\frac{N}{10}$ iodine = 0·02 gm. Hg.

Where the mercurial solution contains nitric acid, or the metal exists as peroxide, it may be converted into protochloride by the reducing action of ferrous sulphate, as in Mohr's method. The solution must contain hydrochloric acid or common salt in sufficient quantity to transform all the mercury into calomel. At least three times the weight of mercury present of ferrous sulphate in solution is to be added, then caustic soda in excess, the muddy liquid well shaken for a few minutes, then dilute sulphuric acid added in excess, and the mixture stirred till the dark-coloured precipitate has become perfectly white. The calomel so obtained is collected on a filter, well washed, and titrated with $\frac{N}{10}$ iodine and thiosulphate as above.

### 4. Direct Titration with Sodic Thiosulphate (Scherer).

*The standard thiosulphate* is made by dissolving $\frac{1}{20}$ eq. = 12·4 gm. of the salt in 1 liter of water.

The reaction which takes place with thiosulphate in the case of mercurous nitrate is

$$Hg^2(NO^3)^2 + Na^2S^2O^3 = Hg^2S + Na^2SO^4 + N^2O^5.$$

With mercuric nitrate—

$$3Hg(NO^3)^2 + 2Na^2S^2O^3 = 2HgS.Hg(NO^3)^2 + 2Na^2SO^4 + 2N^2O^5.$$

With mercuric chloride—

$$3HgCl^2 + 2Na^2S^2O^3 + 2H^2O = 2HgS.HgCl^2 + 2Na^2SO^4 + 4HCl.$$

(*a*) *Mercurous Salts:* The solution containing the metal only as a protosalt is diluted, gently heated, and the thiosulphate delivered in from the burette at intervals, meanwhile well shaking until the last drop produces no brown colour. The sulphide settles freely, and allows the end of the reaction to be easily seen. 1 c.c. of thiosulphate=0·020 gm. Hg., or 0·0208 gm. $Hg^2O$.

(*b*) *Mercuric Nitrate:* The solution is considerably diluted, put into a stoppered flask, nitric acid added, and the thiosulphate cautiously delivered from the burette, vigorously shaken meanwhile until the last drop produces no further yellow precipitate. Scherer recommends that when the greater part of the metal is precipitated, the mixture should be diluted to a definite volume, the precipitate allowed to settle, and a measured quantity of the clear liquid taken for titration; the analysis may then be checked by a second titration of the clear liquid, if needful. 1 c.c. thiosulphate=0·015 gm. Hg., or 0·0162 gm. HgO.

(c) *Mercuric Chloride:* With mercuric chloride (sublimate) the end of the process is not so easily seen. The procedure is as follows:—The very dilute solution is acidified with hydrochloric acid, heated nearly to boiling, and the thiosulphate cautiously added so long as a white precipitate is seen to form; any great excess of the precipitant produces a dirty-looking colour. Filtration is necessary to distinguish the exact ending of the reaction, for which purpose Beale's filter (fig. 16) is useful.

Liebig's method is the reverse of that used for determining chlorides in urine, sodic phosphate being used as indicator in the estimation of mercury, instead of the urea occurring naturally in urine. The method is capable of very slight application.

### 5. As Mercuric Iodide (Personne), Compt. Rend. lvi. 63.

This process is founded on the fact that if a solution of mercuric chloride be added to one of potassic iodide, in the proportion of 1 equivalent of the former to 4 of the latter, red mercuric iodide is formed, which dissolves to a colourless solution until the balance is overstepped, when the brilliant red colour of the iodide appears as a precipitate, which, even in the smallest quantity, communicates its tint to the liquid. The mercuric solution must always be added to the potassic iodide; a reversal of the process, though giving eventually the same quantitative reaction, is nevertheless much less speedy and trustworthy. The mercurial compounds to be estimated by this process must invariably be brought into the form of neutral mercuric chloride.

The standard solutions required are decinormal, made as follows:—

*Solution of Potassic Iodide.*—33·2 gm. of pure salt to 1 liter. 1 c.c.=0·01 gm. Hg, or 0·01355 gm. $HgCl^2$.

*Solution of Mercuric Chloride.*—13·537 gm. of the salt, with about 30 gm. of pure sodic chloride (to assist solution), are dissolved to 1 liter. 1 c.c.=0·1 gm. Hg.

The conversion of various forms of mercury into mercuric chloride is, according to Personne, best effected by heating with caustic soda or potash, and passing chlorine gas into the mixture, which is afterwards boiled to expel excess of chlorine (the mercuric chloride is not volatile at boiling temperature when associated with alkaline chloride). The solution is then cooled and diluted to a given volume, placed in a burette, and delivered into a measured volume of the decinormal potassic iodide until the characteristic colour occurs. It is preferable to dilute the mercuric solution considerably, and make up to a given measure, say 300 or 500 c.c.; and as a preliminary trial take 20 c.c. or so of iodide solution, and titrate it with the mercuric solution approximately with a graduated pipette; the exact strength may then be found by using a burette of sufficient size.

### 6. By Potassic Cyanide (Hannay).

This process is exceedingly valuable for the estimation of almost all the salts of mercury when they occur, or can be separated, in a tolerably pure state. Organic compounds are of no consequence unless they affect the colour of the solution.

The method depends on the fact that free ammonia produces a precipitate, or (when the quantity of mercury is very small) an opalescence in mercurial solutions, which is removed by a definite amount of potassic cyanide. The operation is performed in a flask or beaker standing upon a dull black ground, such as unglazed black paper or black velvet.

The delicacy of the reaction is interfered with by excessive quantities of ammoniacal salts, or by caustic soda or potash; but this difficulty is set aside by the modification suggested by Tuson and Neison (*J. C. S.* 1877, 679).

Mercury compounds, insoluble in water, must be dissolved in nitric, sulphuric, or hydrochloric acid, or in some cases it may be necessary to use *aqua regia*. The solution so obtained is then mixed with a certain proportion of ammonic chloride and potassic carbonate, when the characteristic precipitate is at once formed, and may be removed by standard cyanide.

The standard solutions are :—

*Decinormal Mercuric Chloride.*—13·537 gm. per liter.

*Solution of Potassic Cyanide* of corresponding strength, made by dissolving about 17 gm. of pure crystals of potassic cyanide in a liter of water.

It is also desirable to have—

*Solution of Ammonic Chloride.*—5·36 gm. per liter.

*Solution of Potassic Carbonate.*—69 gm. per liter.

*Ammonic Hydrate.*—One part of strong solution to nine parts of water.

These latter solutions are used according to the judgment of the operator as may be necessary, bearing in mind that in no case should there be present during titration an amount of ammoniacal salt more than ten or fifteen times that of the mercury to be estimated. It is best to have the conditions as nearly as possible the same in any given analysis as existed in the original titration of the standard solutions.

Where the mercury compound is only slightly acid, the free ammonia may be used for neutralizing; on the other hand, in the case of much free acid, potassic carbonate should be used for this purpose, preceded by some ammonic chloride in moderate quantity to produce the precipitate. If any mercurial solution should be largely contaminated with ammonia compounds, potassic carbonate is added in excess, and the mixture boiled to remove the ammonia. No mercury is lost by this method, but on the other hand it is unsafe to attempt the removal of free acid by boiling, as mercury is easily lost under such conditions.

*Titration of the Potassic Cyanide:* 50 c.c. of the standard mercuric chloride being measured into a beaker standing on a black surface, there are added to it 2 or 3 c.c. of ammonic chloride and a drop or two of ammonia. The cyanide is then run cautiously in from the burette with constant stirring, until the last trace of opalescence disappears. If the volume of cyanide is less than 50 c.c. it may be diluted to the requisite strength, or if more, a factor found for calculation. The solution varies slightly from time to time, and hence must be verified before used.

Tuson found the process exceedingly accurate in a long series of experiments upon various salts of mercury. In the case of very small quantities of the metal $\frac{N}{100}$ cyanide should be used.

## NICKEL.

§ 66. The estimation of this metal volumetrically is tedious and difficult. If a solution of it in a tolerably pure state can be obtained by the removal of other metals and substances liable to interfere with its precipitation as oxalate, it may be titrated in that form in the same way as zinc (§ 78). The estimation in conjunction with cobalt is given in § 53.

## NITROGEN AS NITRATES AND NITRITES.

### Nitric Anhydride.

$N^2O^5 = 108$.

### Nitrous Anhydride.

$N^2O^3 = 76$.

### Factors.

| | | |
|---|---|---|
| Normal acid | × | $0{\cdot}0540 = N^2O^5$ |
| Ditto | × | $0{\cdot}1011 = KNO^3$ |
| Metallic iron | × | $0{\cdot}3750 = HNO^3$ |
| Ditto | × | $0{\cdot}6018 = KNO^3$ |
| Ditto | × | $0{\cdot}3214 = N^2O^5$ |

§ 67. The accurate estimation of nitric acid in combination presents great difficulties, and can only be secured by indirect means; the methods here given are sufficient for most purposes. Very few of them can be said to be simple, but it is to be feared that no simple process can ever be obtained for the determination of nitric acid in many of its combinations.

### 1. Gay Lussac's Method modified by Abel (applicable only to Alkaline Nitrates).

This process depends upon the conversion of potassic or sodic nitrates into carbonates by ignition with carbon, and the titration of the carbonate so obtained, by normal acid. The number of c.c. of normal acid required multiplied by 0·101 will give the weight of pure potassic nitrate in grams; by 0·085, the weight of sodic nitrate in grams.

The best method of procedure is as follows:—

The sample is finely powdered and dried in an air bath, and 1 gram, or an equivalent quantity in grains, weighed, introduced into a platinum crucible, and mixed with a fourth of its weight of pure graphite (prepared by Brodie's process), and four times its weight of pure ignited sodic chloride. The crucible is then covered and heated moderately for twenty minutes over a Bunsen's burner, or for eight or ten minutes in a muffle (the heat must not be so great as to volatilize the chloride of sodium to any extent). If sulphates are present they will be reduced to sulphides; and as these would consume the normal acid, and so lead to false results, it is necessary to sprinkle the fused mass with a little powdered potassic chlorate, and heat again moderately till all effervescence has ceased. The crucible is then set aside to cool, warm water added, the contents brought upon a filter, and washed with hot water till the washings are no longer alkaline. The filtrate is then titrated with normal acid in the ordinary way.

### 2. Estimation of Nitrates by Distillation with Sulphuric Acid.

This method is of very general application, but particularly so with the impure alkaline nitrates of commerce. The process needs careful manipulation, but yields accurate results.

There are two methods of procedure.

(*a*) To bring the weighed nitrate into a small tubulated retort with a cooled mixture of water and strong sulphuric acid, in the proportion of 10 c.c. of water and 5 c.c. of sulphuric acid for 1 gm. of nitrate. The neck of the retort is drawn out to a point and bent downward, entering a potash or other convenient bulb apparatus containing normal caustic alkali. The retort is then buried to its neck in the sand-bath, and heated to 170° C. (338° Fahr.) so long as any liquid distils over; the heat must never exceed 175° C. (347° Fahr.), otherwise traces of sulphuric acid will come over with the nitric acid. The quantity of acid distilled over is found by titrating the fluid in the receiver with normal acid as usual.

(*b*) *Distillation in a Partial Vacuum* (Finkener).—By this arrangement there is no danger of contaminating the distillate with sulphuric acid, inasmuch as the operation is conducted in a water bath, and when once set going needs no superintendence.

The retort is the same as before described, but the neck is not drawn out or bent; the stopper of the tubulure must be well ground. The receiver is a 200-c.c. flask with narrow neck, containing the requisite quantity of normal alkali diluted to about 30 c.c. The receiver is bound, air-tight, to the neck of the retort (which should reach nearly to the middle of the flask) by means of a vulcanized tube: the proportions of acid and water before mentioned are introduced into the retort with a tube funnel. The stopper of the retort is then removed, and the contents, both of the receiver and retort, heated by spirit or gas lamp to boiling, so as to drive out the air; the weighed nitrate contained in a small tube is then dropped into the retort, the stopper inserted, the lamps removed, and the retort brought into the water bath, while the receiver is kept cool with wet tow, or placed in cold water. The distillate is titrated as before. 1 or 2 gm. of saltpetre require about four hours for the completion of the process.

Finkener obtained very accurate results by this method.

When chlorides are present in the nitrate, a small quantity of moist oxide of silver is added to the mixture before distillation.

### 3. Estimation by conversion into Ammonia (Schulze and Vernon Harcourt).

The principle of this method is based on the fact that when a nitrate is heated with a strong alkaline solution, and zinc added, ammonia is evolved; when zinc alone is used, however, the quantity of ammonia liberated is not a constant measure of the nitric acid present. Vernon Harcourt and Siewert appear to have arrived independently at the result that by using a mixture of zinc and iron the reaction was perfect (*J. C. S.* 1862, 381; *An. Chem. u. Phar.* cxxv. 293).

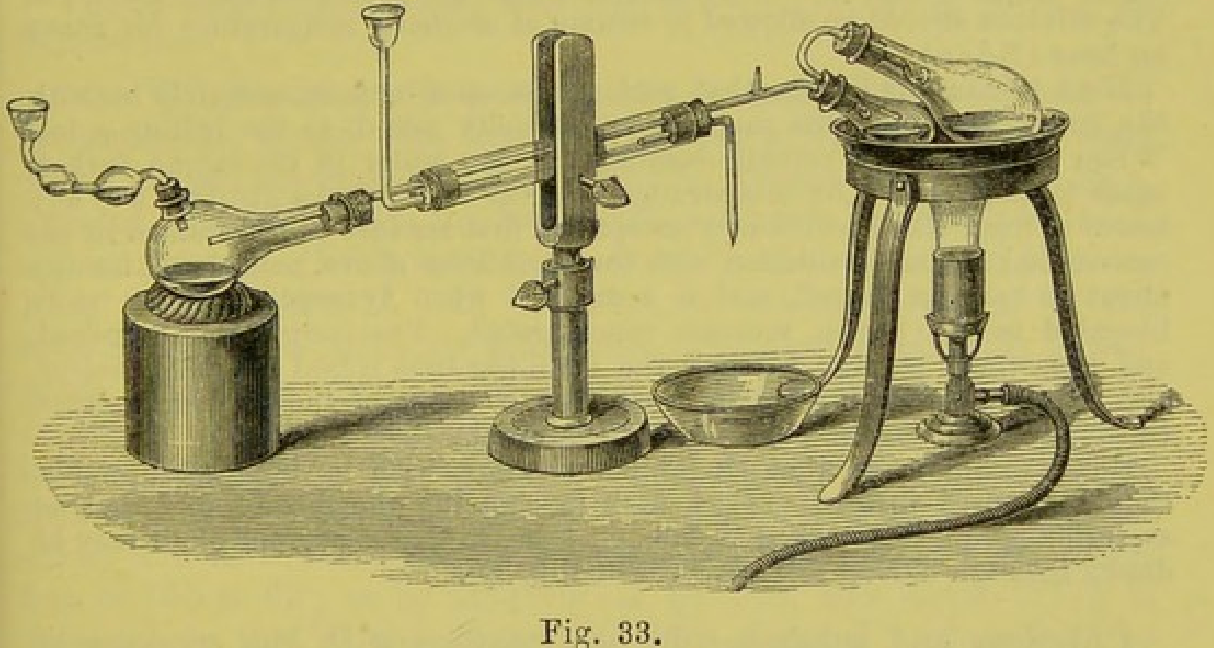

Fig. 33.

A convenient form of apparatus is shown in fig. 33.

The distilling flask holds about 200 c.c., and is closely connected by a bent tube with another smaller flask, in such a manner that both may be placed obliquely upon a sand-bath, the bulb of the smaller flask coming just under the neck of the larger. The oblique direction prevents the spirting of the boiling liquids from entering the exit tubes, but as a further precaution, these latter are in both flasks turned into the form of a hook; from the second flask, which must be somewhat wide in the mouth, a long tube passes through a Liebig's condenser (which may be made of wide glass tube) into an ordinary tubulated receiver, containing normal sulphuric acid coloured with an indicator. The end of the distilling tube reaches to about the middle of the receiver, through the tubulure of which Harcourt passes a bulb apparatus of peculiar form, containing also coloured normal acid; instead of this latter, however, a chloride of calcium tube, filled with broken glass, and moistened with acid, will answer the purpose. The distilling tube should be cut at about two inches from the cork of the second flask, and connected by means of a well-fitting vulcanized tube; by this means water may be passed through the tube when the distillation is over so as to remove any traces of ammonia which may be retained on its sides. All the corks of the apparatus should be soaked in hot paraffine, so as to fill up the pores.

All being ready, about 50 gm. of finely granulated zinc (best made by pouring molten zinc into a warm iron mortar while the pestle is rapidly being rubbed round) are put into the larger flask with about half the quantity of clean iron filings which have been ignited in a covered crucible (fresh iron and zinc should be used for each analysis); the weighed nitrate is then introduced, either in solution, or with water in sufficient quantity to dissolve it, strong solution of caustic potash added, and the flask immediately connected with the apparatus, and placed on a small sand-bath, which can be heated by a gas-burner, a little water being previously put into the second flask. Convenient proportions of material are ½ gm. nitre, and about 25 c.c. each of water, and solution of potash of spec. grav. 1·3. The mixture should be allowed to remain at ordinary temperature for about an hour (Eder).

Heat is now applied to that part of the sand-bath immediately beneath the larger flask, and the mixture is gradually raised to the boiling point. When distillation has actually commenced, the water in the second flask is made to boil gently; by this arrangement the fluid is twice distilled, and any traces of fixed alkali which may escape the first are sure to be retained in the second flask. The distillation with the quantities above named will occupy about an hour and a half, and is completed when hydrogen is pretty freely liberated as the potash becomes concentrated. The lamp is then removed, and the whole allowed to cool, the distilling tube rinsed into the receiver, also the tube containing broken glass; the contents of the receiver are then titrated with $\frac{N}{10}$ caustic potash or soda as usual.

Eder recommends that an ordinary retort, with its beak set upwards, should be used instead of the flask for holding the nitrate, and that an aspirator should be attached to the exit tube, so that a current of air may be drawn through during and after the distillation.

Chlorides and sulphates do not interfere with the accuracy of the results. Harcourt, Eder, and many others, including myself, have obtained very satisfactory results by this method.

Siewert has suggested a modification of this process. The distilling apparatus is a 300—350 c.c. flask with tube leading to two small flasks connected together as wash bottles, and containing standard acid. For 1 gm. of nitre, 4 gm. of iron, and 10 gm. of zinc filings, with 16 gm. of caustic potash, and 100 c.c. of alcohol of sp. gr. 0·825 are necessary. After digesting for half an hour in the cold or in slight warmth, a stronger heat may be applied to drive out all the ammonia into the acid flasks. Finally, 10—15 c.c. of fresh alcohol are admitted to the distilling flask, and distilled off to drive over the last traces of ammonia, and the acid solution then titrated residually as usual. The alcohol is used to prevent bumping, but this is also avoided in the original process by adopting the current of air recommended by Eder.

The copper-zinc couple devised by Gladstone and Tribe has been used by Thorpe for the reduction of nitrates and nitrites occurring in water residues, etc. (*J. C. S.* 1873, 545). The resulting ammonia is distilled into weak hydrochloric acid, and an aliquot portion then Nesslerized in the usual way.

M. W. Williams (*J. C. S.* 1881, 100) has shown that this reduction, in the case of small quantities of nitric or nitrous acids may be carried on by mere digestion with a properly arranged couple at ordinary temperatures, and may safely be hastened by increasing the temperature to about 25° C. in the presence of certain saline or acid substances; alkaline substances, on the contrary, retard the action. The details are further described in Part VI.

### 4. By Oxidation of Ferrous Salts (Pelouze). Not available in the presence of Organic Matter.

The principle upon which this well-known process is based is as follows:—

(*a*) When a nitrate is brought into contact with a solution of ferrous oxide, mixed with free hydrochloric acid, and heated, part of the oxygen contained in the nitric acid passes over to the iron, forming a persalt, while the base combines with hydrochloric acid, and nitric oxide ($NO^2$) is set free. 3 eq. iron=168 are oxidized by 1 eq. nitric acid=63. If, therefore, a weighed quantity of the nitrate be mixed with an acid solution of ferrous chloride or sulphate of known strength, in excess, and the solution boiled, to expel the liberated nitric oxide, then the amount of unoxidized iron remaining in the mixture, found by a suitable method of titration, the quantity of iron converted from ferrous into ferric oxide, will be the measure of the original nitric acid in the proportion of 168 to 63; or by dividing 63 by 168, the factor 0·375 is obtained, so that if the amount of iron changed as described be multiplied by this factor, the product will be the amount of nitric acid present.

This method, though theoretically perfect, is in practice liable to serious errors, owing to the readiness with which a solution of ferrous oxide absorbs oxygen from the atmosphere. On this account accurate results are only obtained by conducting hydrogen or carbonic acid gas through the apparatus while the boiling is carried on. This modification has been adopted by Fresenius with very satisfactory results.

The boiling vessel may consist of a small tubulated retort, supported in such a manner that its neck inclines upward: a cork is fitted into the tubulure, and through it is passed a small tube connected with a vessel for generating either carbonic acid or hydrogen. If a weighed quantity of pure metallic iron is used for preparing the solution, the washed carbonic acid or hydrogen should be passed through the apparatus while it is being dissolved; the solution so obtained, or one of double sulphate of iron and ammonia of known strength, being already in the retort, the nitrate is carefully introduced, and the mixture heated gently by a small lamp, or by the water bath, for ten minutes or so, then boiled until the dark-red colour of the liquid disappears, and gives place to the brownish-yellow of ferric compounds. The retort is then suffered to cool, the current of carbonic acid or hydrogen still being kept up, then the liquid diluted freely, and titrated with $\frac{N}{10}$ permanganate.

Owing to the irregularities attending the use of permanganate with hydrochloric acid, it is preferable, in case this acid has been used, to dilute the solution less, and titrate with bichromate. Two grams of pure iron, or its equivalent in double iron salt, 0·5 gm. of saltpetre, and about 60 c.c. of strong hydrochloric acid, are convenient proportions for the analysis.

Eder (*Z. a. C.* xvi. 267) has modified Fresenius' improvements as follows:

1·5 gm. of very thin iron wire is dissolved in 30 to 40 c.c. of pure fuming hydrochloric acid, placed in a retort of about 200 c.c. capacity; the beak of the retort points upwards, at a moderately acute angle, and is connected with a U-tube, which contains water. Solution of the iron is hastened by applying a small flame to the retort. Throughout the entire process a stream of $CO^2$ is passed through the apparatus. When the iron is all dissolved the solution is allowed to cool, the stream of $CO^2$ being maintained; the weighed quantity of nitrate contained in a small glass tube (equal to about 0·2 gram $HNO^3$) is then quickly passed into the retort through the neck; the heating is continued under the same conditions as before, until the liquid assumes the colour of ferric chloride. The whole is allowed to cool in a stream of $CO^2$; water is added in quantity, and the unoxidized iron is determined by titration with permanganate. The results are exceedingly good.

If the $CO^2$ be generated in a flask, with a tube passing downwards for the reception of the acid, air always finds its way into the retort, and the results are unsatisfactory. Eder recommends the use of Kipp's $CO^2$ apparatus. By carrying out the operation exactly as is now to be described, he has obtained very good results with ferrous sulphate in place of chloride.

The same apparatus is employed; the tube through which $CO^2$ enters the retort passes to the bottom of the liquid therein, and the lower extremity of this tube is drawn out to a fine point. The bubbles of $CO^2$ are thus reduced in size, and the whole of the nitric oxide is removed from the liquid by the passage of these bubbles. The iron wire is dissolved in excess of dilute sulphuric acid (strength 1 : 3 or 1 : 4). When the liquid in the retort has become cold, a small tube containing the nitrate is quickly passed, by means of a piece of platinum wire attached to it, through the tubulus of the retort, and the cork is replaced before the tube has touched the liquid; $CO^2$ is again passed through the apparatus for some time, after which, by slightly loosening the cork, the tube containing the nitrate is allowed to fall into the liquid. The whole is allowed to remain at the ordinary temperature for about an hour—this is essential—after which time the contents of the retort are heated to boiling, $CO^2$ being passed continuously into the retort, and the boiling continued till the liquid assumes the light yellow colour of ferric sulphate. After cooling, water is added (this may be omitted with bichromate), and the unoxidized iron is determined by means of permanganate.

Eder also describes a slight modification of this process, allowing of the use of a flask in place of the retort, and of ammonio-ferrous sulphate in place of iron wire. Although the titration with permanganate is more trustworthy when sulphuric acid is employed than when hydrochloric acid is used, he nevertheless thinks that the use of ferrous chloride is generally to be recommended in preference to that of ferrous sulphate. When the chloride is employed, no special concentration of acid is necessary ; the nitric oxide is more readily expelled from the liquid, and the process is finished in a shorter time.

The final point in the titration with permanganate, when the sulphate is employed, is rendered more easy of determination by adding a little potassic sulphate to the liquid.

(*b*) *Direct titration of the resulting Ferric salt by Stannous Chloride.*—Fresenius has adopted the use of stannous chloride for titrating the ferric salt with very good results.

The following plan of procedure is recommended by the same authority.

A solution of ferrous sulphate is prepared by dissolving 100 gm. of the crystals in 500 c.c. of hydrochloric acid of spec. grav. 1·10 ; when used for the analysis, the small proportion of ferric oxide invariably present in it is found by titrating with stannous chloride, as in § 60.1. The nitrate being weighed or measured, is brought together with 50 c.c. (more or less, according to the quantity of nitrate) of the iron solution into a long-necked flask, through the cork of which two glass tubes are passed, one connected with a $CO^2$ apparatus, and reaching to the middle of the flask, the other simply an outlet for the passage of the gas. When the gas has driven out all the air, the flask is at first gently heated, and eventually boiled, to dispel all the nitric oxide. The $CO^2$ tube is then rinsed into the flask, and the liquid, while still boiling hot, titrated for ferric chloride, as in § 60.1.

The liquid must, however, be suffered to cool before titrating with iodine for the excess of stannous chloride. While cooling, the stream of $CO^2$ should still be continued. The quantity of iron changed into peroxide, multiplied by the factor 0·375, will give the amount of nitric acid.

*Example:* (1) A solution of stannous chloride was used for titrating 10 c.c. of solution of pure ferric chloride, containing 0·215075 gm. Fe. 25·65 c.c. of tin solution were required, therefore that quantity was equal to 0·0807 gm. of $HNO^3$, or 0·069131 gm. of $N^2O^5$.

(2) 50 c.c. of acid ferrous sulphate were titrated with tin solution for ferric oxide, and 0·24 c.c. was required.

(3) 1 c.c. tin solution=3·3 c.c. iodine solution.

(4) 0·2177 gm. of pure nitre was boiled, as described, with 50 c.c. of the acid ferrous sulphate, and required 45·03 c.c. tin solution, and 4·7 c.c. iodine—

4·7 c.c. iodine solution = 1·42 c.c. $SnCl^2$
The peroxide in the protosulphate solution = 0·24 c.c.
1·66

45·03—1·66=43·37, therefore 25·65 : 0·069131=43·37 : $x$,=0·1169 $N^2O^5$ instead of 0·1163, or 53·69 per cent. instead of 53·41. A mean of this, with three other estimations, using variable proportions of tin and iron solutions, gave exactly 53·41 per cent. The process is therefore entirely satisfactory in the case of pure materials.

The above process is slightly modified by Eder. About 10 gm. of ammonio-ferrous sulphate are dissolved in a flask, in about 50 c.c. of hydrochloric acid (sp. gr. 1·07) in a stream of $CO^2$. The tube through which the $CO^2$ enters is drawn to a point; an exit-tube, somewhat trumpet-shaped, to admit of any liquid that may spirt finding its way back into the flask passes downwards into water. After solution of the double salt, the nitrate is dropped in with the precautions already detailed, and the liquid is boiled until the nitric oxide is all expelled. The hot liquid is diluted with twice its own volume of water, excess of standard stannous chloride solution is run in, the whole is allowed to cool in a stream of $CO^2$, and the excess of tin is determined by means of standard iodine.

(*c*) *Direct Titration of the resulting Ferric Chloride by Iodine and Thiosulphate.*—Mohr proceeds as follows :—

The dry nitrate, with twelve times its weight of double iron salt, is placed in a 100—150 c.c. flask, with about 50 c.c. of hydrochloric acid and a little water. The flask is closed with a cork through which is passed a glass tube cut obliquely below the cork; about 1½ inch of stout vulcanized tube is then fixed over the upper end of the glass tube and closed with a piece of solid glass rod. A slit is cut vertically in the elastic tube, so that when the contents of the flask boil the steam may escape from the valve so formed; the atmospheric pressure closes this valve when boiling ceases. The contents are boiled till all the nitric oxide is driven off and the solution is the colour of ferric chloride, then cooled, and a sufficiency of potassic iodide added to decompose the ferric chloride; when this is complete, starch is added, and the mixture titrated with thiosulphate. As the oxygen in nitric acid represents three times its equivalent of thiosulphate,

$$\frac{0{\cdot}0063}{3}=0{\cdot}0021\ HNO^3 \text{ or } \frac{0{\cdot}0101}{3}=0{\cdot}00337\ KNO^3$$

The quantity of thiosulphate used multiplied by these factors will give the quantity of nitric acid or potassic nitrate respectively.

Mohr obtained by this method very good results. My own trials, however, have not been very satisfactory.

(*d*) *Holland's Modification of the Pelouze process.*—The arrangement of apparatus shown in fig. 34 obviates the use of an atmosphere of H or $CO^2$. A is a long-necked assay flask drawn off at B, so as to form a shoulder, over which is passed a piece of stout pure india-rubber tube, D, about 6 centimeters long, the other end terminating in a glass tube, F, drawn off so as to leave only a small orifice. On the elastic connector D is placed a screw clamp. At C, a distance of 3 centimeters from the shoulder, is cemented with a blow-pipe a piece of glass tube about 2 centimeters long, surmounted by one of stout elastic tube rather more than twice that length. The elastic tubes must be securely

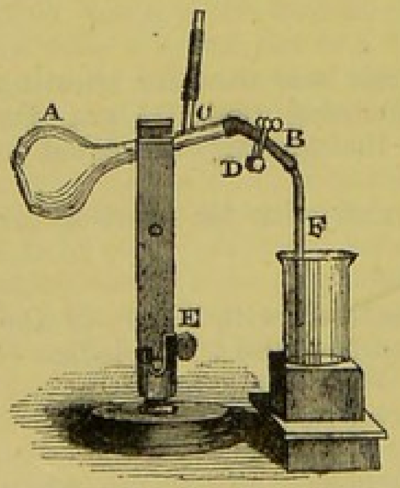

Fig. 34.

attached to the glass by binding with wire. After binding, it is as well to turn the end of the conductor back and smear the inner surface with fused caoutchouc, and then replace it to render the joint air-tight.

*The Analysis:* A small funnel is inserted into the elastic tube at C, the clamp at D being for the time open; after the introduction of the solution, followed by a little water which washes all into the flask, the funnel is removed, and the flask supported by means of the wooden clamp, in the inclined position it occupies in the figure. The contents are now made to boil so as to expel all air and reduce the volume of the fluid to about 4 or 5 c.c. When this point is reached a piece of glass rod is inserted into the elastic tube at C, which causes the water vapour to escape through F.

Into the small beaker is put about 50 c.c. of a previously boiled solution of ferrous sulphate in hydrochloric acid (the amount of iron already existing as persalt must be known).

The boiling is still continued for a moment to ensure perfect expulsion of air from F, the lamp is then removed, and the caoutchouc connector slightly compressed with the first finger and thumb of the left hand. As the flask cools the solution of iron is drawn into it; when the whole has nearly receded the elastic tube is tightly compressed with the fingers, whilst the sides of the beaker are washed with a jet of boiled water, which is also allowed to pass into the flask. The washing may be repeated, taking care not to dilute more than is necessary or admit air. Whilst F is still full of water, the elastic connector previously compressed with the fingers is now securely closed with the clamp, the screw of which is worked with the right hand. Provided the clamp is a good one, F will remain full of water during the subsequent digestion of the flask.

After heating in a water bath at 100° for half an hour, the flask is removed from the water bath and cautiously heated with a small flame, the fingers at the same time resting on the elastic connector at the point nearest the shoulder; as soon as the tube is felt to expand, owing to the pressure from within, the lamp is removed and the screw clamp released, the fingers maintaining a secure hold of the tube, the gas-flame is again replaced, and when the pressure on the tube is again felt, this latter is released altogether, thus admitting of the escape of the nitric oxide through F, which should be below the surface of water in the beaker whilst these manipulations are performed. The contents of the flask are now boiled until the nitric oxide is entirely expelled, and the solution of iron shows only the brown colour of the perchloride. At the completion of the operation the beaker is first removed, and then the lamp.

It now only remains to transfer the ferric solution to a suitable vessel, and determine the perchloride with stannous chloride as in *b*.

A mean of six experiments for the percentage determination of $N^2O^5$ in pure nitre gave 53·53 per cent. instead of 53·41. The process is easy of execution, and gives satisfactory results. The point chiefly requiring attention is that the apparatus should be air-tight, which is secured by the use of good elastic tubes and clamp.

### 5. Schlösing's Method (available in the presence of Organic Matter).

The solution of nitrate is boiled in a flask till all air is expelled, then an acid solution of ferrous chloride drawn in, the mixture boiled, and the nitric oxide gas collected over mercury in a balloon filled with mercury and milk of lime; the gas is then brought, without loss, in contact with oxygen and water, so as to convert it again into nitric acid, then titrated with $\frac{N}{10}$ alkali as usual.

This method was devised by Schlösing for the estimation of nitric acid in tobacco, and is especially suitable for that and similar purposes, where the presence of organic matter would interfere with the direct titration of the iron solution. Where the quantity of nitric acid is not below 0·15 gm. the process is fairly accurate, but needs a special and rather complicated arrangement of apparatus, the description of which may be found in the original paper in *Annal. de Chim.* [3] xl. 479, or in Fresenius' *Quant. Anal.*

An arrangement of apparatus, dispensing with the use of mercury, has been designed by Wildt and Scheibe (*Z. a C.* xxiii. 151), which simplifies the analysis and gives accurate results with not less than 0·25 gm. $N^2O^5$. With smaller quantities the results are too low. Fig. 35 shows the apparatus used.

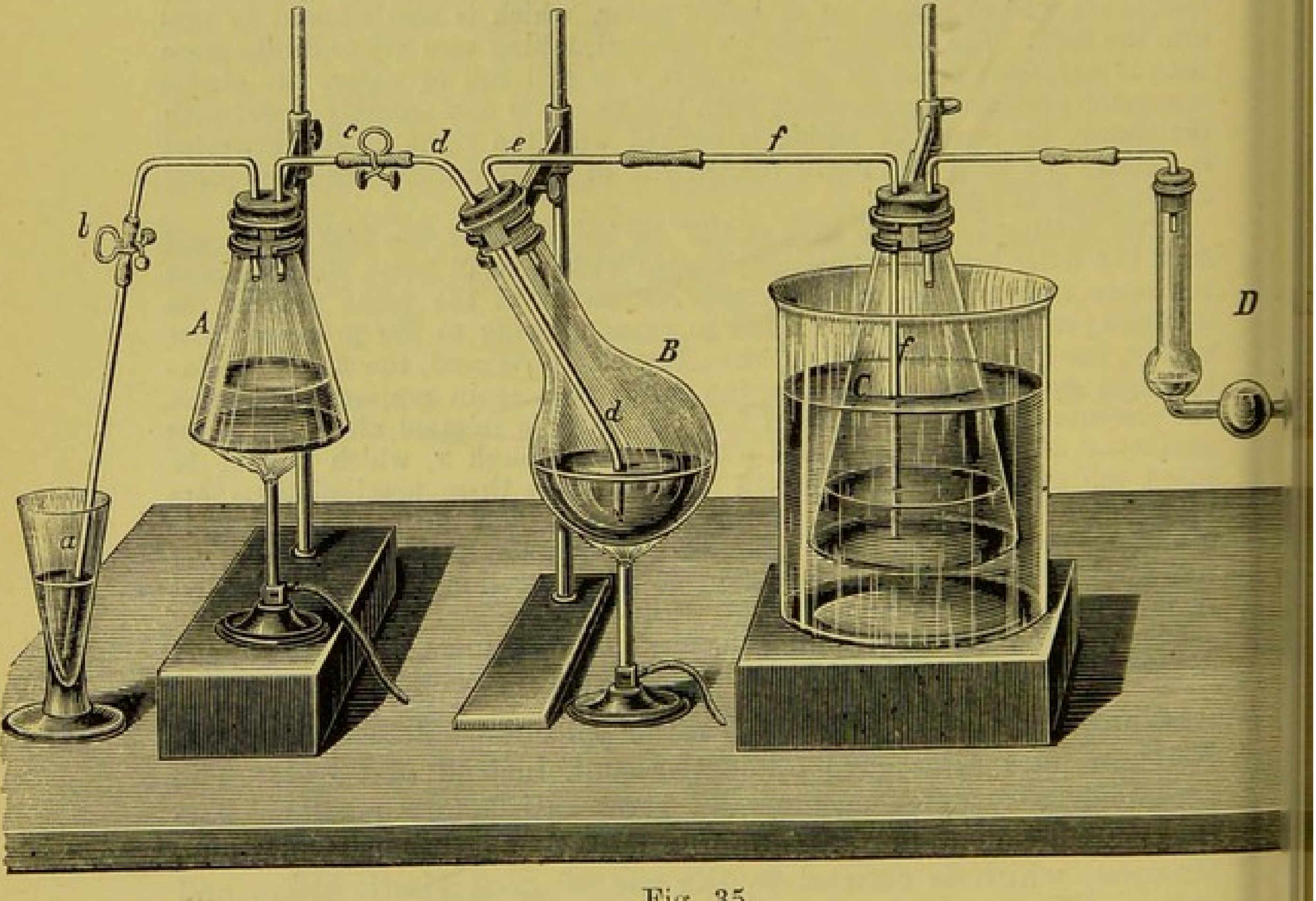

Fig. 35.

A is an Erlenmeyer's flask of 250 c.c. capacity, containing the solution to be analyzed. B is a round-bottomed flask of 250—300 c.c. capacity, half filled with caustic soda, to absorb any HCl which might be carried over from A. C is an Erlenmeyer's flask of 750 c.c. capacity, containing a little water to absorb the nitric acid. D is a tube, containing water to collect any nitric acid not absorbed by the water in C. The tube *d* is bent, as shown in the diagram, and drawn out to a point, to diminish the size of the bubbles. The tube *e* is wide, and cut obliquely to prevent water collecting and passing into C.

The analysis is conducted as follows:—The clip *b* is closed and *c* opened, and the tube *e* disconnected from *f*. The solutions in A and B are then boiled for 20 minutes to remove all oxygen. The tubes *e* and *f* are again connected, the clip *c* is closed, the flame under B increased to prevent the liquid in C from being drawn back, and the clip *b* is opened. As soon as steam issues from the tube *a*, it is dipped into a conical glass containing 50 c.c. of ferrous chloride prepared according to Schlösing's directions, and the flame under A is removed, when the ferrous chloride enters the flask. The clip *b* is regulated with the finger and thumb, so as to prevent the entry of air into the flask. The conical vessel is rinsed two or three times with water, and this is allowed to enter the flask, and the clip *b* is then closed, and the vessel A heated. The liquid in A turns brown in a short time, and nitric oxide is evolved. The clip *c* is opened slightly from time to time until the pressure is high enough, when it is opened entirely. The flames must be regulated so that a slow current of gas bubbles through the water in C. The hydrochloric acid is removed by the caustic soda in B, and the nitric oxide on coming in contact with the air in C is oxidized, and the nitric acid absorbed by the water. In case the current of gas is too rapid, the escaping nitric acid is absorbed in D. After an hour the tubes *e* and *f* are disconnected, while the solutions in A and B are still boiling, and the nitric acid is titrated with dilute caustic soda (about ¼ normal). The vessel C must be well cooled during the whole experiment, which occupies about an hour and a half.

Good results were obtained with nitrates of potash and soda, both alone and mixed with ammonium sulphate, superphosphate, and amido compounds. With superphosphate the solution should be made slightly alkaline, to prevent the liberation of nitric acid.

Warington (*J. C. S.* 1880, 468) has made a series of experiments on the original Schlösing process, for the purpose of testing its accuracy, when small quantities of nitric acid have to be determined in the presence of organic substances, such for instance as in soils, the sap of beet-root, etc.; but instead of converting the nitric oxide back into nitric acid as in the original method, he collected the gas either over caustic soda as recommended by Reichardt, or over mercury, and ascertained its amount by measurement in Frankland's gas apparatus. The results obtained by Warington plainly showed that even on the most favourable circumstances the method as usually worked in Germany, either by the alkalimetric titration or by measurement of the gas, invariably gave results much too low, especially if the quantity of nitrate operated on was small, say 5 or 6 centigrams of nitre; moreover, when sugar or similar organic substance was present the resulting gas was very impure, and the distillates were highly coloured from the presence of some volatile products. The nitric oxide also suffered considerable diminution of volume, when left for any time in contact with the distillate, especially when over caustic soda. This being the case, the following modification originally recommended by Schlösing was adopted, in which $CO^2$ was employed, both to assist in expelling the air from the apparatus, and to chase out the nitric oxide produced.

The form of apparatus adopted by Warington is shown in fig. 36. The vessel in which the reaction takes place is a small tubulated receiver, the tubulure of which has been bent near its extremity to make a convenient junction with the delivery tube, which dips into a trough of mercury on the left. The long supply tube attached to the receiver is of small bore, and is easily filled by a $\frac{1}{2}$ c.c. of liquid. The short tube to the right is also of small bore, and is connected by a caoutchouc tube and clamp with an apparatus for the continuous production of carbonic acid.

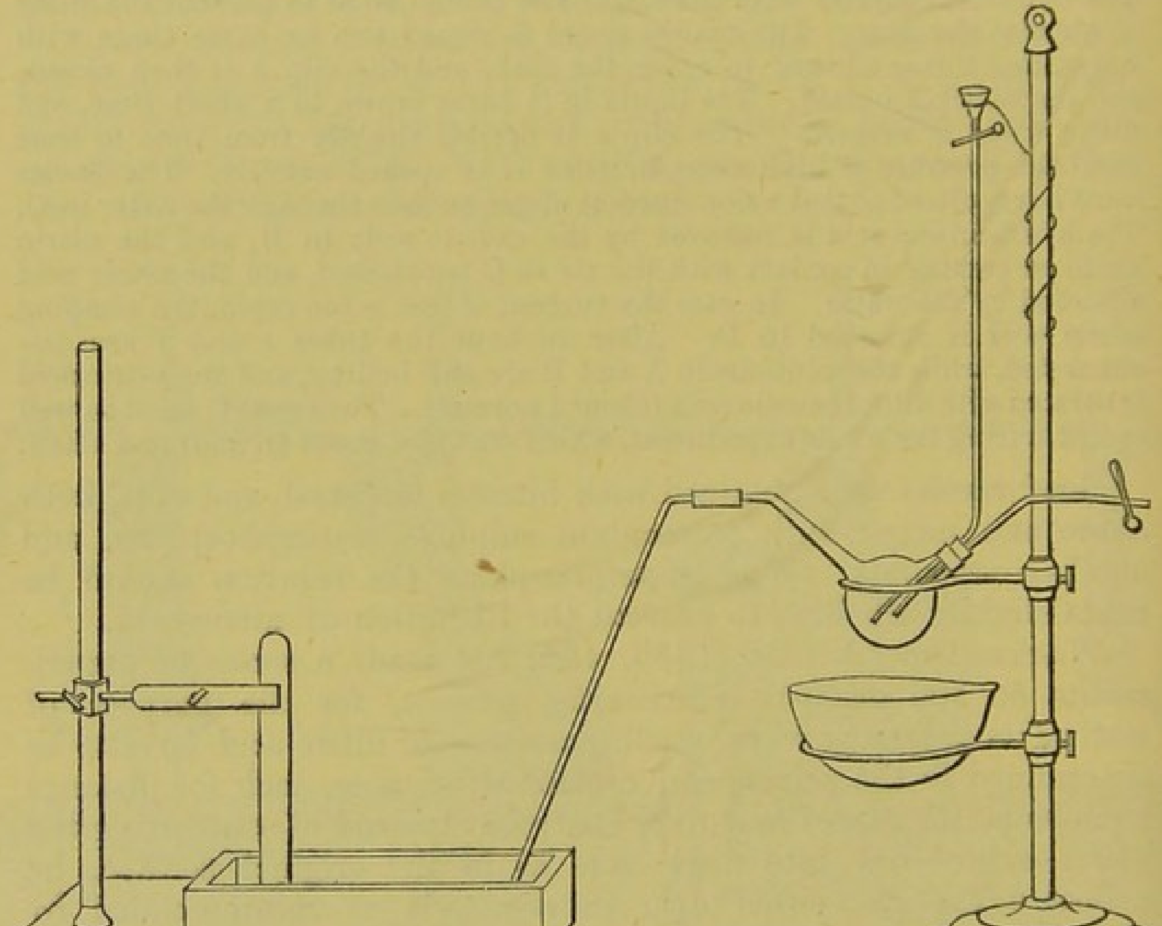

Fig. 36.

In using this apparatus the supply tube is first filled with strong HCl, and $CO^2$ is passed through the apparatus till a portion of the gas collected in a jar over mercury is found to be entirely absorbed by caustic potash. The current of gas is then stopped by closing the clamp to the right. A chloride of calcium bath at 140° is next brought under the receiver, which is immersed one-half or more in the hot fluid; the temperature of the bath is maintained throughout the operation by a gas-burner placed beneath it. By allowing a few drops of HCl to enter the hot receiver, the $CO^2$ it contains is almost entirely expelled. A jar filled with mercury is then placed over the end of the delivery tube, and all is ready for the commencement of a determination.

The nitrate, which should be in the form of a dry residue in a small beaker or basin, is dissolved in about 2 c.c.* of strong ferrous chloride solution, 1 c.c. of strong HCl is added, and the whole is then introduced into the receiver through the supply tube, being followed by successive rinsings with HCl, each rinsing not exceeding a ½ c.c., as the object is to introduce as small a bulk of liquid as possible. The contents of the receiver is in a few minutes boiled to dryness; a little $CO^2$ is admitted before dryness is reached, and again afterwards to drive over all remains of nitric oxide. If the gas will not be analyzed till next day, it is advisable to use more $CO^2$, so as to leave the nitric oxide diluted with several times its volume of that gas. As soon as one operation is concluded the apparatus is ready for another charge.

This mode of working presents the following advantages:—

(1) The volume of liquid introduced into the apparatus is much diminished, and with this of course the amount of dissolved air contributed from this source.

(2) By evaporation to dryness a complete reaction of the nitrate and ferrous chloride, and a perfect expulsion of the nitric oxide formed, is as far as possible attained.

(3) The nitric oxide in the collecting jar is left in contact with a much smaller volume of acid distillate, and its liability to absorption is greatly diminished by its dilution with $CO^2$.

The results obtained with this apparatus by Warington on small quantities of nitre alone, and mixed with variable quantities of ammonic salts and organic substances including sugar, showed a marked improvement upon the method as usually carried out.

A further improvement has been made in this method by Warington (*J. C. S.* 1882, 345), and described by him as follows:—

The apparatus now employed is quite similar to that shown in fig. 36, with the only difference that the bulb retort in which the reaction takes place is now only 1¾ inch in diameter, thus more exactly resembling the form employed by Schlösing. A bulb of this size is sufficient for the analysis of soil extracts; for determinations of nitrates in vegetable extracts a larger bulb is required.

The chief improvement consists in the use of $CO^2$ as free as possible from oxygen. The generator is formed of two vessels. The lower one consists of a bottle with a tubulure in the side near the bottom; this bottle is supported in an inverted position, and contains the marble from which the gas is generated. The upper vessel consists of a similar bottle standing upright; this contains the HCl required to act on the marble. The two vessels are connected by a glass tube passing from the side tubulure of the upper vessel to

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* Supposing the ferrous chloride to contain 2 gm. of iron per 10 c.c., then 1 c.c. of the solution will be nearly equivalent to 0·12 gm. of nitre, or 0·0166 gm. of nitrogen. A considerable excess of iron should, however, always be used.

the inverted mouth of the lower vessel; the acid from the upper vessel thus enters below the marble. $CO^2$ is generated and removed at pleasure by opening a stop-cock attached to the side tubulure of the lower vessel, thus allowing HCl to descend and come in contact with the marble. The fragments of marble used have been previously boiled in water. The boiling is conducted in a strong flask. After boiling has proceeded some time, a caoutchouc stopper is fixed in the neck of the flask, and the flame removed; boiling will then continue for some time in a partial vacuum. The lower reservoir is nearly filled with the boiled marble thus prepared. The HCl has been also well boiled, and before it is introduced into the upper reservoir it has dissolved in it a moderate quantity of cuprous chloride. As soon as the acid has been placed in the upper reservoir it is covered by a layer of oil. The apparatus being thus charged is at once set in active work by opening the stop-cock of the marble reservoir; the acid descends, enters the marble reservoir, and the $CO^2$ produced drives out the air which is necessarily present at starting. As the acid reservoir is kept on a higher level than the marble reservoir, the latter is always under internal pressure, and leakage of air from without cannot occur.

The presence of the cuprous chloride in the hydrochloric acid not only ensures the removal of dissolved oxygen, but affords an indication to the eye of the maintenance of this condition. So long as the acid remains of an olive tint, oxygen will be absent; but should the acid become of a clear blue-green, it is no longer certainly free from oxygen, and more cuprous chloride must be added.

A further slight improvement adopted consists in the use of freshly-boiled reagents, which are employed in as small a quantity as possible. When boiling the hydrochloric acid it is well to add a few drops of ferrous chloride, in order more certainly to remove any dissolved oxygen.

The mode of operation is as follows:—The apparatus is fitted together, the long funnel tube attached to the bulb retort being filled with water. Connection is made with the glass stop-cock of the $CO^2$ generator by means of a short stout caoutchouc tube, provided with a pinch-cock. The pinch-cock being opened, the stop-cock is turned till a moderate stream of bubbles rises in the mercury trough; the stop-cock is left in this position, and the admission of gas is afterwards controlled by the pinch-cock, pressure on which allows a few bubbles to pass at a time. The heated chloride of calcium bath is next raised, so that the bulb retort is almost submerged; the temperature, shown by a thermometer which forms part of the apparatus, should be 130—140°. By boiling small quantities of water or hydrochloric acid in the bulb retort in a stream of $CO^2$ the air present is expelled; the supply of gas must be stopped before the boiling has ceased, so as to leave little in the retort. Previous to very delicate experiments it is advisable to introduce through the funnel tube a small quantity of nitre, ferrous chloride, and hydrochloric acid, rinsing the tube with the latter reagent; any trace of oxygen remaining in the apparatus is then consumed by the nitric oxide formed, and after boiling to dryness, and driving out the nitric oxide with $CO^2$, the apparatus is in a perfect condition for a quantitative experiment.

Soil extracts may be used without other preparation than concentration. Vegetable juices, which coagulate when heated, require to be boiled and filtered, or else evaporated to a thin syrup, treated with alcohol and filtered. A clear solution being thus obtained, it is concentrated over a water-bath to the smallest volume, in a beaker of smallest size. As soon as cool, it is mixed with 1 c.c. of a cold saturated solution of ferrous chloride and 1 c.c. HCl, both reagents having been boiled and cooled immediately before use. In mixing with the reagents care must be taken that bubbles of air are not entangled; this is especially apt to occur with viscid extracts. The quantity of ferrous chloride mentioned is amply sufficient for most soil extracts, but it is well perhaps to use 2 c.c. in the first experiment of a series; the presence of a considerable excess of ferrous chloride in the retort is thus ensured. With bulky vegetable extracts more ferrous chloride should be employed; to the syrup from 20 grams of mangel sap should be added 5 c.c. of ferrous chloride, and 2 c.c. of hydrochloric acid.

The mixture of the extract with ferrous chloride and HCl is introduced through the funnel tube, and rinsed in with three or four successive ½ c.c. of HCl. The contents of the retort is then boiled to dryness, a little $CO^2$ being from time to time admitted, and a more considerable quantity used at the end to expel any remaining nitric oxide. The most convenient temperature is 140°, but in the case of vegetable extracts it is well to commence at 130°, as there is some risk of the contents of the retort frothing over. The gas is collected in a small jar over mercury. As soon as one operation is completed, the jar is replaced by another full of mercury, and the apparatus is ready to receive a fresh extract. A series of five determinations, with all the accompanying gas analyses, may be readily performed in one day. The bulb retort becomes encrusted with charcoal when extracts rich in organic matter are the subject of analysis; it is best cleaned first with water, and then by heating oil of vitriol in it.

Mercury, contrary to the statement in most text books, is gradually attacked by hydrochloric acid in the presence of air; the mercury in the trough is thus apt to become covered with a grey chloride, and it is quite necessary to keep the store of mercury in contact with sulphuric acid to preserve its mobile condition

The gas analysis is of a simple character; the gas is measured after absorption of the $CO^2$ by potash, and again after absorption of the nitric oxide, the difference giving the amount of this gas. For the absorption of nitric oxide, a saturated solution of ferrous chloride was for some time employed. This method is not, however, perfectly satisfactory when the highest accuracy is required, the nitric oxide being generally rather underestimated, except the process of absorption is repeated with a fresh portion of ferrous chloride. The error is greater in proportion to the quantity of unabsorbed gas present. Thus, with a mixture of nitrogen and nitric oxide containing little of the former, absorption of the nitric oxide by successive treatment with oxygen and pyrogallol over potash showed 97·8 per cent. of nitric oxide; while the same gas, analyzed by a single absorption with ferrous chloride (after potash), showed 97·5 per cent. of nitric oxide. With a mixture containing more nitrogen, the oxygen method showed 65·9 per cent. of nitric oxide; while one absorption with ferrous chloride gave 64·2 per cent., and a second absorption, in which the ferrous chloride was plainly discoloured, 66·2 per cent. The use of ferrous chloride as an absorbent for nitric oxide has now been given up, and the oxygen method substituted. All the measurements of the gas are now made without shifting the laboratory vessel; the conditions are thus favourable to extreme accuracy.

The chief source of error attending the oxygen process lies in the small quantity of carbonic oxide produced during the absorption with pyrogallol; this error becomes negligible if the oxygen is only used in small excess. The difficulty of using the oxygen in nicely regulated quantity may be removed by the use of Bischof's gas delivery-tube. This may be made of a test-tube, having a small perforation half an inch from the mouth. The tube is partly filled with oxygen over mercury, and its mouth is then closed by a finely-perforated stopper, made from a piece of wide tube, and fitted tightly into the test-tube by means of a covering of caoutchouc. When this tube is inclined, the side perforation being downwards, the oxygen is discharged in small bubbles from the perforated stopper, while mercury enters through the side opening. Using this tube, the supply of oxygen is perfectly under control, and can be stopped as soon as a fresh bubble ceases to produce a red tinge in the laboratory vessel. The trials made with this apparatus have been very satisfactory. If nitrites are to be estimated by this method, it is necessary first to convert them into nitrates, with excess of hydrogen peroxide, which is entirely destroyed by the subsequent evaporation to dryness.

### Technical method for Alkaline Nitrates and Nitrated Manures.

Wagner uses a simple arrangement of apparatus, which gives fairly good results, and permits of rapid working.

A 200 c.c. flask is fitted with a two-hole rubber stopper. One hole carries an ordinary gas delivery tube, and the other a thistle funnel having a stopcock below the funnel. The end of this tube is narrowed, and does not quite reach the liquid in the flask.

A solution of 200 gm. of iron wire in hydrochloric acid is made and diluted to 1 liter. 40 c.c. of this solution is placed in the flask, and the air expelled by boiling. 10 c.c. of a standard solution of sodic nitrate, containing 33 gm. per liter, are then placed in the funnel, and allowed gradually to drop into the boiling solution of iron. A gas tube graduated to 100 c.c. is filled with boiled and cooled distilled water, and the nitric oxide collected in the usual way. When the nitre solution is nearly all dropped in, the funnel is filled with 20 per cent. HCl, and run down: this is repeated, the liquid being still kept gently boiling. 10 c.c. of the solution to be tested are now put into the funnel, taking care that not more than 100 c.c. of gas will result. The gas is collected as before in a fresh tube precisely as in the case of the pure nitrate. In this manner five or six estimations can be made with the one and the same ferrous solution. Finally a fresh test is made with standard nitre solution; the readings of the tubes are taken, and as they will all be of same temperature and pressure no correction is necessary, all being allowed to cool to the same point.

The calculation is easy. Suppose that the pure nitre gave 90 c.c. of gas, this volume $=0{\cdot}33$ gm. of $NaNO^3$, or 1 c.c. $=0{\cdot}00366$ gm. $=0{\cdot}000604$ gm. N.

### 6. Estimation by Standard Indigo Solution.

This process has commanded a great deal of attention as a ready and convenient one for estimating the nitrogen existing as nitrates and nitrites in waters, etc., but it is subject to great irregularity unless conducted with special precautions. The principle of the method is that of liberating free nitric and nitrous acids from their combinations by the aid of strong sulphuric acid, and measuring the quantity so liberated by the decoloration of a solution of indigo.

As a general rule, in the case of waters, no amount of interference is produced by the presence of chlorides, sulphates, or alkaline and earthy matters usually found.

In the third edition of this book, the process, as modified by Thorp and myself, was given; but since that time Warington has extensively experimented on the method with great discrimination, and found out its weak points, the result being that when the method is carried out in the way adopted by him in the case of potable waters, drainage waters, soil extracts, etc., in the absence of much organic matter, very concordant results are obtained, differing very slightly from other established methods. These valuable contributions by Warington are given in two papers (*C. N.* xxxv. 45, and *J. C. S.* 1879, 578), and may be summarized as follows:—

*Standard Potassic Nitrate.*—1·011 gm. of the pure salt in a liter. This is in reality a $\frac{N}{100}$ solution of nitre.

*Weak Standard Nitre.*—One part of the above solution to three parts of water.

A series of weaker solutions of nitre are also requisite for standardizing the indigo, which are made of $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$, and $\frac{1}{64}$ the original strength by simple dilution with distilled water.

*Strong Standard Solution of Indigo.*—This should be made from pure sublimed indigotin, 2 gm. of which, digested with about 10 gm. of fuming sulphuric acid for some hours, diluted to about a liter and filtered, will give a solution of approximate strength. When actually adjusted so as to agree with the centinormal nitre solution, 4 per cent. by volume of oil of vitriol, or about that proportion, should be contained in it; this prevents alteration by keeping.

*Weak Standard Indigo.*—This is made to agree with the $\frac{1}{4}$ standard nitre solution by actual experiment, as described further on, and should also contain 4 per cent. of its volume of $H^2SO^4$.

In making these solutions of indigo the so-called indigo-carmine has often been used (sodic sulphindylate), but this compound generally gives more red colour when oxidized by nitric acid than pure indigotin; nevertheless, there are some specimens of indigo-carmine which are quite available for the purpose.

A burette divided into $\frac{1}{10}$ c.c. should be used for the indigo, but owing to the deep colour of the solution the reading is difficult. This may be considerably lessened by rubbing with the finger some white lead or chalk, mixed with oil or varnish, over the outside of the burette, then wiping the outside of the instrument clean, so as to leave the graduations and figures filled with white. In the case of using an Erdmann's float, if the ring is deeply cut, and filled with white material, as also the graduations of the burette, a remarkably sharp reading may be obtained in the case of all opaque or highly coloured liquids.

In water analysis it is most convenient to work with 20 c.c. of the water; when this is done it is necessary to standardize the indigo with 20 c.c. of the $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$ and $\frac{1}{64}$ nitre solutions. If 10 c.c. of water are to be employed, the indigo must be also standardized with 10 c.c. of the $\frac{1}{4}$ and $\frac{1}{8}$ nitre solutions. It is most useful to standardize both for 10 c.c. and 20 c.c. of water, as waters of a greater range of strength can then be titrated without dilution. It is unnecessary to standardize with 10 c.c. of the weaker nitre solutions; if the amount of nitrate in a water is no greater than that in the $\frac{1}{8}$ nitre solution, 20 c.c. of the water may be at once taken for analysis.

A large supply of pure oil of vitriol will be required for extensive water analysis. It should be colourless, quite free from nitrous compounds, and contain as little as possible of sulphurous acid, and must be of nearly full gravity. The oil of vitriol is measured for use in a tolerably wide burette provided with a glass stop-cock. A test-tube with foot, marked at each 2 c.c. from 10 to 40 c.c., answers very well for the oil of vitriol and dispenses with the burette; the oil of vitriol is then kept in a stoppered bottle.

A further requisite is a chloride of calcium bath, provided with a thermometer; the bath is conveniently made in a porcelain basin. The temperature to be maintained is 140° C. As the temperature keeps rising from the evaporation of the solution, it is necessary to bring it down to the required point by the addition of a little water, or calcium solution, immediately before each experiment. The bath is not required when strong solutions of nitrate are analyzed by the stronger solution of indigo, the reaction in such cases being almost immediate. With weak solutions of indigo and nitrate the reaction may take some time, in extreme cases as much as five minutes, and it becomes essential for accuracy that the temperature should be maintained throughout at the normal point.

The standardizing of the indigo solution is performed as follows:—

10 c.c. or 20 c.c. of the standard nitre solution are placed in a wide-mouthed flask of about 150 c.c. capacity, as much indigo solution is measured in as is judged sufficient, and the whole mixed. Oil of vitriol is next run from the burette into a test-tube, in quantity exactly equal to the united volumes of the nitre solution and indigo. The contents of the test-tube are then poured as suddenly as possible into the solution in the flask, the whole rapidly mixed, and the flask at once transferred to the chloride of calcium bath. It is essential for concordant results that the oil of vitriol should be uniformly mixed with the solution as quickly as possible. This is especially necessary in the case of strong solutions of nitrate in which the action begins immediately after the addition of the sulphuric acid; with such solutions it is more difficult to get duplicate experiments to agree than with weaker solutions in which the action does not begin at once, and in which therefore time is afforded for mixing. The operator should not attempt to drain the test-tube; the oil of vitriol adhering to the tube is a fairly constant quantity, and after the first experiment the tube will deliver the quantity measured into it.

It is well to have the flask covered by a watch-glass while holding it in the bath. The progress of the reaction should be watched, and as soon as the greater part of the indigo has been oxidized, the contents of the flask should be gently rotated for a moment. With very weak solutions of pure nitre no change is observed for some time, and it may be necessary in some cases to keep the flask in the bath for five minutes. If the colour of the indigo is suddenly discharged, it is a sign that the nitric acid is in considerable excess, and that a considerably larger amount of indigo must be taken for the next experiment. If some of the indigo remains unoxidized, a little experience will enable the operator to judge its probable amount, and so decide on the quantity of indigo suitable for the next experiment.

The amount of indigo which corresponds to the solution of nitrate is found by a series of approximating experiments made as just described with varying quantities of indigo, the oil of vitriol used being always equal in volume to the united volumes of the nitrate solution and indigo. The determination is finished when a quantity of indigo is left unoxidized not exceeding 0·1 c.c. of the indigo solution used; this amount can be readily estimated by the eye. It is well, until considerable experience has been gained, to check the result by making a further experiment with 0·1 c.c. less indigo, when the colour should be entirely discharged. The tint produced by a small excess of indigo is best seen by filling up the flask with water. The estimated excess of indigo is of course deducted from the reading of the burette.

To reduce the number of experiments required to obtain the result it is well to proceed with some boldness, and ascertain as soon as possible what are the limits between which the quantity of indigo must fall. Seven experiments will be a maximum rarely exceeded; four experiments is about the average required where the history of the waters examined is already known.

When the indigo solution has been standardized with the series of nitre solutions already mentioned, it will be found that the quantity of indigo consumed is not strictly in proportion to the nitric acid present, but diminishes as the nitrate solution becomes more dilute. In round numbers, a diminution of the amount of nitre present to $\frac{1}{8}$ is accompanied by diminution of the indigo oxidized to $\frac{1}{10}$; or, in other words, if 20 c.c. of the $\frac{1}{8}$ standard solution of nitre require 10 c.c. of indigo, 20 c.c. of the $\frac{1}{64}$ nitre solution will require only 1 c.c. of indigo. This is a very important fact, and necessitates the standardizing of the indigo with solutions of graduated strength, so that the value of the indigo may be known for all parts of its scale.

In consequence it becomes necessary to form a table of the value in nitrogen corresponding to each part of the indigo scale, and by the help of this table every analysis subsequently made is calculated. Below is given an ideal table of this description. It is assumed, which is very near the truth, that a diminution to one-eighth in the strength of the nitrate solution is accompanied by a diminution to one-tenth in the indigo consumed. It is further assumed, which is also near the truth, that the alteration in the relation of the indigo to the nitrate proceeds at a uniform rate between the limits actually determined. The following will be the results arrived at when using 20 c.c. of the nitrate solution for each experiment :—

*Value of the Indigo in Nitrogen for different strengths of Nitre Solution.*

| Strength of nitre solution used. | Indigo required. | Difference between amounts of indigo. | Nitrogen corresponding to 1 c.c. of indigo. | Difference between the nitrogen values. | Difference in the nitrogen values for a difference of 1 c.c. in the amount of indigo. |
|---|---|---|---|---|---|
| | c.c. | c.c. | gram. | gram. | gram. |
| $\frac{8}{64}$ Standard | 10·00 | — | ·000035000 | — | — |
| $\frac{7}{64}$ " ... | 8·71 | 1·29 | ·000035161 | ·000000161 | ·000000125 |
| $\frac{6}{64}$ " ... | 7·43 | 1·28 | ·000035330 | ·000000169 | ·000000132 |
| $\frac{5}{64}$ " ... | 6·14 | 1·29 | ·000035627 | ·000000298 | ·000000231 |
| $\frac{4}{64}$ " ... | 4·86 | 1·28 | ·000036008 | ·000000381 | ·000000298 |
| $\frac{3}{64}$ " ... | 3·57 | 1·29 | ·000036764 | ·000000756 | ·000000586 |
| $\frac{2}{64}$ " ... | 2·29 | 1·28 | ·000038209 | ·000001445 | ·000001129 |
| $\frac{1}{64}$ " ... | 1·00 | 1·29 | ·000043750 | ·000005541 | ·000004295 |

The mode of using this table is very simple. Supposing that 20 c.c. of a water have required 5·36 c.c. of indigo, this amount is seen to be 0·5 c.c. above the nearest point (4·86 c.c.) given in the table. We learn from the right-hand column that 0·000000149 must consequently be subtracted from the unit value in nitrogen (0·000036008 gm.) belonging to 4·86 c.c. of indigo. We thus find that the 5·36 c.c. of indigo should be reckoned at 0·000035859 gm. of N per c.c. : the water therefore contains 9·6 parts of N as nitric acid per million. If 20 c.c. of the water have required less than 1 c.c. of indigo, the unit-value corresponding to 1 c.c. of indigo is employed for calculating the result. This will give accurate results if the oil of vitriol employed is quite pure.

It is not necessary in practice to form so complete a table as that now given; it will suffice to determine the indigo with nitre solutions of $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$, and $\frac{1}{64}$ strength : if another solution is used, that of $\frac{3}{64}$ strength seems the most important. It may be sufficient, even, in some cases, simply to determine the indigo with the $\frac{1}{8}$ and $\frac{1}{64}$ nitre solutions, and to find all the intermediate values by calculation; examples will be presently given showing the amount of agreement between such calculation and experiment. If 10 c.c. of water are to be employed as well as 20 c.c., separate tables should be formed giving the values of the indigo in each case.

There is one important advantage that follows from this troublesome necessity of standardizing the indigo with various nitrate solutions; it tends to remove the errors due to impurities in the oil of vitriol. As the volume of the oil of vitriol used depends far more on the volume of water taken than on the quantity of nitric acid it contains, all errors due to oxidizing or reducing matter contained in the oil of vitriol fall far more heavily on determinations of small quantities of nitric acid than on larger. Unless, therefore, the oil of vitriol used was absolutely pure, it would always be necessary to standardize the indigo as now recommended, even if the relation of indigo to nitric acid were exactly the same in weak and strong solutions. By standardizing as now described, the errors due to the sulphuric acid affect the figures of the table, but not the result of the analysis. Such standardizing has also the effect, as far as it goes, of calibrating the burette, any inequalities of capacity falling on the table, and not on the analyses calculated from it.

In standardizing the indigo solution, and in the subsequent experiments with it, some regard must be paid to the initial temperature of the solutions. A rise in the initial temperature will be attended by a diminution in the quantity of indigo oxidized; this is most perceptible in the case of the stronger solutions of nitrate. The following table shows the results obtained by standardizing the same indigo solution at two temperatures, representing nearly the extreme limits at which the solution would be used in practice. The temperature of the room during the experiment was 10°; for the trials at the higher temperature, the flask containing the indigo and nitrate, and the test-tube containing the oil of vitriol, were placed for some time in a water bath at 22—23° previously to being mixed.

*Indigo Solution Standardized with* 10 *c.c. of Nitre Solution.*

| Strength of nitre solution. | At 10°. | | At 22°. | |
|---|---|---|---|---|
| | Indigo required (actual). | Indigo calculated from two extremes. | Indigo required (actual). | Indigo calculated from two extremes. |
| | c.c. | c.c. | c.c. | c.c. |
| $\frac{1}{4}$ Standard | 10·28 | 10·28 | 9·76 | 9·76 |
| $\frac{1}{8}$ ,, ... | 4·97 | 4·97 | 4·78 | 4·73 |
| $\frac{1}{16}$ ,, ... | 2·30 | 2·32 | 2·18 | 2·22 |
| $\frac{1}{32}$ ,, ... | 0·99* | 0·99 | 0·96 | 0·96 |

*Standardized with* 20 *c.c. of Nitre Solution.*

| | | | | |
|---|---|---|---|---|
| $\frac{1}{8}$ Standard | 10·26 | 10·26 | 9·74 | 9·74 |
| $\frac{1}{16}$ ,, ... | 4·84 | 4·96 | 4·65 | 4·74 |
| $\frac{1}{32}$ ,, ... | 2·21 | 2·31 | 2·21 | 2.24 |
| $\frac{1}{64}$ ,, ... | 0·99 | 0·99 | 0·99 | 0·99 |

* It must not be supposed that it was possible to work to one-hundredth of a cubic centimeter; in all the figures given, the errors shown by calibrating the measuring vessels employed have been taken account of, and minute fractions thus introduced.

It is seen that a rise of 12° in temperature diminishes the indigo consumed by about 5 per cent. in the case of the stronger solutions of nitrate; it is evident, therefore, that the indigo solution should be standardized at nearly the same temperature at which it is to be used.

In the table the quantity of indigo corresponding to the intermediate strengths of nitre solution has been calculated from the determinations made with the two extreme strengths, to show the amount of accuracy to be attained by this plan; the agreement of calculation with the results actually obtained is sometimes very close, but in others the difference is somewhat greater than the errors of experiment.

If the indigo solution has been standardized with 20 c.c. of the nitre solutions recommended, the operator will be able to titrate waters containing nitric acid up to 17·5 parts of nitrogen per million. If the indigo has also been standardized with 10 c.c. of the $\frac{1}{4}$ and $\frac{1}{8}$ nitre solutions, the operator can, by employing 10 c.c. of the water, extend his range of analysis to waters containing 34 parts of nitrogen per million. Waters stronger than this should be diluted for analysis. The natural error of the determination, shown by the performance of duplicate experiments, will not exceed 1 per cent. of the nitric acid present in the case of waters containing 17 of nitrogen per million, but may amount to 5 per cent. with waters containing as little as 2 of nitrogen per million.

Chlorides are of course generally present in waters containing nitrates; they are not altogether without effect on the determination with indigo.

The presence of an abundance of chlorides occasioned an error of deficiency of about 1·5 per cent. in the case of a $\frac{1}{8}$ standard solution of nitre, and an error of excess of 4·4 per cent. in the case of a solution of one-quarter this strength. At some point between the two the error was probably *nil.* The different direction of the error is apparently due to the effect of chlorides on the duration of the reaction. As nitre solutions become weaker the time occupied by the reaction with indigo is lengthened, and the proportion of indigo consumed diminished. In the presence of chlorides the duration of the reaction in weak solutions is much shortened, and the quantity of indigo consumed is consequently increased.

The error introduced by chlorides is for many purposes insignificant. Thus, two nitre solutions employed contained 17·8 and 4·3 of nitrogen per million; titrated in the presence of excess of chloride they yielded 17·5 and 4·5 per million. As in water analysis the amount of chlorine is always determined, it would be well to make this part of the analysis preliminary to the nitric acid determination. The indigo might also be standardized with nitre solutions containing excess of chloride, and a small quantity of pure chloride added to all waters deficient in this constituent.

Finkener has already recommended the addition of chlorides to the standard nitre solutions.

Nitrites are unfortunately not capable of being determined by indigo; the amount of indigo oxidized is much less than in the case of nitrates, and the reaction is far from being sharp.

Nitrites may be easily converted into nitrates by treatment with permanganate, and may then be determined by indigo. A solution of commercial potassic nitrite, which contained by the Crum-Frankland method 31·5 parts of nitrogen per million, gave only 22·1 parts of nitrogen when tested by indigo previously standardized with a nitrate. The same quantity of nitrite, in a more concentrated form, was treated with permanganate, acidified with sulphuric acid, and permanganate slowly added till decolorization no longer occurred. The solution was finally brought to the same volume as in the first experiment, and tested with indigo; it now yielded 32·4 parts of nitrogen per million.

If chlorides are present as well as nitrites, free chlorine may be produced during treatment with permanganate, and the determination with indigo consequently come out too high; in this case it may be well to make the liquid slightly ammoniacal after the treatment with permanganate, and raise the temperature for an instant to boiling. This mode of proceeding, according to Boussingault, completely removes free chlorine.

The weakest point in the indigo method is its behaviour in the presence of organic matter. Warington found that a small quantity of cane-sugar greatly reduced the quantity of indigo oxidized by a nitrate, the effect of the sugar being greater in dilute solutions, in which the reaction was naturally more prolonged. The use of a large proportion of oil of vitriol also increased the effect of the sugar. Carbolic acid and urea also act as reducing agents, while tartaric acid has been proved by many experiments to be without effect.

The indigo method cannot be employed with safety for the analysis of waters distinctly contaminated with organic matter. There appears to be no method of determining small quantities of nitric acid, save that of Schlösing, which is free from suspicion under these circumstances.

In the case of ordinary drainage waters the agreement between the indigo method and that of Crum-Frankland is very good. The following analyses of drainage waters refer to waters collected from unmanured arable land (Warington). The figures represent nitrogen per million:—

| Crum-Frankland method. | Indigo method. |
|---|---|
| 22·7 | 23·0 |
| 16·6 | 16·9 |
| 13·3 | 13·8 |

In a series of comparative analyses, by the same two methods, of nitrified solutions of ammonic chloride (*J. C. S.* 1879, 448) the agreement between the results was generally good, and the comparisons instituted by Hatton (*J. C. S.* 1881, 258) are equally satisfactory.

The general conclusion respecting the indigo method for determining nitric acid will be, that it is excellently adapted by its simplicity, rapidity, and delicacy for general use in water analysis; but that accuracy can be secured only by working under the same conditions which obtained when the indigo was standardized. In the presence of organic matter the results obtained with indigo must be accepted as probably below the truth.

The above description is given mainly in Warington's own words, and is undoubtedly the best plan of working the process so as to secure accuracy; notwithstanding this, there are some operators who seem disposed to discard it even for water analysis (Dupré, *Analyst*, vi. 39). I am inclined to think that the apparent or alleged inaccuracies arise from want of patience or practice, and that if the manipulations are well understood, the process will give as good average results as most of the processes in use for the determination of small quantities of nitric acid.

It is certainly the most handy process for rapidly ascertaining the approximate amount of nitric acid in any given substance; and as an adjunct to the use of some other methods, where it is necessary to know as nearly as possible the amount of nitric acid to be dealt with, it is without a rival. For such purposes in the case of materials such as guanos, manures, etc., the process may be shortened as follows:—

(1) A rough test is made with 10 c.c. of the nitrate solution and stronger indigo using 20 c.c. of oil of vitriol.

(2) If 10 c.c. of the nitrate solution require less than 1 c.c. of stronger indigo, then 10 c.c. of it may at once be titrated with the weaker indigo; the volume of acid being regulated by the first experiment to equal the volume of nitrate solution, *plus* the volume of weaker indigo required. 1 c.c. or so of acid either way does not influence the experiment. This second titration, if carefully performed, using an ordinary spirit lamp of small flame for heating, will give the value of the nitrate in terms of weak indigo.

(3) If in the preliminary test 10 c.c. of the nitrate solution require more than 1 c.c., but less than 3 c.c. of stronger indigo, the solution may be titrated at once with stronger indigo, using about 12 c.c. of acid.

(4) If in the preliminary test 10 c.c. of nitrate solution require more than 4 c.c. of stronger indigo, the solution must be diluted twice, thrice, or more as the case may be, so as to bring it to about the strength of the weaker standard nitre solution, when it may be finally titrated with the stronger indigo and the correct amount of acid.

### 7. Estimation as Nitric Oxide.

This method of estimating nitrogen existing as nitric and nitrous acids, either separately or together, is an exceedingly delicate one, and capable of great accuracy under proper manipulation.

It is now best known as the Crum-Frankland method, the original idea emanating from Crum, and afterwards improved in detail of manipulation by Frankland and Armstrong, in their well-known method of water analysis.

So far as the use of the method for water analysis is concerned, the process is given in Part VI., where the shaking tube which is used for the decomposition of the nitrogen compounds by mercury and sulphuric acid is figured, and the details of the process as applied to waters fully described.

The method there given, however, requires the use of a gas apparatus. This method obviates that necessity, and though the results cannot be said to be absolutely as exact, they are very satisfactory for some purposes, such as the examination of nitrous vitriol, raw commercial nitrates, manures, etc.

The apparatus used is Lunge's nitrometer, a figure of which is given in the section on technical gas analysis, accompanied with a description of the method of using it. The application of the instrument to the estimation of nitrous and nitric acids in vitriol and other substances, is explained in the same section.

The volume of the nitric oxide obtained can be read off to $\frac{1}{20}$ c.c.; it is reduced by Bunsen's tables to 0° and 760 m.m. mercurial pressure, and the percentage of the acid calculated from it. Each c.c. of NO, measured at 0° and 760 m.m., corresponds to 1·343 m.gm. NO, or 1·701 m.gm. $N^2O^3$, or 2·417 m.gm. $N^2O^5$, or 4·521 m.gm. $KNO^3$, or 3·805 $NaNO^3$. By this process, of course, nitric and nitrous acids cannot be distinguished, but are always estimated together.

The principle of the reaction is explained in the section on Water Analysis (Estimation of Nitrates and Nitrites), and the satisfactory nature of the method for vitriol-testing has been amply demonstrated by Watts, by Davis (*C. N.* xxxvii. 45), and many others. The instrument itself has been made in several modified ways, but the principle of its construction is the same.

Allen (*Analyst*, v. 181) recommends the use of this instrument for the estimation of nitrates and nitrites in water residues; and to obviate the difficulty in reading the volume which sometimes arises from the mercurial froth, he uses two nitrometers side by side, in one of which is worked a pure standard nitrate solution, and in the other the material for analysis under precisely the same conditions of temperature, pressure, etc. If the apparatus containing the comparative test is free from leakage, it may be retained for a long period for the purpose of comparison.

## NITRITES.

Very dilute solution of nitrous acid in combination with alkaline or earthy bases, such as naturally occur in drinking waters, can be titrated with very fair results, according to Fresenius, as follows:—

250 c.c. of the water is acidified with acetic acid, placed in a retort, and about 100 c.c. distilled into a 250 c.c. flask, the measure being afterwards made up with pure distilled water; this fluid is then acidified with pure sulphuric acid, and titrated with a very weak standard solution of permanganate.

Nitrous acid may be thus separated without any danger of oxidation; the presence of nitrates or other ordinary constituents of water do not in the slightest interfere with the accuracy of results; the greater part of the acid distils over in the first 20 or 30 c.c.

It is necessary that the solution should be very dilute, not exceeding about 6 m.gm. of nitrous acid per liter; if much stronger than this, irregularities occur which interfere with accuracy.

The usual qualitative test for nitrites is, to acidify the water moderately with pure sulphuric acid, then adding potassic iodide and starch liquor; the occurrence of the dark blue colour of starch iodide reveals the presence of nitrites immediately. This test may be conveniently applied before distilling any sample of water, so as to form a judgment of the amount of nitrites present.

*Example:* Some solution of potassic nitrite was added to pure water, and on testing in the above manner a deep blue solution was obtained.

250 c.c. of the same liquid were then acidified with sulphuric acid, and titrated with a permanganate solution of which 35 c.c. represented 0·02 gm. of iron or 0·0068 gm. of nitrous acid. The quantity required was 8·2 c.c. 250 c.c. were then acidified with acetic acid, and about half the liquid distilled and diluted to 250 c.c., then acidified with sulphuric acid and titrated with the permanganate; the quantity required was 7·5 c.c.

The first experiment showed the presence of 0·00159 gm. of nitrous acid and the second 0·00146 gm., or a loss in the 250 c.c. of 0·00013 gm.

The colorimetric method of Trommsdorf (*Z. a C.* viii. 358) depends upon the reaction just mentioned; the re-agents used being zinc iodide, sulphuric acid, and starch. Leeds has investigated the conditions under which this method is best carried out, and has found that, without special care, the error due to dissolved air and exposure to light may be enormous.

The testing solution is made by dissolving about 20 gm. of zinc chloride and 2 gm. of zinc iodide in water, adding about 5 gm. of starch previously emulsified with boiling water, and diluting the whole to about 1 liter.

The proportions used in analysis are 100 c.c. of the water to be tested, 3 c.c. of the above-described zinc iodide and starch, and 1 c.c. of pure concentrated sulphuric acid. The effect of this zinc iodide is found by a standard solution of potassic nitrite. Leeds states that about 0·04 m.gm. of $N^2O^3$ in 100 c.c. is the superior limit at which this process can be safely worked. Waters containing more than this amount must be diluted before testing quantitatively. The inferior limit is probably about 0·002 m.gm. per 100 c.c.

The delicacy of the test is seriously influenced by the dissolved organic colouring matters in natural waters, and probably by various inorganic constituents; and the reaction can only be depended on by discharging all atmospheric oxygen out of the water, and the re-agents themselves, by a current of pure carbonic anhydride.

Leeds prefers to use the method as an absolute volumetric one by operating as just described, and finding the amount of liberated iodine by weak standard thiosulphate.

### Analysis of Alkaline Nitrites.

Kinnicutt and Nef (*Amer. Chem. Journ.*) have experimented on the following method, and obtained very fair results.

The sample of nitrite is dissolved in cold water in the proportion of about 1 to 300: to this liquid $\frac{N}{10}$ permanganate is added, drop by drop, till it has a permanent red colour; then 2 or 3 drops of dilute $H^2SO^4$, and immediately afterwards a known excess of the permanganate. The liquid, which should now be of a dark red colour, is strongly acidified with pure $H^2SO^4$, heated to boiling, and the excess of permanganate determined by means of freshly prepared $\frac{N}{10}$ oxalic acid. 1 c.c. permanganate = 0·0069 gm. $NaNO^2$, or 0·0085 gm. $KNO^2$.

Of course there must be no other reducing substance than the nitrite present in the material examined, and, to ensure accuracy, a blank experiment should be made with the like proportions of $H^2SO^4$ and oxalic acid.

### Mixtures of Alkaline Sulphites, Thiosulphates, and Nitrites.

Lunge and Smith (*J. S. C. I.* ii. 465) have shown that the only satisfactory method of completely oxidizing sulphites and thiosulphates by permanganate is to add to the solution a large excess of permanganate, more than sufficient for complete oxidation, and with formation of $MnO^2$. Excess of $FeSO^4$ is then added, and again permanganate till pink. When such a mixture contains nitrites, they will of course be oxidized to nitrates.

To find the amount of nitrites present, therefore, the following method is adopted:—

The solution of the substance in not too large quantity is exactly oxidized as described, a known volume of standard ferrous sulphate is added, together with a large excess of strong $H^2SO^4$. The mixture is boiled nearly to dryness in a flask with slit valve, diluted, and, when cool, titrated with permanganate. The difference between the volume then required and that required by the original $Fe^2SO^4$, represents the nitric acid which has been reduced and escaped as NO.

The exceedingly delicate colorimetric method of estimating nitrites originally devised by Griess with meta-diamido-benzol, and afterwards elaborated by Preusse and Tiemann, will be described in the section on Water Analysis.

## OXYGEN.

$O=16$.

§ 68. The estimation of free oxygen in liquids such as waters, beer worts, etc., by methods other than gasometric has been investigated by many operators, but, until Dupré and Dibdin carried out the experiments detailed in the *Analyst* (x. 156), no such methods were used to any extent in England. The method by Mohr of finding the oxidizing power of weak alkaline solutions of oxygen upon ferrous compounds, and subsequent titration by permanganate, is manifestly of very limited application. The original method of Schützenberger with sodic hyposulphite ($NaHSO^2$) and ammoniacal copper solution, regulated by indigo (*Compt. rend.* lxv. 879), seems to be the only one worthy of notice, and this has been adopted with some modifications by the operators mentioned.

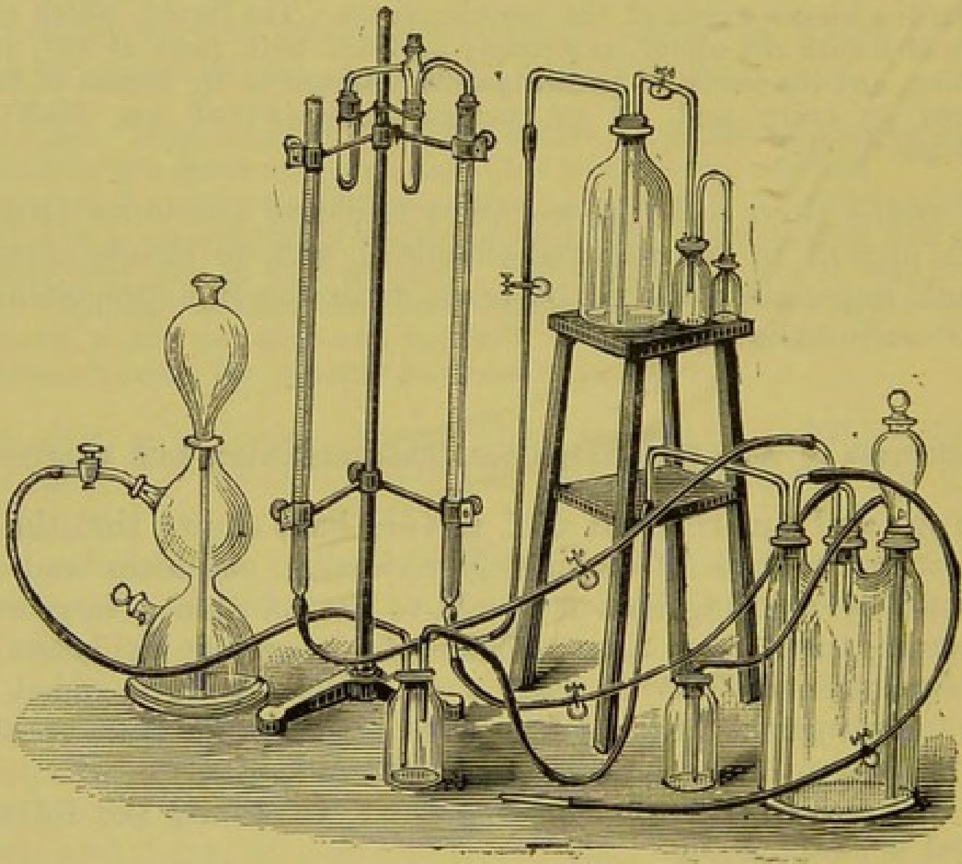

Fig. 37.

The apparatus as arranged by Dupré for the examination of waters, which differs little from Schützenberger's, is shown in fig. 37, and though seemingly complicated, is by no means difficult to work. Its description is as follows :—

One neck of a three-necked Woulf's bottle, of about one-quart capacity, is connected, by means of a doubly-perforated india-rubber stopper, with two burettes for containing indigo and hyposulphite solutions respectively. The hyposulphite burette is connected, at its lower end, in the usual manner, with a supply bottle holding the hyposulphite solution, and both burette and supply bottle are connected at the top with a small wash-bottle, containing an alkaline pyrogallol solution, through which all the air entering, when some of the solution is withdrawn, has to pass and is deprived of most of its oxygen. The second neck carries the vessel for holding the water, usually a pear-shaped vessel of about ¼ liter capacity, with a stop-cock below (not shown in figure), by means of which the water can be run into the Woulf's bottle. The delivery tube from this vessel should be carried nearly to the bottom of the bottle. Through the india-rubber stopper of the third neck, three tubes are passed; one, reaching nearly to the bottom, is connected with an apparatus for generating hydrogen; the second, also reaching nearly to the bottom, is used as a syphon for drawing off the contents of the Woulf's bottle without admission of air. The lower, outer end of this syphon tube is closed by a pinchcock. The third tube passes only just through the stopper, and is connected, outside, with a wash-bottle, through which the hydrogen, passing through the whole apparatus, can escape, while at the same time access of air to the apparatus is cut off by the water contained in the bottle.

An experiment is carried out as follows:—

The two burettes having been filled, the Woulf's bottle is entirely filled with water, all communications with the air are cut off, the syphon is opened, and the hydrogen turned on. The hydrogen entering the bottle, presses the water out through the syphon, and by the time all the water is expelled, the bottle is filled with hydrogen; after this a gentle current of hydrogen is kept up, as long as the experiment lasts. The syphon is closed, and a small quantity of water is run into the bottle through the separator (20 to 30 c.c., or thereabouts). This water is slightly coloured by running in a small quantity of indigo, and the colour of this indigo cautiously discharged by the careful dropping in of hyposulphite solution. When this is accomplished, the contents of the pear-shaped vessel, which has meanwhile been filled with the water to be examined, are run into the bottle, and the blue colour thereby restored to the contents, once more cautiously discharged. The amount of hyposulphite solution required for this is noted, the contents of the Woulf's bottle withdrawn by means of the syphon, and the same process repeated; the mean of the two experiments gives the amount of hyposulphite required by the water under examination. It now only remains to standardize the hyposulphite solution, which is accomplished by repeating the above process, with fully aërated water of known temperature, taking also the mean of the hyposulphite required in two experiments. From the respective quantities of hyposulphite required, the amount of oxygen contained in the water under examination is calculated.

At first, it was assumed that the proportions of oxygen dissolved in the two waters stood in the same relation as the amount of hyposulphite solutions required to discharge the blue colour in the two, but experiment showed that this was not so. The amount of indigo added to the water is, after its reduction, as a rule, entirely insufficient to take up the whole of the oxygen dissolved in the quantity of water taken for an experiment, and this necessitates a correction. On carrying out the experiment, as described above, it will be noticed that when the blue colour has been discharged, by the cautious addition of hyposulphite, it will very speedily return, and when again discharged, will return again, and this will continue until twice the amount of hyposulphite required to bring about the first decolouration has been added, after which the blue colour does not reappear, if the apparatus contains hydrogen only. This same amount of hyposulphite is required, if instead of taking a small amount of indigo merely, an amount is taken sufficient, after reductions, to take up the whole of the oxygen in the quantity of water used. This proves that the action of the dissolved oxygen on the reduced indigo is not the same as, at any rate, the immediate action taking place between the dissolved oxygen and the hyposulphite, but that in the first case twice the amount of oxygen is taken up at once than in the latter. The amounts of hyposulphite solution required to discharge the blue colour for the first time have therefore to be corrected, according to the amount of indigo employed, before they fairly represent the relative proportions of oxygen contained in the two waters compared. This correction is one half the amount of hyposulphite solution required simply to reduce the indigo added, so long as this is insufficient to take up all the oxygen present in the water, and to divide the amount of hyposulphite required by two whenever the indigo used was sufficient, or more than sufficient, to take up the whole of the oxygen of the water. The following table, giving one series of experiments out of many, will render the point clearer:—

| Amount of water taken. | Amount of indigo taken. | Amount of hyposulphite required. | Corrected amount proportional to the amount of oxygen in the water. |
|---|---|---|---|
| 50 c.c. | 4 drops* | 0·65 c.c. | 0·60 c.c. = 0·65 — 0·05 |
| 50 „ | 8 „ | 0·70 „ | 0·60 „ = 0·70 — 0·10 |
| 50 „ | 12 „ | 0·75 „ | 0·60 „ = 0·75 — 0·15 |
| 50 „ | 60 „ † | 1·25 „ | 0·62 „ = 1·25 — 0·20 |
| 100 „ | 12 „ | 1·35 „ | 0·60 „ = 1·35 — 0·15 |

When the water to be examined is fully aërated, this correction has no influence on the result; its influence is but slight if the water is near its full aëration, but it becomes very noticeable if the water falls considerably short of full aëration. This correction would be unnecessary if the amount of indigo taken were always sufficient to take up, after reduction, the whole of the oxygen present in the water, but in fully aërated water this amount is so great that it is difficult to fix the point at which the last trace of blue has been discharged with any degree of accuracy, since the solution never

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* 4 drops indigo required 0·1 c.c. hyposulphite for their decolouration, corrections to be applied, therefore 0·05 c.c. for every 4 drops indigo taken.

† In this case more indigo was taken than could be oxidized, after its reduction, by the oxygen of the water.

becomes colourless, but remains more or less yellow. Dupré therefore prefers to use much less indigo and to take the point of first disappearance of the blue colour, afterwards applying the correction as above described. The amount of indigo he takes is such that for its decolouration or reduction about $\frac{1}{10}$ the amount of hyposulphite will be required than that used in the examination of a water fully aërated at mean temperature.

The actual amount of oxygen contained in the water used for standardizing, is calculated by means of Bunsen's formula, but in order to save trouble, Dibdin has calculated the amount contained in a gallon of water at various temperatures, so that it can at once be read off.

**Table showing the quantity of oxygen dissolved by water at various temperatures. Corrected to 0° C. at 760 m.m. pressure.**

The table is calculated for a barometer pressure of 760 m.m. and would require corrections for variations from this, but such correction is mostly within the limits of experimental error.

| Temperature Fahrenheit. | Temperature Centigrade. | Cubic inches of Oxygen per Gallon. |
|---|---|---|
| 41° | 5·00 | 2·101 |
| 42 | 5·55 | 2·074 |
| 43 | 6·11 | 2·048 |
| 44 | 6·66 | 2·022 |
| 45 | 7·22 | 1·997 |
| 46 | 7·77 | 1·973 |
| 47 | 8·33 | 1·949 |
| 48 | 8·89 | 1·927 |
| 49 | 9·44 | 1·905 |
| 50 | 10·00 | 1·884 |
| 51 | 10·55 | 1·864 |
| 52 | 11·11 | 1·844 |
| 53 | 11·66 | 1·826 |
| 54 | 12·22 | 1·808 |
| 55 | 12·77 | 1·791 |
| 56 | 13·33 | 1·775 |
| 57 | 13·89 | 1·760 |
| 58 | 14·44 | 1·746 |
| 59 | 15·00 | 1·732 |
| 60 | 15·55 | 1·719 |
| 61 | 16·11 | 1·706 |
| 62 | 16·66 | 1·695 |
| 63 | 17·22 | 1·683 |
| 64 | 17·77 | 1·674 |
| 65 | 18·33 | 1·667 |
| 66 | 18·89 | 1·660 |
| 67 | 19·44 | 1·652 |
| 68 | 20·00 | 1·644* |
| 69 | 20·55 | 1·639 |
| 70 | 21·11 | 1·634 |

* 1·644 cubic inch of oxygen at 0° C. and 760 m.m. pressure weigh 0·594 grain.

The result of the analysis may be given in different forms. Either the amount of oxygen found in the sample under examination may be given in cubic inches per gallon, or, in per cent. of possible amount, or in both. Thus, say a water, having a temperature of 20° C., required 4 c.c. hyposulphite, the fully aërated water, at the same temperature, requiring 6 c.c. of the same solution, while the amount of indigo used took 0·6 c.c. of the same hyposulphite for its reduction. The corrected amounts of hyposulphite are $4 - 0·3 = 3·7$ and $6 - 0·3 = 5·7$. From the above table we learn that a fully aërated water at 20° C., holds in solution 1·644 cubic inch oxygen per gallon, and we get the proportion $5·7 : 1·644 = 3·7 : x$.

$$x = 1·067.$$

$$\text{or, [2] } 5·7 : 100 :: 3·7 : x ; \; x = 64·9.$$

that is, the water contained 1·067 cubic inches of oxygen dissolved per gallon, and its degree of aëration was 64·9 per cent. of the total possible.

One final precaution, sometimes required, should be mentioned. In every case the water to be examined, must, of course, be transferred to the measuring vessel in a manner to avoid aëration. This can generally be done by introducing it by means of a syphon passing to the bottom of the vessel, and thus filling it from below. In case, however, the water is but very partially aërated, it will absorb oxygen even while thus filling it into and running it out from the measuring vessel. In order to avoid this, the vessel is filled, in such cases, with carbonic acid, previous to putting in the water, which is allowed only to enter as the water runs out again. The effect of this is well shown in the following experiment:—A water which, by boiling, had been deprived of most of its dissolved oxygen required, when tested as usual, 0·83 c.c. hyposulphite, whereas, when carbonic acid was used as above directed, it required only 0·15 c.c. of the same; fully aërated water required 10·3 c.c. hyposulphite and the amount of indigo taken required 0·8 c.c. hypo. According to the first experiment, the degree of aëration of the boiled water was 4·34 per cent., according to the second 0·75 per cent. only.

*Indigo Solution.*—This is made by dissolving indigo carmine in distilled water and diluting to appropriate strength.

*Preparation of the Hyposulphite Solution.*—A concentrated solution of sodic bisulphite is saturated with sulphurous acid, a bottle of a few ounces capacity is nearly filled with this solution, a small quantity of zinc dust is added, the bottle is closed and shaken for about ten minutes; should it become warm, it must be cooled—easiest under a running tap. The bottle is then allowed to rest, and after the excess of zinc has settled, the clear solution is decanted into a second bottle, of about ten times the capacity of the first. In this bottle thin milk of lime is added to alkaline reaction, after which, the bottle is completely filled with water, stoppered, shaken, and left at rest. The clear liquid, after the precipitate has settled, is the hyposulphite solution required. If too strong, it can easily be reduced by further dilution with pure water. The strength preferred is such, that $\frac{1}{4}$ liter of fully aërated water requires about 5 c.c. of the hypo solution. It may, however, be used both stronger and considerably weaker.

The application of this process to water analysis with the necessary interpretations is given in the section devoted to that subject.

While the foregoing matter was in type, my attention was called to a series of experiments by Williams and Ramsay (*J. C. S.* 1886, 751). These operators employed the original method of Schützenberger, and their conclusion is, that in the case of estimating free oxygen in water, the process is rapid, fairly reliable, and easy of execution.

*The Standard Hyposulphite* is prepared as before described, and it is recommended to keep the strong filtered solution under a layer of benzene, removing small quantities for dilution as required.

*Standard Copper Solution.*—This is made by dissolving 4·46 gm. of crystallized cupric sulphate in water, precipitating, and redissolving in ammonia, then diluting to 1 liter. 10 c.c. = 1 c.c. O at normal temperature and pressure. On titrating this cupric solution with hyposulphite, which is always done in a hydrogen atmosphere, the blue colour gives place to clear yellow, a cuprous salt being formed.

*Solution of Indigo Carmine.*—The strength is estimated by titration with hyposulphite till the blue colour is discharged.

The hydrogen gas used for driving out the air from the vessels was purified by passing over stick potash and through $H^2SO^4$. The solution of hyposulphite was so diluted, that about 7 to 9 c.c. were required for 10 c.c. of copper solution.

The solution of indigo was made weaker than Schützenberger's, in order the better to detect loss of blue colour. The best strength is about 20 c.c. for 10 c.c. of hyposulphite.

The experiments were all conducted at ordinary temperature, and in apparatus similar to that of Dupré.

It will be readily seen that, in Dupré's method, the reducing power of the hyposulphite is determined by using water in a full state of aëration, whose contents of oxygen are known at a given temperature, while in Schützenberger's the standard is fixed by a weighed amount of copper. Schützenberger employed two methods of using his process. In the first, the water to be examined is placed in the apparatus, the air removed by hydrogen, indigo added in small quantity, then hyposulphite till blue colour is discharged. This is the first stage alluded to below. In the second method warm water is placed in the apparatus, 40 c.c. of indigo added, and carefully decolourized with hyposulphite. A known volume of the water to be tested is then run in, the oxygen in which restores the colour by oxidation. The colour is again removed by a known volume of hyposulphite, whose strength has been previously determined by standard copper.

Schützenberger was of opinion that, in the first method, only half of the oxygen was obtained, the other half combining with hydrogen to form hydroxyl. But the operators come to the conclusion, that the ratio of the oxygen estimated by stopping at the first discharge of colour to the total oxygen is not 1 : 2, but 3 : 5 approximately. Schützenberger took it for granted that, if hydroxyl was formed, it had no effect on the $NaHSO^2$, but this was found by actual trial not to be true. The experimental mean ratio obtained between methods 1 (first stage) and 2 was 1·66.

The experiments were all conducted on Bristol tap water, shaken with air, and as follows:—

1. All air being expelled from the bottle, the water to be tested was introduced and tinged with a few c.c. of indigo, then hyposulphite till yellow. On standing some minutes it again turned blue, more hyposulphite was added from time to time, until the yellow was permanent. The relative strengths of the solutions being known, the calculation for O is easy.

2. About 100 c.c. of water were placed in the bottle, together with a large excess of indigo, the colour of which was destroyed with hyposulphite. The water to be tested was then added, and the resulting blue colour again destroyed. In this case the O is calculated directly from the hyposulphite.

*Example:* Method 1, first stage.—The strength of indigo in relation to hypo was 4 : 1, and 9·41 c.c. hypo = 10 c.c. copper. 300 c.c. water required in 4 trials a mean of 8·82 c.c. hypo, therefore O per liter 3·124 c.c.

Second stage.—7·21 c.c. hypo = 10 c.c. copper. 1 liter water required 39·52 c.c. hypo = O 5·48 c.c.

Method 2.—9·41 c.c. hypo = 10 c.c. copper. 1 liter water required 52·36 c.c. hypo = O 5·554 c.c.

The first method gave, when pushed to its last stage, as a mean result of three series = 5·474 c.c. O per liter. The second 5·396 c.c.

These numbers were checked by direct gas measurement of the O expellable by boiling the same water, and resulted in a mean of 5·402 c.c.

From these experiments it appears that either of the methods of Schützenberger, when the first method is carried out to its fullest extent, is capable of giving good results.

**Hydrogen Peroxide.**—This substance is now largely used commercially for bleaching and other purposes, and it is frequently necessary to ascertain its oxygenating power, which fortunately can be done volumetrically with accuracy and dispatch.

Schöne (*Z. a. C.* xviii. 133) gives a *résumé* of the various methods in use for this purpose, comprising the permanganate estimation originally proposed by Brodie, the estimation by iodine and thiosulphate, Thenard's gasometric method, and the indigo and colorimetric methods. He gives the preference to the permanganate and colorimetric methods; but Kingzett (*J. C. S.* 1880, 792) has clearly shown that the best and most rapid estimation is made by iodine and thiosulphate in the presence of a tolerably large excess of sulphuric acid, the reaction being

$$2HI + H^2O^2 = 2H^2O + I^2.$$

The function performed by the sulphuric acid is difficult of explanation, but the want of uniformity in the reaction experienced by many operators no doubt has arisen from the use of insufficient acid.

Kingzett's method consists in mixing 10 c.c. of the peroxide solution to be examined with about 30 c.c. of dilute sulphuric acid (1 : 2) in a beaker, adding crystals of potassic iodide in sufficient quantity, and after standing five minutes the liberated iodine is titrated with $\frac{N}{10}$ thiosulphate and starch. The peroxide solution should not exceed the strength of 2 volumes; if stronger, it must be diluted proportionately before the analysis.

In the case of very weak solution it will be advisable to titrate with $\frac{N}{100}$ thiosulphate.

$$1 \text{ c.c. } \tfrac{N}{10} \text{ thiosulphate} = 0{\cdot}0017 \text{ gm. } H^2O^2.$$

The estimation of this substance may also be readily made in the absence of organic or other reducing matters by weak standard permanganate in the presence of free sulphuric acid, the permanganate being added until a faint rose colour occurs: the reaction is—

$$2KMnO^4 + 5H^2O^2 + 3H^2SO^4 = K^2SO^4 + 2MnSO^4 + 8H^2O + 5O^2.$$

The same reaction may be used for the estimation by measuring the oxygen gas evolved in a suitable apparatus, such as the nitrometer.

Carpenter and Nicholson (*Analyst*, ix. 36) report a series of experiments on the analysis of hydrogen peroxide, both by the iodine and permanganate methods.

The conclusion they arrive at is, that the process of Kingzett is accurate, but in their hands somewhat tedious, owing to slow decomposition towards the end. Kingzett, however, states that if a volume of strong sulphuric acid equal to peroxide taken be used, and especially if the dilute solution be slightly warmed, the reaction is complete in a few minutes, and this is my own experience. Nevertheless, for technical purposes, very good results may be quickly obtained, either by natural or artificial light, with simple titration of the dilute acidified solution by $\frac{N}{10}$ permanganate.

## PHOSPHORIC ACID AND PHOSPHATES.

$P^2O^5 = 142$.

§ 69. THE estimation of phosphoric acid volumetrically may be done with more or less accuracy by a variety of processes, among which may be mentioned that of Mohr as lead phosphate, the indirect method as silver phosphate (the excess of silver being found by thiocyanate), by standard uranium nitrate or acetate, or by Pemberton's method as phospho-molybdate, or when existing only as monocalcic phosphate, by standard alkali, as recommended by Mollenda or Emmerling. Further, there is the method of Stolba by separation as ammonio-magnesic phosphate, and the titration of this salt when obtained pure by standard acid. These processes are mainly useful in the case of manures, or the raw phosphates from which manures are manufactured, and for $P^2O^5$ in urine, etc. When, however, phosphorus has to be estimated as it exists in combination with metals or metallic minerals, it is doubtful whether any volumetric method can be relied upon. My experience will not allow the recommendation of any such method. For the purpose mentioned, that is to say, when in combination with alkaline or earthy alkaline bases and moderate quantities of iron or alumina, phosphoric acid may be estimated volumetrically with very fair accuracy, and with much greater rapidity than by gravimetric means as usually carried out. This remark, however, can only be applied to uranium or molybdenum methods, and the alkalimetric method of Stolba; therefore only these will be described.

### 1. Separation of the Phosphoric Acid previous to Titration.

Natural phosphates used for the manufacture of manures differ materially in their composition, and must be treated differently in their analysis. Many of the rock phosphates contain silica in large quantity, and of such a nature that hydrochloric acid readily dissolves a portion of the silica. This must be separated by evaporating the acid solution to dryness, heating to 150° or so, and redissolving the phosphate in dilute HCl or $HNO^3$, and filtering off the gelatinous $SiO^2$. If this is not done, subsequent precipitation either by molybdenum or magnesia will be rendered inaccurate from the presence of $SiO^2$.

In the case of separation by molybdenum, organic matter must be previously destroyed by calcination. Chlorides, if present, should also be removed by repeated evaporation with $HNO^3$, inasmuch as the phospho-molybdate is sensibly soluble in free HCl, or in alkaline or ferric chlorides in the presence of nitric acid. Free sulphuric acid also retards the formation of the precipitate, but neutral sulphates are of no consequence. Nitric acid, therefore, must be the final solvent in all cases where this method of separation is used.

Fluorides are of no consequence, as they are not decomposed by this acid.

In the case of separation direct by magnesia, hydrochloric acid is the usual solvent; but soluble silica must always be removed by evaporation previous to precipitation, especially for the gravimetric method.

Many natural guanos contain only mere traces of $SiO^2$, also some mineral phosphates like the Belgian phosphatic sands. Bones and similar organic phosphates are in like manner almost entirely free from it, and the same is the case with many superphosphates.

These substances may therefore, although contaminated with iron and alumina, be directly treated with magnesic citrate as described further on.

It will be evident to most operators of any experience, that if the uranium method is capable of accurate volumetric results by special precautions, the complete purity of the precipitate either in the case of magnesia or molybdenum is not a matter of great importance. This is true to some extent, but it is always advisable to have the $P^2O^5$ in as clean a form as possible, and especially is this necessary in the citro-uranic method, since the smallest trace of citric acid interferes seriously with the colour reaction.

For many years past I have used very extensively the magnesic citrate method of analysis direct by weight, and with the most satisfactory results, compared with the molybdic method of separation. For superphosphates where iron or alumina is present, or even raw phosphatic materials containing these substances, nothing better can be desired for rapidity, cleanliness, and accuracy. There are instances in which reprecipitation is necessary to purify from large excesses of Fe, Al, Ca, etc.; but these are comparatively rare; and even then less trouble is involved than by molybdenum, unless the modern method of rapid separation in the presence of a large excess of ammonic nitrate, with a small excess of nitric acid, be adopted, as in Pemberton's volumetric method. This is available in many cases, and is much more cleanly than when concentrated nitric acid is present, and the precipitate washed with the molybdic solution itself.

**Citro-Magnesic Solution.**—27 gm. of pure magnesic carbonate are added by degrees to a solution of 270 gm. of citric acid in 350 c.c. of warm water; when all effervescence is over and the liquid cool, about 400 c.c. of solution of ammonia are added, containing 10 per cent. of $NH^3$ (about 9·6 sp. gr.), or if other strength is used, enough to ensure decided excess of $NH^3$; the whole is then diluted to a liter, and preserved in a well-stoppered bottle. 20 c.c. of this solution is sufficient to insure the precipitation of 0·1 gm. of $P^2O^5$ in the presence of a large excess of $NH^3$, unless accompanied by excessive quantities of Fe or Al, which may be known by an immediate precipitate being formed on its being mixed with the phosphate solution and ammonia. In this case a fresh portion of the phosphate must be taken, and 30 or 40 c.c. of the magnesia solution used.

For estimation by weight, it is not advisable to take more phosphate solution than corresponds to 0·05 gm. $P^2O^5$, using 10 or 20 c.c. of magnesia solution, and a considerable excess of 10 per cent. ammonia.

For volumetric purposes double these quantities may be taken. The precipitation is much hastened by cooling the liquid to 12° C. or 50° F., accompanied by rapid stirring. This, however, causes a dense crystalline deposit on the sides of the beaker and on the rod, which is difficult to remove if required to be weighed. But if it has to be estimated volumetrically this is of no consequence, as the titration may take place in the same beaker and with the same rod, after they have been well washed with weak ammonia through the filter containing the main precipitate.

The precipitate of ammonio-magnesic phosphate formed is dense, crystalline, and admits of very easy washing, and the use of very free filtering paper. It is washed with 2½ per cent. ammonia until no ammonic citrate or magnesia is present in the filtrate, then either dried for ignition and weighed as $Mg^2P^2O^7$, or dissolved through the filter with dilute nitric or hydrochloric acid for subsequent titration with uranium.

It is advisable in all cases to have the acids and ammonia of a tolerably uniform strength, and to use as nearly as possible the same proportions in the analysis. Convenient strengths are 10 per cent. $NH^3$ for rendering the phosphate and citrate mixture alkaline, also for neutralizing the free acid in superphosphates, and 2½ per cent. for washing the precipitate; 10 per cent. nitric or hydrochloric acid for dissolving the precipitate for titration. This is far better than pouring in acids or alkalies at random.

**Molybdenum Solution.**—This is the usual solution made by dissolving 150 gm. of ammonic molybdate in a liter of water, and pouring it into a liter of nitric acid sp. gr. 1·20.

50 c.c. of this solution suffices amply to precipitate 0·1 gm. $P^2O^5$, and it should be accompanied by a quantity of ammonic nitrate in clear solution equal to about 15 per cent. of the total weight of liquid. If heated to 80° or 90° C., the precipitation is complete in one hour. Instead of as formerly washing the precipitate with equal parts of molybdic solution and water, a 10 per-cent. solution of ammonic nitrate is used.

The precipitate of yellow phospho-molybdate is dissolved in 2½ per-cent. ammonia solution through the filter, taking care that every trace is removed from its folds, and then the usual magnesia mixture added "dropwise" with gentle stirring in the proportion of not less than 15 c.c. for every 0·1 gm. $P^2O^5$. Two hours amply suffice for this precipitate to separate; it is then filtered and washed with 2½ per-cent. $NH^3$ till clean, when it may be either ignited as $Mg^2P^2O^7$, or titrated with uranium.

**Magnesia Mixture.**—55 gm. of crystallized magnesic chloride and 70 gm. of ammonic chloride are dissolved to a liter with $2\frac{1}{2}$ per cent. ammonic hydrate. 10 c.c. is sufficient to precipitate 0·1 gm. $P^2O^5$, but it is safer to use 15 c.c. as before recommended.

The literature connected with the determination of phosphoric acid is very voluminous, and many competent chemists have contributed thereto in various scientific journals and standard works, which have been consulted and freely used in the compilation of this section.[*]

### 2. Precipitation as Uranic Phosphate in Acetic Acid Solution.

This method is based on the fact that when uranic acetate or nitrate is added to a neutral solution of tribasic phosphoric acid, such, for instance, as sodic orthophosphate, the whole of the phosphoric acid is thrown down as yellow uranic phosphate $2(Ur^2O^3), P^2O^5 + Aq$. Should the solution, however, contain free mineral acid, it must be neutralized with an alkali, and an alkaline acetate added, together with excess of free acetic acid. In case of using ammonia and ammonic acetate, the whole of the phosphoric acid is thrown down as double phosphate of uranium and ammonia, having a light lemon colour, and the composition $2(Ur^2O^3), 2(NH^4O), P^2O^5 + Aq$. When this precipitate is washed with hot water, dried and burned, the ammonia is entirely dissipated, leaving uranic phosphate, which possesses the formula $2(Ur^2O^3) P^2O^5$, and contains in 100 parts 80·09 uranic oxide and 19·91 phosphoric acid. In the presence of fixed alkalies, instead of ammonia, the precipitate consists simply of uranic phosphate. By this method phosphoric acid may be completely removed from all the alkalies and alkaline earths; also, with a slight modification, from iron; not, however, satisfactorily from alumina when present in any quantity.

The details of the gravimetric process were fully described by me (*C. N.* i. 97—122), and immediately after the publication of that article, while employed in further investigation of the subject, I devised the volumetric method now to be described. Since that time it has come to my knowledge that Neubauer[†] and Pincus[‡]

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[*] Fresenius, *Quant. Chem. Analyse*, 6te Aufl. 411.
Abesser, Jani u. Märcker, *Z. a. C.* xii. 239.
Schumann, *ibid.* xi. 382; Janovsky, *ibid.* xi. 153.
Gilbert, *ibid.* xii. 1; Rümpler, *ibid.* xii. 151.
Fresenius, Neubauer, and Luck, *ibid.* ix. 16.
Mohr, *Titrirbuch*, 4te Aufl. 520.
Neubauer, *Anal. des Harns*, 6te Aufl.
Joulie, *Moniteur Scientifique*, 1872—3, et *Annuaire de la Pharmacie*, rédigé par Dr. C. Mehu, 1875, 465, etc., etc. Joulie, *Ann. Agronom.* xi. 97—129.

[†] *Archiv. für wissenschäftliche Heilkunde*, iv. 228.

[‡] *Journal für Prakt. Chem.* lxxvi. 104.

had independently of each other and myself arrived at the same process. This is not to be wondered at, if it be considered how easy the step is from the ordinary determination by weight to that of measure, when the delicate reaction between uranium and potassic ferrocyanide is known. Moreover, the great want of a really good volumetric process for phosphoric acid in place of those hitherto used has been felt by all who have anything to do with it, and consequently the most would be made of any new method possessing so great a claim to accuracy as the gravimetric estimation of phosphoric acid by uranium undoubtedly does.

**Conditions under which accuracy may be insured.**—Objections have been urged, not without reason, that this process is inaccurate, because varying amounts of saline substances have an influence upon the production of colour with the indicator. Again, that very different shades of colour occur with lapse of time. This is all true, and the analysis is unfortunately one of that class which requires uniform conditions; but when the source of irregularity is known, it is not difficult to obviate them. Therefore it is absolutely essential that the standardizing of the uranium solution should be done under the same conditions as the analysis. For instance, a different volume of uranium will be required to give the colour in the presence of salts of ammonia to that which would be necessary with salts of the fixed alkalies or alkaline earths. But if the standard solution is purposely adjusted with ammonia salts in about the same proportion, the difficulties all vanish. Fortunately this can be easily done, and as the chief substances requiring analysis are more or less ammoniacal in their composition, such as urine, manures, etc., no practical difficulty need occur.

Excessive quantities of alkaline or earthy salts modify the colour, but especially is it so with acetate or citrate of ammonia. For this reason I have insisted on the complete washing of the citro-magnesian precipitate, where that method of separating $P^2O^5$ is adopted previous to titration.

### 3. Estimation of Phosphoric Acid in combination with Alkaline Bases, or in presence of small quantities of Alkaline Earths.

The necessary materials are—

(*a*) *A standard solution of uranium*, 1 c.c. $=0{\cdot}005$ gm. $P^2O^5$.

(*b*) *A standard solution of tribasic phosphoric acid.*

(*c*) *A solution of sodic acetate in dilute acetic acid*, made by dissolving 100 gm. of sodic acetate in water, adding 50 c.c. of glacial acetic acid, and diluting to 1 liter. Exact quantities are not necessary.

(*d*) A freshly prepared solution of potassic ferrocyanide, or some finely powdered pure crystals of the same salt.

*Standard Solution of Uranium.*—This solution may consist either of uranic nitrate or acetate. An approximate solution is obtained by using about 35 gm. of either salt to the liter. In the case of using uranic nitrate it is imperative that the sodic acetate should accompany the titration in order to avoid the possible occurrence of free nitric acid in the solution. With acetate, however, it may be omitted at the discretion of the operator, but it is important that the method used in standardizing the uranium be invariably adhered to in the actual analysis. The solution should be perfectly clear and free from basic salt. Whether made from acetate or nitrate, it is advisable to include about 25 c.c. of pure glacial acetic, or a corresponding quantity of weaker acid to each liter of solution; exposure to light has then less reducing action.

My own practice is to use in all cases acetate solution, and dispense entirely with the addition of sodic acetate.

### 4. Titration of the Uranium Solution.

*Standard Phosphoric Acid.*—When the uranium solution is not required for phosphate of lime, it may be titrated upon ammonio-sodic phosphate (microcosmic salt) as follows:—5·886 gm. of the crystallized, non-effloresced salt (previously powdered and pressed between bibulous paper to remove any adhering moisture) are weighed, dissolved in water, and diluted to 1 liter. 50 c.c. of this solution will represent 0·1 gm. $P^2O^5$.

50 c.c. of this solution are measured into a small beaker, 5 c.c. sodic acetate solution added if uranic nitrate is to be used, and the mixture heated to 90° or 100° C. The uranium solution is then delivered in from a burette, divided into $\frac{1}{10}$ c.c., until a test taken shall show the slight predominance of uranium. This is done by spreading a drop or two of the hot mixture upon a clean white level plate, and bringing in contact with the middle of the drop a small glass rod moistened with the freshly made solution of ferrocyanide, or a dust of the powdered salt. The occurrence of a faint brown tinge shows an excess of uranium, the slightest amount of which produces a brown precipitate of uranic ferrocyanide.

A second or third titration is then made in the same way, so as to arrive exactly at the strength of the uranium solution, which is then diluted and re-titrated, until exactly 20 c.c. are required to produce the necessary reaction with 50 c.c. of phosphate.

Suppose 18·7 c.c. of the uranium solution have been required to produce the colour with 50 c.c. of phosphate solution, then every 18·7 c.c. will have to be diluted to 20 c.c. in order to be of the proper strength, or 935 to 1000. After dilution, two or three fresh trials must be made to insure accuracy.

It is of considerable importance that the actual experiment for estimating phosphoric acid by means of the uranium solution should take place with about the same bulk of fluid that has been used in standardizing the solution, and with as nearly as possible the same relative amount of sodic acetate, and the production of the same depth of colour in testing. Hence the proportions here recommended have been chosen, so that 50 c.c. of liquid shall contain 0·1 gm. $P^2O^5$.

*Standard Phosphoric Acid corresponding volume for volume with Standard Uranium.*—This solution is obtained by dissolving 14·715 gm. of microcosmic salt in a liter, and is two and a half times the strength of the solution before described ; it is used for residual titration in case the required volume of uranium is overstepped in any given analysis.

A little practice enables the operator to tell very quickly the precise point, but it must be remembered that when the two drops are brought together for the production of the chocolate colour, however faint it seems at first, if left for some little time the colour increases considerably, owing to the retarding action of the sodic acetate and acetic acid upon the formation of uranic ferrocyanide, but this has no effect upon the accuracy of the process, since the original standard of the solution has been based on an experiment conducted in precisely the same way.

*The Analysis :* In estimating unknown qualities of $P^2O^5$, it is necessary to have an approximate knowledge of the amount in any given material, so as to fulfil as nearly as possible the conditions laid down above ; that is to say, 50 c.c. of solution shall contain about 0·1 gm. $P^2O^5$, or whatever other proportion may have been used in standardizing the uranium.

The compound containing the $P^2O^5$ to be estimated is dissolved in water; if no ammonia is present, 1 c.c. of 10 per-cent. solution is dropped in and neutralized with the least possible quantity of acetic acid (also 5 c.c. of sodic acetate if uranic nitrate has to be used), and the volume made up to about 50 c.c., then heated to about 90° C. on the water bath, and the uranium solution delivered in cautiously, with frequent testing as above described, until the faint brown tinge appears.

The first trial will give roughly the amount of solution required, and taking that as a guide, the operator can vary the amount of liquid and sodic acetate for the final titration, should the proportions be found widely differing from those under which the strength of the uranium was originally fixed.

Each c.c. of uranium solution = 0·005 gm. $P^2O^5$.

### 5. Estimation of Phosphoric Acid in combination with Lime and Magnesia (Bones, Bone Ash, Soluble Phosphates, and other Phosphatic Materials, free from Iron and Alumina).

The procedure in these cases differs from the foregoing in two respects only ; that is to say, the uranium solution is preferably standardized by tribasic calcic phosphate ; and in the process of titration it is necessary to add nearly the full amount of uranium required before heating the mixture, so as to prevent the precipitation of calcic phosphate, which is apt to occur in acetic acid solution when heated ; or the modification adopted by Fresenius, Neubauer, and Luck, may be used, which consists in reversing the process by taking a measured volume of uranium, and delivering into it the solution of phosphate until a drop of the mixture ceases to give a brown colour with ferrocyanide. This plan gives, however, much more trouble, and possesses no advantage on the score of accuracy, because in any case at least two titrations must occur, and the first being made somewhat roughly, in the ordinary way, shows within 1 or 2 c.c. the volume of standard uranium required; and in the final trial it is only necessary to add at once nearly the quantity, then heat the mixture, and finish the titration by adding a drop or two of uranium at a time until the required colour is obtained.

This reversed process is strongly advocated by many operators, but except in rare instances I fail to see its superiority to the direct method for general use. The best modification to adopt in the reverse process is to use invariably an excess of uranium, and to titrate back with standard phosphate solution till the colour disappears; this avoids all the trouble of preparing and cleaning a burette for the solution to be analyzed, and if a standard phosphate is made to correspond volume for volume with the uranium, an analysis may always be brought into order at any stage.

*Standard Calcic Phosphate.*—It is not safe to depend upon the usual preparations of tricalcic phosphate by weighing any given quantity direct, owing to uncertainty as to the state in which the phosphoric acid may exist; therefore, in order to titrate the uranium solution with calcic phosphate, it is only necessary to take rather more than 5 gm. of precipitated pure tricalcic phosphate such as occurs in commerce, dissolve it in a slight excess of dilute hydrochloric acid, precipitate again with a slight excess of ammonia, re-dissolve in a moderate excess of acetic acid, then dilute to a liter; by this means is obtained a solution of acid monocalcic phosphate, existing under the same conditions as occur in the actual analysis. In order to ascertain the exact amount of tribasic phosphoric acid present in a given measure of this solution, two portions of 50 c.c. each are placed in two beakers, each holding about half a liter. A slight excess of solution of uranic acetate or nitrate is then added to each, together with about 10 c.c. of the acetic solution of sodic acetate, heated to actual boiling on a hot plate or sand-bath, and the beakers filled up with boiling distilled water, then set aside to settle, which occurs very speedily. The supernatant fluid should be faintly yellow from excess of uranium. When perfectly settled, the clear liquid is withdrawn by a syphon or poured off as closely as possible without disturbing the precipitate, and the beakers again filled up with boiling water. The same should be done a third time, when the precipitates may be brought on two filters, and need very little further washing.

When the filtration is complete, the filters are dried and ignited separate from the precipitate, taking care to burn off all carbon. Before being weighed, however, the uranic-phosphate must be moistened with strong nitric acid, dried perfectly in the water bath or oven, and again ignited; at first, very gently, then strongly, so as to leave a residue when cold of a pure light lemon colour; this is uranic phosphate $2(Ur^2O^3), P^2O^5$, the percentage composition of which is 80·09 of uranic oxide, and 19·91 of phosphoric acid.

The two precipitates are accurately weighed, and should agree to within a trifle. If they differ, the mean is taken to represent the amount of $P^2O^5$ in the given quantity of tricalcic phosphate, from which may be calculated the strength of the solution to be used as a standard. Of course any other accurate method of determining the $P^2O^5$ may be used in place of this.

The actual standard required is 5 gm. of pure tricalcic phosphate per liter; and it should be adjusted to this strength by dilution, after the actual strength has been found. In this way is obtained a standard which agrees exactly with the analysis of a superphosphate or other similar manure.

*Standard Uranium Solution.*—This is best adjusted to such strength that 25 c.c. are required to give the faint chocolate colour with ferrocyanide, when 50 c.c. of the standard acetic solution of calcic phosphate are taken for titration. Working in this manner each c.c. of uranium solution represents 1 per cent. of soluble tricalcic phosphate, when 1 gm. of manure is taken for analysis, because 50 c.c. of the calcic phosphate will contain monocalcic phosphate equal to 0·25 gm. of $Ca^3P^2O^8$ and will require 25 c.c. of uranium solution to balance it.

These standards are given as convenient for manures, but they may be modified to suit any particular purpose.

*The Analysis in case of Superphosphate free from Fe and Al, except in mere traces:*—10 gm. of the substance is weighed, placed in a small glass mortar and gently broken down by the pestle, cold water being used to bring it to a smooth cream. The material should not be ground or rubbed hard, which might cause the solution of some insoluble phosphate in the concentrated mixture. The creamy substance is washed gradually without loss into a measuring flask marked at 503·5 c.c., the 3·5 c.c. being the space occupied by the insoluble matters in an ordinary 25 to 30 per cent. superphosphate. The flask is filled to the mark with cold water, and shaken every few minutes during about half-an-hour. A portion is then filtered through a dry filter into a dry beaker, and 50 c.c.=1 gm. of manure measured into a beaker holding about 100 c.c. Sufficient 10 per cent. ammonia is then added to precipitate the monocalcic phosphate in the form of $Ca^3P^2O^8$ (in all ordinary superphosphates there is enough Ca present as sulphate to ensure this, and four or five drops of ammonia generally suffices to effect the precipitation). Acetic acid is then added in just sufficient quantity to render the liquid clear. Should traces of gelatinous $AlPO^4$ or $FePO^4$ occur at this stage, the liquid will be slightly opalescent; but this may be disregarded if only slight, as the subsequent heating will enable the uranium to decompose it. If more than traces occur, the method will not be accurate, and recourse must be had to separation by the citro-magnesic solution.

While the liquid is still cold, a measured volume of the standard uranium is run in with stirring, and occasional drops are taken out with a glass rod, put in contact with some ferrocyanide indicator sprinkled on a white plate until a faint colour occurs. The beaker is then placed in the water-bath for a few minutes, and again the mixture tested with the indicator: after heating in this way the testing ought to show no colour. More uranium is then added with stirring, and drop by drop till the proper reaction occurs. This titration is only a guide for a second, which may be made more accurate by running in at once very nearly the requisite volume of uranium.

This operation may be reversed, if so desired, by making the clear solution of phosphate up to a definite volume (say 60 c.c.), and running it into a measured volume of uranium until a test taken shows no colour.

### 6. Estimation of Phosphoric Acid in Minerals or other substances containing Iron, Alumina, or other disturbing matters.

In order to make use of any volumetric process for this purpose, the phosphoric acid must be separated. As has been already described, this may be done either by the molybdic precipitation followed by solution in $NH^3$, again precipitated with ordinary magnesia mixture, or direct separation by citro-magnesia mixture. In either case the ammonio-magnesic salt is dissolved in the least possible quantity of nitric or hydrochloric acid, neutralized with ammonia, acidified with acetic acid, and the titration with uranium carried out as before described.

### 7. Joulie's Method.

This differs somewhat from the foregoing, and may be summarized as follows (Munro, *C. N.* lii. 85).

Joulie applies the citro-magnesia method to all phosphates, whether containing iron and alumina or not, and prefers nitrate to acetate of uranium.

1 to 10 gm. of the sample are dissolved in HCl. Some chemists use nitric acid with a view of leaving as much ferric oxide as possible undissolved. This course is condemned by the author, because the presence of ferric salts in no way interferes with the process, and because HCl is a much better solvent of mineral phosphates than nitric acid, and leaves a residue free from iron, by the whiteness of which one may judge of the completeness of the attack. In the case of phosphates containing a little pyrites, nitric acid should be used in conjunction with hydrochloric. The removal of silica by evaporation to dryness is necessary only in those cases where the sample contains silicates decomposable by HCl, with separation of gelatinous silica. The sample is boiled with the acid in a measuring flask until the residue is perfectly white, the contents are cooled, made up to the mark with cold water, mixed, filtered through a dry filter, and such a fraction of the filtrate withdrawn by a pipette as contains about 50 m.gm. of $P^2O^5$. The sample being delivered from the pipette into a small beaker, 10 c.c. of citro-magnesia solution are added, and then a large excess of ammonia. If this quantity of citro-magnesia liquor is sufficient, no precipitate will form until the lapse of a few moments; should an *immediate* precipitate form, it is iron or aluminium phosphate. In this case a fresh sample must be pipetted off, and 20 c.c. citro-magnesia liquor added; it is of no use adding another 10 c.c. of the citric solution to the original sample, as the precipitated phosphates of iron and aluminium do not readily redissolve when once formed. The citro-magnesia liquor is the same as described on p. 239. The old plan of adding first citric acid and then "magnesia mixture" to the solution under analysis frequently leads to incomplete precipitation of the phosphoric acid, because

the ammonio-magnesic phosphate is slightly soluble in ammonic citrate unless a sufficient excess of magnesium salt is present, and therefore the quantity of magnesium salt should be increased *pari passu* with the citric acid required, which is best done when they are in solution together. The liquid after precipitation is allowed to stand from 2 to 12 hours (covered to prevent evaporation of ammonia), and then decanted through a small filter. The precipitate remaining in the beaker is washed with weak ammonia by decantation, and then on the filter until the filtrate gives no precipitate with sodic phosphate. Dilute nitric acid is next poured into the beaker to dissolve the precipitate adhering to the glass, thence on to the precipitate on the filter. The nitric solution is received in a beaker holding about 150 c.c. and marked at 77 c.c. After two or three washings with acidulated water the filter itself is detached from the funnel and added to the contents of the beaker, as the paper is found to retain traces of $P^2O^5$ even after many washings. Dilute ammonia is next added until a slight turbidity is produced, which is removed by the addition of one or two drops nitric acid, the liquid is heated to boiling, 5 c.c. of the sodium acetate solution added (page 242, 3*c*.) and the titration with uranium nitrate immediately proceeded with.

*The Standard Uranic Nitrate* is made by dissolving about 40 gm. of the pure crystals in 800 c.c. water, adding a few drops of ammonia to produce a slight turbidity, then acetic acid until cleared, and diluting to 1 liter. Acetate of uranium should not be used, as it impairs the sensibility of the end-reaction. The uranium solution is titrated with 10 c.c. of a standard solution of acid ammonium phosphate containing 8·10 gm. of the pure dry salt per liter (1 c.c. = 0·005 gm. $P^2O^5$). The ammonium phosphate solution is verified by evaporating a measured quantity (say 50 c.c.) of it to dryness with a measured quantity of a solution of pure ferric nitrate containing an excess of ferric oxide, and calcining the residue. The difference in weight between this calcined residue and that from an equal volume of ferric nitrate solution evaporated alone, is the weight of phosphoric anhydride contained in the 50 c.c. of ammonium phosphate solution. The actual verification of the uranic nitrate is performed by measuring accurately 10 c.c. of the ammonium phosphate into a beaker marked at 75 c.c., adding 5 c.c. of the sodium acetate, making up with water to about 30 c.c., and heating to boiling. 9 c.c. uranium are then run in from a burette, and the liquid tested in the usual way with ferrocyanide. From this point the uranium is added two or three drops at a time, until the end-reaction just appears, the burette being read off at each testing. As soon as the faintest colouration appears, the beaker is immediately filled to the mark with boiling distilled water, and another test made. If the operation has been properly conducted no brown colour will be detected, owing to the dilution of the liquid, and one or two drops more of the uranium solution must be added before the colour becomes evident, and the burette is finally read off. A constant *correction* is subtracted from all readings obtained in this way: it is the quantity of uranium found necessary to give the end-reaction with 5 c.c. of the sodium acetate solution alone, diluted to 75 c.c. with boiling water as above described. The end-point must always be verified by adding three or four drops of uranium in excess, and testing again, when a strongly marked colour should be produced. The standard uranium is made of the same strength as the standard ammonium phosphate, in order to eliminate the error caused by changes in the temperature of the laboratory. The actual analysis is made in the same way as the titration of the standard uranium, except that a slight error is introduced by the number of tests that have to be made abstracting a small fraction of the assay. To correct this, a second estimation should always be made, and nearly the whole of the uranium found necessary in the first trial should be added at once. Tests are then made at intervals of two or three drops, and the final and correct result should slightly exceed that obtained in the first trial.

### 8. Stolba's Alkalimetric Method.

This process has given me very good results in the analysis of superphosphates containing iron and alumina, even if the quantity of these substances is very considerable, such as mostly occurs when the total $P^2O^5$ has to be estimated in a given manure, and where the hydrochloric acid solution has necessarily extracted all the iron or alumina present in the substance.

*The Analysis :* The clear aqueous solution of 1 gm. of a superphosphate, or the acid solution of the soluble and insoluble phosphates, is placed into a beaker holding about 150 c.c., and from 30 to 50 c.c. of citro-magnesia solution added according to the proportion of $P^2O^5$. A good excess of strong ammonia is added, and vigorously stirred, regardless of rubbing the sides of the beaker. If the stirring is done at intervals of a few minutes, it is possible to separate the whole of the $P^2O^5$ in half an hour, but for safety the mixture may be left at rest for another half-hour; then the liquid filtered through a porous filter, washing the main precipitate and the filter with alcohol or methylated spirit of 50 per cent. until all free ammonia is removed. The stirring rod and sides of the beaker will be covered with crystals, which need not be detached, but must be carefully washed with the dilute alcohol; and finally, the main precipitate may be transferred to the filter to drain; but before this is done, the first strong ammoniacal filtrate should be removed from beneath the funnel, so that no volatile ammonia may contaminate the precipitate or filter. In fact, all care must be taken to remove ammonia, except that which is chemically combined with the magnesia and the phosphoric acid; this being done, the original beaker and stirring rod are placed under the funnel, and a measured excess of $\frac{N}{10}$ sulphuric, nitric, or hydrochloric acid is poured over the filter and precipitate in repeated small quantities until the double phosphate is completely dissolved. Finally, the whole is washed with repeated portions of hot water, so that all the salt is extracted from the folds of the filter, and a perfectly clear solution of all the crystals from the rod and sides of the beaker is obtained.

The titration is made by cooling the liquid to ordinary temperature, and adding a drop or two of methyl orange or rosolic acid, then titrating residually with $\frac{N}{10}$ ammonia or other alkali.

The volume of $\frac{N}{10}$ acid neutralized by the alkaline double phosphate, when multiplied by 0·00355, will give the weight of $P^2O^5$, or by 0·00775, the weight of $Ca3P^2O^8$ in the 1 gm. of material used.

The process is one of delicacy, and cannot be used except by experienced manipulators.

### 9. Pemberton's Molybdic Method.

This process, with all the steps that led to its adoption, and the difficulties involved, is described in a paper read before the chemical section of the Franklin Institute in 1882 (*C. N.* xlvi. 4).

The process is based on the fact that, if a standard aqueous solution of ammonic molybdate be added to one of phosphoric acid, in the presence of a large proportion of ammonic nitrate, accompanied with a small excess of nitric acid, and heat applied to the mixture, the whole of the $P^2O^5$ is immediately and completely carried down as phospho-molybdate quite free from $MoO^3$. A small excess of the precipitant renders the supernatant liquid clear and colourless, and the ratio of molybdic trioxide to phosphoric anhydride is always the same.

The weak part of the method is the difficulty in finding the exact point at which the precipitation is ended, because the yellow precipitate does not settle in a clotty form like silver chloride, and hence filtration is necessary, in order to obtain a portion of clear liquid for testing with a drop of the molybdate. Very good results may be obtained with some little patience and practice by using the Beale filter (fig. 16). When the precipitation is thought to be nearly complete, the filter is dipped into the hot liquid, so as to obtain 2 c.c. or so in a clear condition: this is transferred to a clean test tube or small short beaker, and a drop or two of the precipitant added, then heated in the bath to see if a yellow colour occurs; if it does, the filter and beaker are washed again into the bulk with hot water in very small quantities from a small wash bottle. A second titration ought to result in a very near approximation, and a third will be exact. A convenient small suction asbestos filter is figured and described by Professor Caldwell as well adapted to this process (*C. N.* xlviii. 61). As each titration can be made in a very short time, and iron or alumina may be totally disregarded in moderate quantity, the process may be made valuable for technical purposes.

It is, however, imperative here, as it is in the usual molybdic process, to avoid the presence of soluble silica, organic matter, and organic acids. Chlorides in moderate quantity do not interfere.

The necessary solutions and reagents are—

*Standard Ammonic Molybdate.* 89·543 gm. of the crystallized salt are dissolved in about 900 c.c. of water; if not quite clear, a very few drops of ammonia may be added to ensure perfect solution; the flask is then filled to the liter mark. The weight of salt used is based on the proportion of 24 $MoO^3$ to 1 of $P^2O^5$, and each c.c. precipitates 3 m.gm. $P^2O^5$. If any doubt exists as to the purity of the molybdate, the solution should be standardized with a solution of $P^2O^5$ of known strength. In any case this is to be recommended.

*Ammonic Nitrate* in granular form and neutral.

*Nitric Acid*, sp. gr. not less than 1·4; or if of less strength, a proportionate increase must be used in the titration.

*The Analysis:* The phosphate to be titrated is taken in quantity containing not over 0·1 gm. $P^2O^5$ or 0·15 gm. at the utmost. If silica is present, the solution is evaporated to dryness. In presence of organic matter ignite gently and evaporate to dryness twice with $HNO^3$. There is no advantage in filtering off the $SiO^2$. The solution is transferred to a beaker of 100 to 125 c.c., using as little water as possible to prevent unnecessary dilution, and is just neutralized with $NH^4HO$, *i.e.*, until a slight precipitate is formed.

If much iron is present the ammonia is added until the yellow colour *begins* to change to a darker shade. 2 c.c. of nitric acid are added. Care must be taken that the sp. gr. of the acid is not less than 1·4, otherwise more must be added. 10 gm. of granular nitrate of ammonia are now added. After a little experience the quantity can be judged with sufficient accuracy by the eye without the trouble of weighing. The solution is now heated to 140° F. or over and the molybdate solution run in (most conveniently from a Gay Lussac burette), meanwhile stirring the liquid. The beaker is now left undisturbed for about a minute on the water-bath or hot plate until the precipitate settles, leaving the supernatant liquid not clear but containing widely disseminated particles, in which the yellow cloud can easily be seen on the further addition of the molybdate. This addition is continued as long as the precipitate is thick and of a deep colour. But as soon as it becomes rather faint and thin, a little of the solution, about 2 to 3 c.c., after settling of the precipitate, is filtered into a very small beaker, and this is heated on a hot plate and 4 or 5 drops of the molybdate added. If a precipitate is produced, the whole is poured back into the large beaker, and a further addition of the molybdate (1, 2, or 3 c.c.) added, according to the quantity of the precipitate in the small beaker. After stirring and settling, another small quantity is filtered and again tested. If the mark has been overstepped and too much molybdate added, a measured quantity of $P^2O^5$ solution of known strength is added, and the corresponding amount of $P^2O^5$ deducted. The results may be checked by adding 1 c.c. of standard $P^2O^5$ solution, and then again testing. This can be repeated as often as desired. The portion that finally produces a cloud is the end-point; from this is deducted 0·5 c.c. (for neutralizing the solvent action of the nitric acid), the remainder multiplied by 3 gives the weight of $P^2O^5$ in milligrams. 0·1 gm. of $P^2O^5$ gives about 2·75 gm. of the yellow precipitate, and the accuracy of the method is largely due to the low percentage of $P^2O^5$.

## SILVER.

Ag=107·66.

1 c.c. or 1 dm. $\frac{N}{10}$ sodic chloride=0·010766 gm. or 0·10766 grn. Silver; also 0·016966 gm. or 0·16966 grn. Silver nitrate.

### 1. Precipitation with $\frac{N}{10}$ Sodic Chloride.

§ 70. The determination of silver is precisely the converse of the operations described under chlorine (§ 37, 1 and 2), and the process may either be concluded by adding the sodic chloride till no further precipitate is produced, or potassic chromate may be used as an indicator. In the latter case, however, it is advisable to add the salt solution in excess, then a drop or two of chromate, and titrate residually with $\frac{N}{10}$ silver, till the red colour is produced, for the excess of sodic chloride.

### 2. By Ammonic Sulphocyanate (Thiocyanate).

The principle of this method is fully described in § 39, and need not further be alluded to here. The author of the method

(Volhard) states, that comparative tests made by this method and that of Gay Lussac gave equally exact results, both being controlled by cupellation, but claims for this process that the end of the reaction is more easily distinguished, and that there is no labour of shaking, or danger of decomposition by light, as in the case of chloride.

### 3. Estimation of Silver, in Ores and Alloys, by Starch Iodide (Method of Pisani and F. Field).

If a solution of blue-starch-iodide be added to a neutral solution of silver nitrate, while any of the latter is in excess the blue colour disappears, the iodine entering into combination with the silver; as soon as all the silver is thus saturated, the blue colour remains permanent, and marks the end of the process. The reaction is very delicate, and the process is more especially applicable to the analysis of ores and alloys of silver containing lead and copper, but not mercury, tin, iron, manganese, antimony, arsenic, or gold in solution.

The solution of starch iodide, devised by Pisani, is made by rubbing together in a mortar 2 gm. of iodine with 15 gm. of starch and about 6 or 8 drops of water, putting the moist mixture into a stoppered flask, and digesting in a water bath for about an hour, or until it has assumed a dark bluish-grey colour; water is then added till all is dissolved. The strength of the solution is then ascertained by titrating it with 10 c.c. of a solution of silver containing 1 gm. in the liter, to which a portion of pure precipitate calcic carbonate is added; the addition of this latter removes all excess of acid, and at the same time enables the operator to distinguish the end of the reaction more accurately. The starch iodide solution should be of such a strength that about 50 c.c. are required for 10 c.c. of the silver solution (=0·01 gm. silver).

F. Field (*C. N.* ii. 17), who discovered the principle of this method simultaneously with Pisani, uses a solution of iodine in potassic iodide with starch. Those who desire to make use of this plan can use the $\frac{N}{10}$ and $\frac{N}{100}$ solutions of iodine described in § 34.

In the analysis of silver containing copper, the solution must be considerably diluted in order to weaken the colour of the copper; a small measured portion is then taken, calcic carbonate added, and starch iodide till the colour is permanent. It is best to operate with about from 60 to 100 c.c., containing not more than 0·02 gm. silver; when the quantity is much greater than this, it is preferable to precipitate the greater portion with $\frac{N}{10}$ sodic chloride, and to complete with starch iodide after filtering off the chloride. When lead is present with silver in the nitric acid solution, add sulphuric acid, and filter off the lead sulphate, then add calcic carbonate to neutralize excess of acid, filter again if necessary, then add fresh carbonate and titrate as above.

### 4. Assay of Commercial Silver (Plate, Bullion, Coin, etc.). Gay Lussac's Method modified by J. G. Mulder.

For more than thirty years Gay Lussac's method of estimating silver in its alloys has been practised intact, at all the European mints, under the name of the "humid method," in place of the old system of cupellation. During that time it has been regarded as one of the most exact methods of quantitative analysis. The researches of Mulder, however, into the innermost details of the process have shown that it is capable of even greater accuracy than has hitherto been gained by it.

The principle of the process is the same as described in § 37, depending on the affinity which chlorine has for silver in preference to all other substances, and resulting in the formation of chloride of silver, a compound insoluble in dilute acids, and which readily separates itself from the liquid in which it is suspended.

The plan originally devised by the illustrious inventor of the process for assaying silver, and which is still followed, is to consider the weight of alloy taken for examination to consist of 1000 parts, and the question is to find how many of these parts are pure silver. This empirical system was arranged for the convenience of commerce, and being now thoroughly established, it is the best plan of procedure. If, therefore, a standard solution of salt be made of such strength that 100 c.c. will exactly precipitate 1 gm. of silver, it is manifest that each $\frac{1}{10}$ c.c. will precipitate 1 m.gm. or $\frac{1}{1000}$ part of the gram taken; and consequently in the analysis of 1 gm. of any alloy containing silver, the number of $\frac{1}{10}$ c.c. required to precipitate all the silver out of it would be the number of thousandths of pure silver contained in the specimen.

In practice, however, it would not do to follow this plan precisely, inasmuch as neither the measurement of the standard solution nor the ending of the process would be gained in the most exact manner; consequently, a decimal solution of salt, one-tenth the strength of the standard solution, is prepared, so that 1000 c.c. will exactly precipitate 1 gm. of silver, and, therefore, 1 c.c. 1 m.gm.

The silver alloy to be examined (the composition of which must be approximately known) is weighed so that about 1 gm. of pure silver is present; it is then dissolved in pure nitric acid by the aid of a gentle heat, and 100 c.c. of standard solution of salt added from a pipette in order to precipitate exactly 1 gm. of silver; the bottle containing the mixture is then well shaken until the chloride of silver has curdled, leaving the liquid clear.

The question is now: Which is in excess, salt or silver? A drop of decimal salt solution is added, and if a precipitate be produced 1 c.c. is delivered in, and after clearing, another, and so on as long as a precipitate is produced. If on the other hand the one drop of salt produced no precipitate, showing that the pure silver present was less than 1 gm., a decimal solution of silver is used, prepared by dissolving 1 gm. pure silver in pure nitric acid and diluting to 1 liter. This solution is added after the same manner as the salt solution just described, until no further precipitate occurs; in either case the quantity of decimal solution used is noted, and the results calculated in thousandths for 1 gm. of the alloy.

The process thus shortly described is that originally devised by Gay Lussac, and it was taken for granted that when equivalent chemical proportions of silver and sodic chloride were brought thus in contact, that every trace of the metal was precipitated from the solution, leaving sodic nitrate and free nitric acid only in solution. The researches of Mulder, however, go to prove that this is not strictly the case, but that when the most exact chemical proportions of silver and salt are made to react on each other, and the chloride has subsided, a few drops more of either salt or silver solution will produce a further precipitate, indicating the presence of both silver nitrate and sodic chloride in a state of equilibrium, which is upset on the addition of either salt or silver. Mulder decides, and no doubt rightly, that this peculiarity is owing to the presence of sodic nitrate, and varies somewhat with the temperature and state of dilution of the liquid.

It therefore follows that when a silver solution is carefully precipitated, first by concentrated and then by dilute salt solution, until no further precipitate appears, the clear liquid will at this point give a precipitate with dilute silver solution; and if it be added till no further cloudiness is produced, it will again be precipitable by dilute salt solution.

*Example:* Suppose that in a given silver analysis the decimal salt solution has been added so long as a precipitate is produced, and that 1 c.c. (=20 drops of Mulder's dropping apparatus) of decimal silver is in turn required to precipitate the apparent excess, it would be found that when this had been done, 1 c.c. more of salt solution would be wanted to reach the point at which no further cloudiness is produced by it, and so the changes might be rung time after time; if, however, instead of the last 1 c.c. (=20 drops) of salt, half the quantity be added, that is to say 10 drops (=½ c.c.), Mulder's so-called neutral point is reached; namely, that in which, if the liquid be divided in half, both salt and silver will produce the same amount of precipitate. At this stage the solution contains silver chloride dissolved in sodic nitrate, and the addition of either salt or silver expels it from solution.

A silver analysis may therefore be concluded in three ways—

(1) By adding decimal salt solution until it just ceases to produce a cloudiness.

(2) By adding a slight excess of salt, and then decimal silver till no more precipitate occurs.

(3) By finding the neutral point.

According to Mulder the latter is the only correct method, and preserves its accuracy at all temperatures up to 56° C. (=133° Fahr.), while the difference between 1 and 3 amounts to ½ a m.gm., and that between 1 and 2 to 1 m.gm. on 1 gm. of silver at 16° C. (=60° Fahr.), and is seriously increased by variation of temperature.

It will readily be seen that much more trouble and care is required by **Mulder's** method than by that of **Gay Lussac**, but, as a compensation, much greater accuracy is obtained.

On the whole, it appears to me preferable to weigh the alloy so that slightly more than 1 gm. of silver is present, and to choose the ending No. 1, adding drop by drop the decimal salt solution until just a trace of the precipitate is seen, and which, after some practice, is known by the operator to be final. It will be found that the quantity of salt solution used will slightly exceed that required by chemical computation; say 100·1 c.c. are found equal to 1 gm. of silver, the operator has only to calculate that quantity of the salt solution in question for every 1 gm. of silver he assays in the form of alloy, and the error produced by the solubility of silver chloride in sodic nitrate is removed.

If the decimal solution has been cautiously added, and the temperature not higher than 17° C. (=62° Fahr.), this method of conclusion is as reliable as No. 3, and free from the possible errors of experiment; for it requires a great expenditure of time and patience to reverse an assay two or three times, and each time cautiously adding the solutions, drop by drop, then shaking and waiting for the liquid to clear, besides the risk of discolouring the chloride of silver, which would at once vitiate the results.

The decimal silver solution, according to this arrangement, would seldom be required; if the salt has been incautiously added, or the quantity of alloy too little to contain 1 gm. pure silver, then it is best to add once for all 2, 3, or 5 c.c., according to circumstances, and finish with decimal salt as No. 1, deducting the silver added.

### The Standard Solutions and Apparatus.

(*a*) *Standard Salt Solution:* Pure sodic chloride is prepared by treating a concentrated solution of the whitest table-salt first with a solution of caustic baryta to remove sulphuric acid and magnesia, then with a slight excess of sodic carbonate to remove baryta and lime, warming and allowing the precipitates to subside, then evaporating to a small bulk that crystals may form; these are separated by a filter, and slightly washed with cold distilled water, dried, removed from the filter, and heated to dull redness, and when cold preserved in a well-closed bottle for use. The mother-liquor is thrown away, or used for other purposes. Of the salt so prepared, or of chemically pure rock-salt (Steinsalz, a substance to be obtained freely in Germany), 5·4145 gm. are to be weighed and dissolved in 1 liter of distilled water at 16° C. 100 c.c. of this solution will precipitate exactly 1 gm. of silver. It is preserved in a well-stoppered bottle, and shaken before use.

(*b*) *Decimal Salt Solution:* 100 c.c. of the above solution are diluted to exactly 1 liter with distilled water at 16° C. 1 c.c. will precipitate 0·001 gm. of silver.

(*c*) *Decimal Silver Solution:* Pure metallic silver is best prepared by galvanic action from pure chloride; and as clean and secure a method as any is to wrap a lump of clean zinc, into which a silver wire is melted, with a piece of wetted bladder or calico, so as to keep any particles of impurity contained in the zinc from the silver. The chloride is placed at the bottom of a porcelain dish, covered with dilute sulphuric acid, and the zinc laid in the middle; the silver wire is bent over so as to be immersed in the chloride. As soon as the acid begins to act upon the zinc the reduction commences in the chloride, and grows gradually all over the mass; the resulting finely-divided silver is well washed, first with dilute acid, then with hot water, till all acid and soluble zinc are removed.

The moist metal is then mixed with a little sodic carbonate, saltpetre, and borax, say about an eighth part of each, dried perfectly, then melted. Mulder recommends that the melting should be done in a porcelain crucible immersed in sand contained in a common earthen crucible; borax is sprinkled over the surface of the sand so that it may be somewhat vitrified, that in pouring out the silver when melted no particles of dirt or sand may fall into it. If the quantity of metal be small it may be melted in a porcelain crucible over a gas blowpipe.

The molten metal obtained in either case can be poured into cold water and so granulated, or upon a slab of pipe-clay, into which a glass plate has been pressed when soft so as to form a shallow mould. The metal is then washed well with boiling water to remove accidental surface impurities, and rolled into thin strips by a goldsmith's mill, in order that it may be readily cut for weighing. The granulated metal is, of course, ready for use at once without any rolling.

1 gm. of this silver is dissolved in pure dilute nitric acid, and diluted to 1 liter; each c.c. contains 0·001 gm. of silver. It should be kept from the light.

(*d*) *Dropping Apparatus for Concluding the Assay.*—Mulder constructs a special affair for this purpose, consisting of a pear-shaped vessel fixed in a stand, with special arrangements for preventing any continued flow of liquid. The delivery tube has an opening of such size that 20 drops measure exactly 1 c.c. The vessel itself is not graduated. As this arrangement is of more service to assay than to general laboratories, it need not be further described here. A small burette divided in $\frac{1}{10}$ c.c., with a convenient dropping tube, will answer every purpose, and possesses the further advantage of recording the actual volume of fluid delivered.

The 100-c.c. pipette, for delivering the concentrated salt solution, must be accurately graduated, and should deliver exactly 100 gm. of distilled water at 16° C.

The test bottles, holding about 200 c.c., should have their stoppers well ground and brought to a point, and should be fitted into japanned tin tubes reaching as high as the neck, so as to preserve the precipitated chloride from the action of light, and, when shaken, a piece of black cloth should be covered over the stopper.

(*e*) *Titration of the Standard Salt Solution.*—From what has been said previously as to the principle of this method, it will be seen that it is not possible to rely absolutely upon a standard solution of salt containing 5·4145 gm. per liter, although this is chemically correct in its strength. The real working power must be found by experiment. From 1·002 to 1·004 gm. of absolutely pure silver is weighed on the assay balance, put into a test bottle with about 5 c.c. of pure nitric acid, of about 1·2 sp. gr., and gently heated in the water or sand bath till it is all dissolved. The nitrous vapours are then blown from the bottle, and it is set aside to cool down to about 16° C. or 60° Fahr.

The 100 c.c. pipette, which should be securely fixed in a support, is then carefully filled with the salt solution, and delivered into the test bottle contained in its case, the moistened stopper inserted, covered over with the black velvet or cloth, and shaken continuously till the chloride has clotted, and the liquid becomes clear; the stopper is then slightly lifted, and its point touched against the neck of the bottle to remove excess of liquid, again inserted, and any particles of chloride washed down from the top of the bottle by carefully shaking the clear liquid over them. The bottle is then brought under the decimal salt burette, and $\frac{1}{2}$ c.c. added, the mixture shaken, cleared, another $\frac{1}{2}$ c.c. put in, and the bottle lifted partly out of its case to see if the precipitate is considerable; lastly, 2 or 3 drops only of the solution are added at a time until no further opacity is produced by the final drop. Suppose, for instance, that in titrating the salt solution it is found that 1·003 gm. of silver require 100 c.c. concentrated, and 4 c.c. decimal solution, altogether equal to 100·4 c.c. concentrated, then—

$$1{\cdot}003 \text{ silver} : 100{\cdot}4 \text{ salt} :: 1{\cdot}000 : x. \quad x = 100{\cdot}0999.$$

The result is within $\frac{1}{10000}$ of 100·1, which is near enough for the purpose, and may be more conveniently used. The operator therefore knows that 100·1 c.c. of the concentrated salt solution at 16° C. will exactly precipitate 1 gm. silver, and calculates accordingly in his examination of alloys.

In the assay of coin and plate of the English standard, namely, 11·1 silver and 0·9 copper, the weight corresponding to 1 gm. of silver is 1·081 gm, therefore in examining this alloy 1·085 gm. may be weighed.

When the quantity of silver is not approximately known, a preliminary analysis is necessary, which is best made by dissolving $\frac{1}{2}$ or 1 gm. of the alloy in nitric acid, and precipitating very carefully with the concentrated salt solution from a $\frac{1}{10}$ c.c. burette. Suppose that in this manner 1 gm. of alloy required 45 c.c. salt solution,

$$100{\cdot}1 \text{ salt} : 1{\cdot}000 \text{ silver} :: 45 : x. \quad x = 0{\cdot}4495.$$
$$\text{Again } 0{\cdot}4495 : 1 :: 1{\cdot}003 : x = 2{\cdot}231.$$

2·231 gm. of this particular alloy are therefore taken for the assay.

Where alloys of silver contain sulphur or gold, with small quantities of tin, lead, or antimony, they are first treated with a small quantity of nitric acid so long as red vapours are disengaged, then boiled with concentrated sulphuric acid till the gold has become compact, set aside to cool, diluted with water, and titrated as above.

### Assaying on the Grain System.

It will be readily seen that the process just described may quite as conveniently be arranged on the grain system by substituting 10 grains of silver as the unit in place of the gram; each decem of concentrated salt solution would then be equal to $\frac{1}{10}$ of a grain of silver, and each decem of decimal solution to $\frac{1}{100}$ of a grain.

### 5. Analysis of the Silver Solutions used in Photography.

The silver bath solutions for sensitizing collodion and paper frequently require examination, as their strength is constantly lessening. To save calculation, it is better to use an empirical solution of salt than the systematic one described above.

This is best prepared by dissolving 43 grains of pure sodic chloride in 10,000 grains of distilled water. Each decem (= 10 grn.) of this solution will precipitate 0·125 grn. (*i.e.* $\frac{1}{8}$ grn.) of pure silver nitrate; therefore, if one fluid drachm of any silver solution be taken for examination, the number of decems of salt solution required to precipitate all the silver will be the number of grains of silver nitrate in each ounce of the solution.

*Example:* One fluid drachm of an old nitrate bath was carefully measured into a stoppered bottle, 10 or 15 drops of pure nitric acid and a little distilled water added; the salt solution was then cautiously added, shaking well after each addition until no further precipitate was produced. The quantity required was 26·5 dm.=26½ grains of silver nitrate in each ounce of solution.

Crystals of silver nitrate may also be examined in the same way, by dissolving say 30 or 40 grn. in an ounce of water, taking one drachm of the fluid and titrating as above.

In consequence of the rapidity and accuracy with which silver may be determined, when potassic chromate is used as indicator, some may prefer to use that method. It is then necessary to have a standard solution of silver, of the same chemical power as the salt solution: this is made by dissolving 125 grains of pure and dry neutral silver nitrate in 1000 dm. of distilled water; both solutions will then be equal, volume for volume.

Suppose, therefore, it is necessary to examine a silver solution used for sensitizing paper. One drachm is measured, and if any free acid be present, cautiously neutralized with a weak solution of sodic carbonate; 100 dm. of salt solution are then added with a pipette. If the solution is under 100 grn. to the ounce, the quantity will be sufficient. 3 or 4 drops of chromate solution are then added, and the silver solution delivered from the burette until the red colour of silver chromate is just visible. If 25·5 dm. have been required, that number is deducted from the 100 dm. of salt solution, which leaves 74·5 dm., or 74½ grains to the ounce.

This method is much more likely to give exact results in the hands of persons not expert in analysis than the ordinary plan by precipitation, inasmuch, as with collodion baths, containing as they always do silver iodide, it is almost impossible to get the supernatant liquid clear enough to distinguish the exact end of the analysis.

## SUGAR.

§ 71. THE term sugar is applied to several bodies possessing distinct properties, and differing somewhat in molecular composition, also differing materially in their effects upon various reagents.

The methods in general use for the estimation of the various kinds of sugar are, the optical method, by the polariscope or polarizing saccharometer; by gravimetric analysis with copper solution, and volumetric analysis by copper or mercury solutions. The two last depend upon the reducing power possessed by various kinds of saccharine substances upon the oxides of copper or mercury.

The study of the nature of the various sugars, and their effects upon certain reagents, is one of great interest and importance, and has given rise to very extensive researches, including the transformation products of starch, malt, etc.[*]

The discussion of the intricate organic changes which occur in vegetable juices, or the starches, in relation to the sugar they contain, or are capable of developing, is far too complicated a matter to be entered upon here; but those who may be concerned in the study of such subjects will derive great advantage from the perusal of the admirable papers of O'Sullivan and Brown and Heron, which may be regarded as models of research in this particular branch of organic chemistry. The varieties of sugar of general importance are—

(1) Those that possess the chemical composition of grape sugar or glucose, $C^6H^{12}O^6$, such as the sugar contained in the juice of grapes, apples, and other ripe fruit; also that which occurs in urine in *Diabetes mellitus*.

(2) Common cane sugar, $C^{12}H^{22}O^{11}$, contained in the juice of the sugar cane, beet root, maple, malt sugar, etc.

Sugars of the latter class, and also those contained in milk, may all be altered in character by boiling for a short period with weak sulphuric or hydrochloric acid.

These inverted sugars are not identically the same as grape sugar, and they each have their peculiar effect upon the copper or mercury solutions used for estimating them. Cane sugar in a pure state has no reducing action upon the metallic solutions.

The volumetric method of estimating glucose by Fehling's

[*] Rumpf and Heintzerling, *Z. a. C.* ix. 358.
O'Sullivan, *J. C. S.* 1872, 579, etc., etc.
Märker, *Landw. Versuchs-Stat.* xxii. 69.
Musculus and Gruber, *Bull. Soc. Chim.* xxx. 54.
Hüfner, *Jour. f. pract. Chem.* [2] v. 372.
Brown and Heron, *J. C. S.* 1879, 596.
Soxhlet, *Jour. f. pract. Chem.* [2] xxi. 227.

copper solution has for a long time been thought open to question on the score of accuracy, and the extensive and elaborate experiments of Soxhlet have clearly shown, that only under identical conditions of dilution, etc., can concordant results be obtained. The high official position of this chemist, together with the evident care shown in his methods, leave no doubt as to the general accuracy of his conclusions. His rather sweeping statement, however, that the accurate gravimetric estimation of glucose by Fehling's solution is impossible, is strongly controverted by Brown and Heron, whose large experience leads them to a different conclusion. It is probable, however, that both authorities are right from their own points of view, and that Brown and Heron do obtain concordant results when working in precisely the same way; whereas Soxhlet is equally correct in stating that the gravimetric estimation, as usually performed under varying conditions, is open to serious errors.

*The Solution of Sugar.*—For all the processes of titration this must be so diluted as to contain $\frac{1}{2}$ or at most 1 per cent. of sugar: if on trial it is found to be stronger than this, it must be further diluted with a measured quantity of distilled water.

If the sugar solution to be examined is of dark colour, or likely to contain extractive matters which might interfere with the distinct ending of the reaction, it is advisable to heat a measured quantity to boiling, and add a few drops of milk of lime, allow the precipitate to settle, then filter through animal charcoal, and dilute with the washings to a definite volume. In some instances basic lead acetate may be used to clarify highly coloured or impure solution.

From thick mucilaginous liquids, or those which contain a large proportion of albuminous or extractive matters, the sugar is best extracted by Graham's dialyser.

The methods may be applied directly to fresh diabetic urine (see Analysis of Urine), as also to brewer's wort or distiller's mash. Dextrine does not interfere, except the boiling of the liquid under titration is long continued.

Cane, beet, and maple sugar juice, or prepared sugars, are inverted by heating 30 or 40 c.c. of the clarified liquid in a water bath, with 30 or 40 drops of dilute sulphuric or hydrochloric acid (1 to 5), for twenty minutes, replacing the evaporated water from time to time, so as not to char the sugar. The acid is then neutralized with calcic carbonate, and the liquid diluted to 15 or 20 times its volume before being titrated.

Starch and dextrine, or substances containing them, require to be heated longer with the acid in order to insure their inversion. To invert 1 gm. of starch, it should be mixed with 30 c.c. of cold water smoothly, heated gently until thick, 30 drops of dilute acid are then added, boiled in a small flask, supported obliquely on a sand-bath for 8 or 10 hours, replacing the water from time to time; the solution is then neutralized and diluted as before.

100 parts of grape sugar so found represent 90 parts of starch or dextrine. When dextrine is present with grape sugar, care must be taken not to boil the mixture too long with the alkaline copper solution, as it has been found that a small portion of the copper is precipitated by the dextrine (Rumpf and Heintzerling, *Z. a. C.* ix. 358).

An inversion of starch may be produced more rapidly, and at lower temperature, by using some form of diastase in place of acid. An infusion of malt is best suited to the purpose, but the temperature must not exceed 71° C. (160° Fahr.). The digestion may vary from fifteen minutes to as many hours. The presence of unchanged starch may be found by occasionally testing with iodine. If the digestion is carried beyond half an hour, a like quantity of the same malt solution must be digested alone, at the same temperature, and for the same time, then titrated for its amount of sugar, which is deducted from the total quantity found in the mixture. O'Sullivan (*J. C. S.* 1872, 579) has, however, clearly shown that the effect of the so-called diastase is to produce a body called maltose, which has only the power of reducing the copper solution to the extent of about three-fifths that of dextrose or true grape sugar, the rest being probably various grades of dextrine. Brown and Heron's experiments clearly demonstrate that no dextrose is produced from starch by even prolonged treatment with malt extract; the only product is maltose. Sulphuric or other similar acids cause complete inversion.

Sugar of milk ($C^{12}H^{22}O^{11}$) may also be inverted by boiling for a short time with dilute acid, before being estimated.

### Preparation of the Standard Solutions.

*Fehling's Standard Copper Solution.*—Crystals of pure cupric sulphate are powdered and pressed between unsized paper to remove adhering moisture; 69·28 gm. are weighed, dissolved in water, about 1 c.c. of pure sulphuric acid added, and the solution diluted to 1 liter.

*Alkaline Tartrate Solution.*—350 gm. of Rochelle salt (sodio-potassic tartrate) are dissolved in about 700 c.c. of water, and the solution filtered, if not already clear; there is then added to it a clear solution of 100 gm. of caustic soda in about 200 c.c. of water. The volume is made up to 1 liter.

These solutions, when mixed in equal proportions, form the original Fehling solution, which should contain in each c.c. 0·03464 gm. of cupric sulphate, and has hitherto been taken to represent 0·005 gm. of pure anhydrous grape sugar, the supposition being that 10 equivalents of copper are reduced from the state of cupric to cuprous oxide by 1 equivalent of grape sugar. Soxhlet, however, has with great pains prepared specimens of pure sugars of various types which have been used as standards for the verification of these hitherto-received conclusions of Fehling, Neubauer, and others, and which show that the ratio of reduction is dependent upon various conditions of dilution, duration of experiment, etc., hitherto not taken into account; the results will be given further on. The principle of Fehling's method is based on the fact that although the copper solution, as described above, may be heated to boiling without change, the introduction into it of the smallest quantity of grape sugar, at a boiling temperature, at once produces a precipitate of cuprous oxide, the amount of reduction being in the ratio above mentioned.

*Knapp's Standard Mercuric Cyanide.*—10 gm. of mercuric cyanide are dissolved in about 600 c.c. of water; 100 c.c. of caustic soda solution (sp. gr. 1·145) are added, and the liquid diluted to 1 liter.

This solution, if well preserved, will hold its strength unaltered for a long period.

*Sachsse's Standard Mercuric Iodide.*—18 gm. of pure dry mercuric iodide and 25 gm. of potassic iodide are dissolved in water, and to the liquid is added a solution of 80 gm. of caustic potash; the mixture is finally diluted to 1 liter.

These solutions are very nearly, but not quite, the same in mercurial strength, Knapp's containing 7·9365 gm. Hg in the liter, Sachsse's 7·9295 gm. 100 c.c. of the former are equal to 100·1 c.c. of the latter.

*Indicator for the Mercurial Solutions.*—In the case of Fehling's solution, the absence of blue colour acts as a sufficient indicator, but with mercury solutions the end of reaction must be found by an external indicator. The substance best adapted for this purpose is a strongly alkaline solution of stannous chloride spotted on a porcelain tile. An excess of mercury gives a brown colour.

*The Analytical Process with Mercury Solutions:* 40 c.c. of either are placed in a porcelain basin or a flask, and heated to boiling. The solution of sugar of $\frac{1}{2}$ per-cent. strength is then delivered in until all the mercury is precipitated, the theory being in either case that 40 c.c. should be reduced by 0·1 gm. of dextrose.

The results of Soxhlet's experiments show that this estimate is entirely wrong; nevertheless, it does not follow that these mercurial solutions are useless. It is found that, using them by comparison with Fehling's solution, it is possible to define to some extent the nature of mixed sugars, on the principle of indirect analysis.

*The Analytical Process with Fehling's Solution.*—As hitherto carried out the method is as follows :—

5 c.c. each of standard copper and alkaline tartrate solutions are measured into a thin white porcelain basin, 40 c.c. of water added, and the basin quickly heated to boiling on a sand-bath or by a small flame. No reduction or change of colour should occur; if it does, the alkaline tartrate solution is probably defective from age. This may probably be remedied by the addition of a little fresh caustic alkali on second trial, but it is advisable to use a new solution. The ½ or 1 per cent. sugar solution is then delivered in from a burette * in small quantities at a time, with subsequent boiling, until the blue colour of the copper solution is just discharged, a point which is readily detected by inclining the basin, so that the colour of the clear supernatant fluid may be observed against the white sides of the basin. Some operators use a small thin boiling flask instead of the basin.

It is almost impossible to hit the exact point of reduction in the first titration, but it affords a very good guide for a more rapid and exact addition of the sugar solution in a second trial, when the sugar may be added with more boldness, and the time of exposure of the copper solution to the air lessened, which is a matter of some importance, since prolonged boiling has undoubtedly a prejudicial effect on the accuracy of the process.

When the exact point of reduction is obtained, it is assumed that the volume of sugar solution used represents 0·05 gm. of grape sugar or dextrose, or that 1 equivalent of dextrose (= 180) exactly reduces 10 equivalents of cupric oxide (= 397).

With this assumption, however, Soxhlet does not agree, but maintains from the results of his experiments on carefully prepared standard sugars, that the accuracy of the reaction is interfered with by varying concentration of the solutions, duration of the experiment, and the character of the sugar.

The critical experiments of Soxhlet † were both volumetric and gravimetric, and may be summarized as follows :—

The reducing power of a sugar was volumetrically determined in the following manner :—Varying quantities of the copper solution were heated to boiling in a dish, equal volumes of the alkaline tartrate solution being previously added. Then 50 c.c. or 100 c.c. of the 1 per cent. or ½ per cent. sugar solutions respectively were added, and the whole was boiled for two, four, or six minutes, according to the variety of the sugar. The contents of the dish are then thrown on a filter, the filtrate is acidified with acetic acid, and potassic ferrocyanide at once added to ascertain the presence of copper. This process is repeated until two quantities of the copper

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* The instrument should be arranged as described on page 11.

† A very admirable and complete *résumé* of Soxhlet's results is given in a paper read before the School of Pharmacy Students' Association by C. H. Hutchinson, F.C.S. *Pharm. Journ.* Feb. 1881, 720).

solution, differing from each other by $\frac{1}{10}$ c.c., give, the one a filtrate containing copper, the other a filtrate free from copper. The mean of these two readings is taken as the result.

The gravimetric method of determining the copper reduced by the sugars acting on Fehling's or Löwe's solution (hydrated cupric oxide dissolved in an alkaline solution of glycerine) is to boil a measured quantity of the sugar solution with an excess of the Fehling's or Löwe's solution, and then to filter by means of gentle suction, through a weighed tube filled with asbestos; wash with hot water, then with absolute alcohol, and finally ether. On passing hydrogen through the heated tube, the cuprous oxide is reduced to the metallic state in two or three minutes, and then weighed. The following are the chief results:—

*Dextrose.*—0·5 gm. in 1 per cent. solution reduces 105·2 c.c. Fehling (undiluted), or 101·1 c.c. Fehling (diluted with 4 volumes of water).

Ratio of reduction, 1 : 10·52—1 : 10·11.

*Invert Sugar* (*i.e.* equal molecules of dextrose and levulose obtained by the action of acids on cane-sugar).—0·5 gm. in 1 per cent. solution reduces 101·2 c.c. Fehling (undiluted), or 97·0 c.c. Fehling (diluted with 4 volumes of water).

Ratio of reduction, 1 : 10·12—1 : 9·7.

In the case of dextrose and invert sugar, dilution of the solution lowers, excess of copper raises, the reducing power.

*Milk Sugar.*—0·5 gm. in 1 per cent. solution reduces 74 c.c. Fehling.

Ratio of reduction, 1 : 7·4.

Dilution has no noteworthy influence on the reducing power. Excess of copper raises it, but to a much slighter extent than with dextrose or invert sugar.

*Galactose.*—0·5 gm. in 1 per cent. solution reduces 98 c.c. Fehling (undiluted), or 94 c.c. Fehling (diluted with 4 volumes of water).

Ratio of reduction, 1 : 9·8—1 : 9·4.

Dilution lessens the reducing power to the same extent as with dextrose and invert sugar. Excess of copper raises the reducing power, but to somewhat slighter extent than with dextrose and invert sugar.

*Levulose* (calculated from the results with dextrose and invert sugar).—0·5 gm. in 1 per cent. solution reduces 97·2 c.c. Fehling (undiluted), or 93 c.c. Fehling (diluted with 4 volumes of water).

Ratio of reduction, 1 : 9·72—1 : 9·3.

Dilution and excess of copper act respectively as with dextrose and invert sugar. The reducing power of levulose is probably equal to that of galactose.

*Inverted Milk Sugar* (made by heating ordinary milk sugar with acids).—Reducing power equal to that of invert sugar.

*Maltose.*—0·5 gm. in 1 per cent. solution reduces 64·2 c.c. Fehling (undiluted), or 67·5 c.c. Fehling (diluted with 4 volumes of water).

Ratio of reduction, 1 : 6·09—1 : 6·41.

Dilution raises the reducing power. Excess of copper has no effect with undiluted Fehling, but in highly dilute solutions raises the reducing power to a slight extent.

With the exception of the determination of sugar in diabetic urine (where, owing to the constant formation of ammonia, some of the cuprous oxide is dissolved and passes through the filter, and consequently the end of the reaction must be decided, as usual, by the disappearance of the blue colour), the following plan is adopted for the estimation of the various sugars. The approximate strength of the sugar solution is first determined in the usual manner, by the disappearance of the blue, operating on 25 c.c. Fehling. The sugar solution is now diluted so as to contain 1 per cent. of the sugar, and the determination is proceeded with as described above, operating on 50 c.c. Fehling, undiluted with water.

In the case of highly coloured fluids, the indication with potassic ferrocyanide is difficult to recognize, the reaction with sulphuretted hydrogen giving still worse results. In such cases the following device is adopted :—The filtrate is boiled with a few drops of the sugar solution in a beaker, allowed to settle, and then poured off; on wiping the bottom and sides of the beaker with a piece of white filter-paper, it will be coloured red if any copper still remain in the solution.

The remarks which Soxhlet appends to these experiments are thus classified :—

(1) The reducing power of inverted sugar, for alkaline copper solution, is importantly influenced by the concentration of the solutions: a smaller quantity of sugar being required to decompose Fehling's solution in the undiluted state than when it is diluted with 1, 2, 3, or 4 volumes of water. It is immaterial whether the sugar solution be added to the cold or boiling copper re-agent.

(2) If inverted sugar acts on a larger quantity of copper solution than it is just able to reduce, its reducing power will be increased, the increment varying according to the amount of copper in excess and the concentration of the cupric liquid; in the previous experiments the equivalents varied from 1 : 9·7 to 1 : 12·6, these numbers being by no means the limit of possible variation.

(3) In a volumetric estimation of inverted sugar by means of Fehling's solution, the amount of copper reduced by each successive addition of sugar solution is a decreasing quantity; the results obtained are therefore perfectly empirical, and are only true of that particular set of conditions.

(4) The statement that 1 equivalent of inverted sugar reduces 10 equivalents of cupric oxide is not true, the hypothesis that 0·5 gm. inverted sugar reduces 100 c.c. of Fehling's solution being shown to be incorrect;

the real amount under the conditions laid down by Fehling (1 volume of alkaline copper solution, 4 volumes of water, sugar solution ½—1 per cent.) being 97 c.c., the results obtained under this hypothesis are, therefore, 3 per cent. too low. Where, however, the above conditions have been fulfilled, the results, although not absolutely, are relatively correct; not so, however, those obtained by gravimetric processes, since the interference of concentration and excess has not been previously recognized.

The behaviour of the sugars with alkaline mercury solutions was tested both with Knapp's solution (alkaline mercuric cyanide) and Sachsse's solution (alkaline mercuric iodide in potassic iodide).

It was found that different results are obtained from Knapp's solutions, according as the sugar solution is added gradually, or all at once; when gradually added more sugar being required; with Sachsse's, however, the reverse is the case.

To get comparable results the sugar must be added all at once, the solution boiled for two or three minutes, and the liquid tested for mercury, always using the same indicator; in using the alkaline tin solution as indicator, 0·200—0·202 gm. of grape sugar was always required for 100 c.c. Knapp, in a large number of experiments. It is remarkable that these two solutions, although containing almost exactly the same amount of mercury, require very different quantities of sugar to reduce equal volumes of them. This is shown to be due, to a great extent, to the different amounts of alkali present in them.

The amounts of mercury solutions which 1 gm. of sugar in 1 per cent. solution reduces are :—

| | | |
|---|---|---|
| Grape sugar......... | 497·5 c.c. (Knapp), | 302·5 c.c. (Sachsse). |
| Invert sugar......... | 502·5 ,, | 376·0 ,, |
| Levulose ............ | 508·5 ,, | 449·5 ,, |
| Milk sugar ......... | 322·5 ,, | 214·5 ,, |
| Galactose............ | 413·0 ,, | 226·0 ,, |
| Inverted milk sugar | 448·0 ,, | 258·0 ,, |
| Maltose ............ | 317·5 ,, | 197·6 ,, |

The various sugars have different reducing powers for the alkaline mercury solutions, and there is no definite relation between the amount of Knapp's and Sachsse's solutions required by them; the amount of Sachsse's solution, to which 100 c.c. Knapp's correspond, varying from 54·7 c.c. in the case of galactose, to 74·8 c.c. in the case of invert sugar.

Taking the reducing power of grape sugar=100, the reducing powers of the other sugars are :—

| | Fehling (undiluted). | Knapp. | Sachsse. |
|---|---|---|---|
| Grape sugar.................. | 100 | 100 | 100 |
| Invert sugar.................. | 96·2 | 99·0 | 124·5 |
| Levulose (calculated) ...... | 92·4 | 102·2 | 148·6 |
| Milk sugar .................. | 70·3 | 64·9 | 70·9 |
| Galactose...................... | 93·2 | 83·0 | 74·8 |
| Inverted milk sugar......... | 96·2 | 90·0 | 85·5 |
| Maltose ...................... | 61·0 | 63·8 | 65·0 |

The two mercury methods have no advantage in point of accuracy or convenience over Fehling's method, the latter having the preference on account of the great certainty of the point at which the reduction is finished.

The mercury methods are, however, of great importance, both for the identification of a sugar and for the estimation of two sugars in presence of each other, as proposed by Sachsse. For instance, in the estimation of grape and invert sugars in presence of each other, there are the two equations: $ax + by = \mathrm{F}$, $cx + dy = \mathrm{S}$.

Where—
$a$ = number of 1 c.c. Fehling, reduced by 1 gm. grape sugar.
$b$ = ” ” ” ” invert sugar.
$c$ = ” Sachsse ” ” grape sugar.
$d$ = ” ” ” ” invert sugar.
F = ” Fehling, used for 1 vol. sugar solution.
S = ” Sachsse ” ” ”
$x$ = amount of grape sugar in gms. in 1 vol. of the solution.
$y$ = ” invert sugar ” ” ”

It need hardly be mentioned that the above, like all other indirect methods, leaves room for increased accuracy; but nevertheless the combination of a mercury method with a copper method in the determination of a sugar whose nature is not exactly known, gives a more serviceable result than the hitherto adopted plan, by which a solution that reduced 10 c.c. Fehling was said to contain 0·05 gm. of sugar (*J. C. S.* Abstracts, 1880, 758).

### Pavy's modified Fehling Process.

This method consists in adding ammonia to the ordinary Fehling solution, by which means the precipitation of cuprous oxide is entirely prevented, the end of the reaction being shown by the disappearance of the blue colour in a perfectly clear solution (*C. N.* xxxix. 77).

The solution finally recommended by Pavy as equivalent in action to the usual Fehling test is made as follows:—Cupric sulphate 34·65 gm., Rochelle salt 170 gm., caustic potash 170 gm., dissolved to 1 liter with distilled water. 120 c.c. are then mixed with 400 c.c. of ammonia (sp. gr. 0·88) and diluted to a liter. This liquid constitutes the Pavy-Fehling solution, of which 10 c.c. = 1 c.c. Fehling, the glucose reduction ratio being 1 to 6 instead of 1 to 5, as has been hitherto accepted in the case of Fehling. If well stoppered it keeps perfectly.

The experiments of Hehner (*C. N.* xxxix. 197) and Yoshida (*C. N.* xliii. 29), as also my own, show that the ratio of reduction is seriously influenced by the amount of fixed caustic alkali in the solution and by the strength of the ammonia, consequently the result can only be depended on when the solution is standardized under precisely the same conditions as are adopted in the actual analysis.

The variations with sugars, other than dextrose, appear to be even greater than occur in the usual Fehling process.

In order to avoid the nuisance of filling the laboratory with strong ammoniacal vapours, the titration should be made in a small boiling flask, through the cork of which the elongated end of the burette is passed. A small escape tube is also passed through the same cork, leading into a vessel containing water or weak acid, in order to condense the ammonia.

Stillingfleet Johnson (*C. N.* xlvii. 57) points out that in this process it is possible to verify the results of titration on one and the same portion of cupric solution, by passing air in sufficient volume through the liquid to re-oxidize the reduced copper to the blue cupric state.

In carrying out this arrangement it is necessary to use a wide-mouthed boiling flask having a cork with three holes—one for the burette spit, one for the escape tube, and the other carrying a tube reaching to the bottom of the flask, and to which is attached a Dancer's aspirator. About 1½ liter of air passed through in fifteen minutes suffices to restore the full colour, the liquid being kept boiling the whole time. It is hardly necessary to say that a larger excess than usual of $NH^3$ must be used in order to prevent precipitation of $Cu^2O$ by loss on long boiling. This, it appears to me, is a serious drawback in point of accuracy, because the conditions of titration cannot be the same.

The method is well adapted for the examination of diabetic urine and milk, also mixtures of milk and cane sugars, and certainly has the advantage over the ordinary Fehling method by its definite end-action.

### Some technical applications of these Solutions for mixtures of various Sugars.

It cannot be claimed for these estimations that they are absolutely exact; but with care and practice, accompanied with uniform conditions, they are probably capable of the best possible results whatever methods may be used.

**Cane Sugar, Grape Sugar, and Dextrine** (Biard and Pellet, *Z. a C.* xxiv. 275). The solution containing these three forms is first titrated with the usual Fehling solution for grape sugar. A second portion is boiled with acetic acid (which only inverts cane sugar) and titrated. Finally, a third portion is completely inverted with sulphuric acid and titrated. The difference of the first and second titrations gives the cane sugar, and that of the second and third the dextrine.

**Milk and Cane Sugar.**—If the estimation of milk sugar is alone required, and by the usual Fehling solution, the casein and albumen must be first removed. Acidify the liquid with a few drops of acetic acid, warm until coagulation is effected, and filter. Boil the filtrate to coagulate the albumen. Filter again, and neutralize with soda previous to treatment for sugar by the copper test. The number of c.c. of Fehling's solution required, multiplied by 0·006786, will give the weight of milk sugar in grams. Direct estimation by Pavy-Fehling is preferable to this method.

Cane sugar in presence of milk sugar may be estimated as follows:—Dilute the milk to 10 times its bulk, having previously coagulated it with a little citric acid, filter, and make up to a definite volume, titrate a portion with Pavy-Fehling solution, and note the result. Then take 100 c.c. of the filtrate, add 2 gm. of citric acid, and boil for 10 minutes, cool, neutralize, make up to 200 c.c., and titrate with copper solution as before. The difference between the reducing powers of the solutions before and after conversion is due to the cane sugar, the milk sugar not being affected by citric acid.

Stokes and Bodmer (*Analyst*, x. 62) have experimented largely on this method, and with satisfactory results. The plan adopted by them is to use 40 c.c. of Pavy-Fehling liquid (=0·02 gm. glucose), and to dilute the sugar solution (without previous coagulation), so that from 6 to 12 c.c. are required for reduction. By using a screw-clamp on the rubber burette tube, the sugar solution is allowed to drop into the boiling liquid at a moderate rate. If $Cu^2O$ should be precipitated before the colour disappears, a fresh trial must be made, adding the bulk of the sugar at once, then finishing by drops. If, on the other hand, the sugar has been run in to excess, which owing to the rather slow reaction is easily done, fresh trial must be again made until the proper point is reached: this gives the milk sugar. Meanwhile a portion of the mixed sugar solution is boiled with 2 per cent. of citric acid, neutralized with $NH^3$, made up to double its original volume, and titrated as before.

These operators have determined the reducing action of milk, cane, and grape sugar on the Pavy-Fehling liquid, the result being that 100 lactose represents respectively 52 glucose, or 49·4 sucrose.

The Pavy-Fehling liquid is admirably adapted for the estimation of lactose in milk direct after dilution, no coagulation being necessary.

## SULPHUR.

$S=32.$

### Estimation in Pyrites, Ores, Residues, etc.

### 1. Alkalimetric method (Pelouze).

§ 72. This process, designed for the rapid estimation of sulphur in iron and copper pyrites, has hitherto been thought tolerably accurate, but experience has shown that it cannot be relied upon except for rough technical purposes.

The process is based on the fact, that when sulphur is ignited with potassic chlorate and sodic carbonate, the sulphur is converted entirely into sulphuric acid, which expels its equivalent proportion of carbonic acid from the soda, forming neutral sodic sulphate; if therefore, an accurately weighed quantity of the substance be fused with a known weight of pure sodic carbonate in excess, and the resulting mass titrated with normal acid, to find the quantity of unaltered carbonate, the proportion of sulphur is readily calculated from the difference between the volume of normal acid required to saturate the original carbonate, and that actually required after the ignition.

It is advisable to take 1 gm. of the finely levigated pyrites, and 5·3 gm. of pure sodic carbonate for each assay; and as 5·3 gm. of sodic carbonate represent 100 c.c. of normal sulphuric acid, it is only necessary to subtract the number of c.c. used after the ignition from 100, and multiply the remainder by 0·016, in order to arrive at the weight of sulphur in the 1 gm. of pyrites, and by moving the decimal point two places to the right, the percentage is obtained.

*Example:* 1 gm. of finely ground $FeS^2$ was mixed *intimately* with 5·3 gm. sodic carbonate, and about 7 gm. each of potassic chlorate, and decrepitated sodic chloride, in powder; then introduced into a platinum crucible, and gradually exposed to a dull red heat for ten minutes; the crucible suffered to cool, and warm water added; the solution so obtained was brought on a moistened filter, the residue emptied into a beaker and boiled with a large quantity of water, brought on the filter, and washed with boiling water till all soluble matter was removed; the filtrate coloured with methyl orange, and titrated. 67 c.c. of normal acid were required, which deducted from 100, left 33 c.c.; this multiplied by 0·016 gave 0·528 gm. or 52·8 per cent. S.

An iron spoon or ladle may be used instead of the platinum crucible.

If roasted pyrites are to be examined by this method, it is unnecessary to add the salt, and equal quantities of the substance, sodic carbonate and potassic chlorate, may be taken for the combustion.

Kolb (*Journ. de Pharm. et Chim.* [4] x. 401) has experimented very fully upon Pelouze's process, as described above, and found the sources of error to be various—formation of ferric sulphate, loss of chlorine, sulphur chloride, etc. The process recommended in its place, and which is not open to the objection existing in the Pelouze method, consists in mixing sodic carbonate and cupric oxide with the finely powdered ore and igniting the mixture in an iron, copper, or platinum vessel to a low red heat for about fifteen minutes; the whole of the sulphur is oxidized to sulphuric acid, and combines quietly with the soda; the remaining unchanged sodic carbonate is then estimated by titration as usual. The method is particularly applicable to roasted pyrites, the details being as follows:—

From 5 to 10 gm. of the ore, according to its richness in sulphur (if more than 10 per cent. 5 gm., less than 10 per cent. 10 gm.), are weighed and intimately mixed with 5 gm. of sodic carbonate, and about 50 gm. of dry cupric oxide, placed in the crucible, and heated over a small gas-flame with frequent stirring for twelve or fifteen minutes, the heat never exceeding a low red; the crucible is then cooled, the contents treated with hot water filtered, and the filtrate and washings titrated with normal acid.

### 2. Estimation of Sulphur in Coal Gas.

A most convenient and accurate process for this estimation is that of Wildenstein (§ 73.2). The liquid produced by burning the measured gas in a Letheby or Vernon Harcourt apparatus is well mixed, and brought to a definite volume; a portion representing a known number of cubic feet of gas is then poured into a glass, porcelain, or platinum basin, acidified slightly with HCl, heated to boiling, and a measured excess of standard baric chloride added; the excess of acid is then cautiously neutralized with ammonia (free from carbonate), and the excess of barium ascertained by standard potassic chromate exactly as described in § 73.2.

The usual method of stating results is in grains of sulphur per 100 cubic feet of gas. This may be done very readily by using semi-normal solutions of baric chloride and potassic chromate on the metric system, and multiplying the number of c.c. of baric solution required with the factor 0·1234, which at once gives the amount of sulphur in grains.

Standard solutions can of course be made in the same manner on the grain system.

### 3. Estimation of Sulphur in Sulphides decomposable by Hydrochloric or Sulphuric Acids (Weil).

This process, which has just been communicated to me by M. Weil, is based on the fact that, in the case of sulphides where the whole of the sulphur is given off as $H^2S$ by heating with HCl or $H^2SO^4$, the $H^2S$ may be evolved into an excess of a standard alkaline copper solution. After the action is complete, the amount of Cu left unreduced is estimated by standard stannous chloride. The method is available for the sulphides of lead, antimony, zinc, iron, etc. Operators should consult and practise the methods described in § 54.6, in order to become accustomed to the special reaction involved.

*The Analysis:* From 1 to 10 gm. of material (according to its richness in sulphur) in the finest state of division, are put into a long necked flask of about 200 c.c. capacity, to which is fitted a bent delivery tube, so arranged as to dip to the bottom of a tall cylinder, containing 50 or 100 c.c. of standard copper solution (10 c.c.=0·1 gm. Cu) and 20 c.c. of ammonia sp. gr. 0·96. When this is ready, a few pieces of granulated zinc are added to the sulphide. 75 c.c. of strong HCl are then poured over them, the cork with delivery tube immediately inserted, connected with the copper solution, and the flask heated on a sand-bath until all evolution of $H^2S$ is ended. The blue solution and black precipitate are then brought on a filter, filtrate and washings collected in a 200 or 250 c.c. flask, and diluted to the mark. 20 c.c. of the clear blue liquid are then measured into a boiling flask, placed on hot plate, and evaporated to 10 or 15 c.c. 25 to 50 c.c. of strong HCl are then added, and the standard tin solution dropped in while boiling, until the blue gives place to a clear pure yellow.

Each c.c. of standard copper solution represents 0·50393 gm. sulphur. The addition of the granulated zinc facilitates the liberation of the $H^2S$, and sweeps it out of the flask; moreover, in the case of dealing with lead sulphide, which forms insoluble lead chloride, it materially assists the decomposition. Alkaline tartrate solution of copper may be used in place of ammoniacal solution if so desired.

*Examples* (Weil): 1 gm. of galena was taken, and the gas delivered into 50 c.c. of standard copper solution (=0·5 gm. Cu). After complete precipitation the blue liquid was diluted to 200 c.c. 20 c.c. of this required 12·5 c.c. of stannous chloride, the titre of which was 16·5 c.c. for 0·04 gm. Cu. Therefore 16·5 : 0·04 : : 12·5 : 0·0303. Thus 200 c.c. (=1 gm. galena) represent 0·303 gm. Cu. Then 0·5 gm. Cu, less 0·303=0·197 gm. for 1 gm. galena or 19·7 for 100 gm. Consequently 19·7 × 0·50393=9·92 per cent. S. Estimation by weight gave 9·85 per cent. Again, 1 gm. zinc sulphide was taken with 100 c.c. copper solution and made up to 250 c.c., 25 c.c. of which required 14·3 c.c. of same stannous chloride, or 143 c.c. for the 1 gm. sulphide. This represents 0·347 gm. Cu. Thus 1—0·347=0·653 gm. Cu (precipitated as CuS) or 65·3 per 100. Consequently 65·3 × 0·50393=32·9 per cent. S. Control estimation by weight gave 33 per cent.

The process has given me good technical results with $Sb^2S^3$, but the proportion of sulphur to copper is too great to expect strict accuracy.

### 4. Estimation of Alkaline Sulphides by Standard Zinc Solution.

This method, which is simply a counterpart of § 78.3, is especially applicable for the technical determination of alkaline sulphides in impure alkalies, mother-liquors, etc.

If the zinc solution be made by dissolving 3·253 gm. of pure metallic zinc in hydrochloric acid, supersaturating with ammonia, and diluting to 1 liter, or 32·53 grn. to 1000 dm., 1 c.c. or dm. will respectively indicate—

| | | | |
|---|---|---|---|
| 0·0016 gm. | or 0·016 grn. | Sulphur |
| 0·0039 ,, | 0·039 ,, | Sodic sulphide |
| 0·00551 ,, | 0·0551 ,, | Potassic sulphide |
| 0·0034 ,, | 0·034 ,, | Ammonic sulphide. |

The zinc solution is added from a burette until a drop, brought in contact with the lead solution on filtering paper, no longer gives a black stain at the edge.

### 5. Sulphurous Acid and Sulphites.

Solutions of sulphurous acid are very readily titrated by iodine, as described in § 34, but it is necessary to remember that, in order to secure the proper reaction as defined by Bunsen, the solution must not contain more than 0·05 per cent. of sulphur dioxide. Mohr, however, has found that the difficulty as to concentration is overcome by the use of an alkaline bicarbonate (see § 34, note), which has no effect on starch iodide.

$$1 \text{ c.c. } \tfrac{N}{10} \text{ iodine} = 0\text{·}0032 \text{ gm. } SO^2.$$

The serious drawback to this method is the oxidizing influence which dilution with water has on the one hand, and exposure to the atmosphere on the other, whether the free acid or its salts are concerned. These effects are not satisfactorily remedied by the use of alkaline bicarbonates. The difficulties, however, are now fortunately quite overcome by the modification devised by Giles and Schearer (*J. S. C. I.* iii. 197 and iv. 303). A valuable series of experiments on the estimation of $SO^2$, either free or combined, are detailed in these papers. The modification is both simple and exact, and consists in adding the weighed $SO^2$ or the sulphite in powder to a measured excess of $\frac{N}{10}$ iodine without dilution with water, and when the decomposition is complete, titrating back with $\frac{N}{10}$ thiosulphate. Very concentrated solutions of $SO^2$ are cooled by a freezing mixture, and enclosed in thin bulbs, which can be broken under the iodine solution: this is, however, not required with the ordinary preparations. Sulphites and bisulphites of the alkalies and alkaline earths, also zinc and aluminium, may all be titrated in this way with accuracy; the less soluble salts, of course, requiring more time and agitation to ensure their decomposition. A preliminary titration is first made with a considerable excess of iodine, and a second with a more moderate excess as indicated by the first trial.

The authors found that when perfectly pure iodine and neutral potassic iodide were used for the standard solution, its strength remained intact for a long period; and the same with the thiosulphate, if the addition of about 2 gm. of potassic bicarbonate to the liter was made, and the stock solution kept in the dark (see page 105).

From a large number of experiments, they also deduced the simple law of the ratio between any given percentage of $SO^2$ in aqueous solution at 15·4° and 760 m.m., and its specific gravity; namely, the percentage found by titration multiplied by 5 gives the sp. gr. over and above 1000.

### 6. Estimation of Mixtures of Alkaline Sulphides, Sulphites, and Thiosulphates.

Lunge and Smith (*J. S. C. I.* ii. 463) have established the fact, that both sulphites and thiosulphates may be completely oxidized to sulphates, by treating them with a large excess of standard permanganate, more than sufficient for complete oxidation and formation of $MnO^2$. An excess of standard ferrous sulphate is added, then titrated back with permanganate to the pink colour. Upon this reaction, together with the known accurate estimation of both of these compounds by iodine, in the absence of nitrates and nitrites or other similar oxidizing bodies, they have founded a new and rapid volumetric method, which gives the respective proportions of each substance when occurring together. If sulphides are also present, their amount is first ascertained separately with standard ammoniacal zinc chloride. The whole of the three compounds might be oxidized by permanganate if so chosen, and the sulphide found by difference, but the separation is said to be better.

The process consists of two titrations; one with standard iodine and the other with standard permanganate, adding the latter in large excess to the slightly alkaline or neutral solution, then acidifying with $H^2SO^4$, titrating back with excess of standard $FeSO^4$, and finishing with permanganate.

The following equations represent the action of the permanganate and iodine respectively:—

$$(1)\quad Na^2S^2O^3 + 2O^2 + H^2O = Na^2SO^4 + H^2SO^4.$$
$$(2)\quad 4Na^2SO^3 + 2O^2 = 4Na^2SO^4.$$
$$(3)\quad 2Na^2S^2O^3 + I^2 = Na^2S^4O^6 + 2NaI.$$
$$(4)\quad Na^2SO^3 + I^2 + H^2O = Na^2SO^4 + 2HI.$$

Let W equal the weight of sulphur as thiosulphate oxidized to sulphate by 1 c.c. of $KMnO^4$ solution. Let $W^1$ equal the weight of sulphur as thiosulphate acted on by 1 c.c. of iodine solution. Then it is evident from the above equations that 2W is the weight of sulphur as sulphite oxidized by 1 c.c. of $KMnO^4$ and $\frac{W^1}{4}$ that oxidized by 1 c.c. of iodine. In the given mixture let S = weight of sulphur present as thiosulphate and $s$ = ditto as sulphite, N = number of c.c. $KMnO^4$ and $N^1$ = ditto of iodine required.

Then $$\frac{S}{W} + \frac{s}{2W} = N$$

or $$2S + s = 2WN \qquad (1)$$

and $$\frac{S}{W^1} + \frac{4s}{W^1} = N^1$$

or $$S + 4s = W^1N^1 \qquad (2)$$

$$8S + 4s = 8WN \qquad (1a)$$

$$(1a)\text{—}(2) \qquad 7S = 8WN - W^1N$$

$$\therefore S = \tfrac{1}{7}(8WN - W^1N^1)$$

$$s = 2WN - 2S = 2WN = \tfrac{2}{7}(8WN - W^1N^1) \qquad (1b)$$

$$\therefore s = \tfrac{2}{7}(W^1N^1 - WN)$$

An advantage in point of accuracy arises from the fact that a unit weight of sulphur as thiosulphate requires twice the amount of $KMnO^4$, but only one-fourth the amount of I, that a unit of sulphur as sulphite requires. The permanganate method is therefore more accurate for an estimation of the former and the iodine for the latter. In a mixture of the two the experimental errors tend to counteract each other.

The estimation of nitrites in the presence of sulphites and thiosulphates has been described in § 67.

Davis has devised also a method of titrating mixtures of sulphides, sulphites, and thiosulphates (*J. S. C. I.* i. 88).

## SULPHURIC ACID AND SULPHATES.

### Monohydrated Sulphuric Acid.

$H^2SO^4 = 98$.

### Sulphuric Anhydride.

$SO^3 = 80$.

### 1. Mohr's Method.

§ 73. THE indirect process devised by C. Mohr (*Ann. der Chem. u. Pharm.* xc. 165) consists in adding a known volume of baric solution to the compound, more than sufficient to precipitate the $SO^3$. The excess of barium is converted into carbonate, and titrated with normal acid and alkali.

*Normal Baric Chloride* is made by dissolving 121·77 gm. of pure crystals of baric chloride in the liter; this solution likewise suffices for the determination of $SO^3$ by the direct method.

The following is the method of procedure.

If the substance contains a considerable quantity of free acid, it must be brought near to neutrality by pure sodic carbonate; if alkaline, slightly acidified with hydrochloric acid; a round number of c.c. of barium solution is then added, and the whole digested in a warm place for some minutes; the excess of barium is precipitated by a mixture of carbonate and caustic ammonia in slight excess; if a piece of litmus paper be thrown into the mixture, a great excess may readily be avoided. The precipitate containing both sulphate and carbonate is now to be collected on a filter, thoroughly washed with boiling water, and titrated.

The difference between the number of c.c. of barium solution added, and that of normal acid required for the carbonate, will be the measure of the sulphuric acid present; each c.c. of barium solution is equal to 0·040 gm. $SO^3$.

*Example:* 2 gm. of pure and dry baric nitrate, and 1 gm. of pure potassic sulphate were dissolved, mixed, and precipitated hot with carbonate and caustic ammonia; the precipitate, after being thoroughly washed, gave 1·002 gm. potassic sulphate, instead of 1 gm.

For technical purposes this process may be considerably shortened by the following modification, which dispenses with the washing of the precipitate.

The solution containing the sulphates or sulphuric acid is first rendered neutral; normal baric chloride is then added in excess, then normal sodic carbonate in excess of the baric chloride, and the volume of both solutions noted; the liquid is then made up to 200 or 300 c.c. in a flask, and an aliquot portion filtered off and titrated with normal acid. The difference between the baric chloride and sodic carbonate gives the sulphuric acid.

The solution must of course contain no substance precipitable by sodic carbonate except barium (or if so, it must be previously removed); nor must it contain any substance precipitable by barium, such as phosphoric or oxalic acid, etc.

Another alkalimetric process suitable for technical purposes is that of Bohlig (§ 28), also Grossmann (§ 16.14).

### 2. Titration by Baric Chloride and Potassic Chromate (Wildenstein).

To the hot solution containing the $SO^3$ to be estimated (which must be neutral, or if acid, neutralized with caustic ammonia, free from carbonate), a standard solution of baric chloride is added in slight excess, then a solution of potassic chromate of known strength is cautiously added to precipitate the excess of barium. So long as any barium remains in excess, the supernatant liquid is colourless, when it is all precipitated the liquid is yellow, from the free chromate; a few drops only of the chromate solution are necessary to produce a distinct colour.

Wildenstein uses a baric solution, of which 1 c.c. $=0{\cdot}015$ gm. of $SO^3$, and chromate 1 c.c. $=0{\cdot}010$ gm. of $SO^3$. I prefer to use $\frac{N}{2}$ solutions, so that 1 c.c. of each is equal to 0·020 gm. of $SO^3$. If the chromate solution is made equal to the baric chloride, the operator has simply to deduct the one from the other, in order to obtain the quantity of baric solution really required to precipitate all the $SO^3$.

*The Analysis:* The substance or solution containing $SO^3$ is brought into a small flask, diluted to about 50 c.c., acidified if necessary with HCl, heated to boiling, and precipitated with a slight excess of standard baric chloride delivered from the burette. As the precipitate rapidly settles from a boiling solution, it is easy to avoid any great excess of barium, which would prevent the liquid from clearing so speedily. The mixture is then cautiously neutralized with ammonia free from carbonic acid (to be certain of this, it is well to add to it two or three drops of calcic chloride or acetate solution).

The flask is then heated to boiling, and the chromate solution added in ½ c.c. or so, each time removing the flask from the heat and allowing to settle, until the liquid is of a light yellow colour; the quantity of chromate is then deducted from the barium solution, and the remainder calculated for $SO^3$.

Or the mixture with barium in excess may be diluted to 100 or 150 c.c., the precipitate allowed to settle thoroughly, and 25 or 50 c.c. of the clear liquid heated to boiling, after neutralizing, and precipitated with chromate until all the barium is carried down as baric chromate, leaving the liquid of a light yellow colour; the analysis should be checked by a second titration. The process has yielded me very satisfactory results in comparison with the barium method by weight; it is peculiarly adapted for estimating sulphur in gas when burnt in the Letheby sulphur apparatus, details of which will be found on page 270.

The presence of alkaline and earthy salts is of no consequence—Zn and Cd do not interfere—Ni, Co, and Cu give coloured solutions which prevent the yellow chromate being seen, but this difficulty can be overcome by the use of an external indicator for the excess of chromate. This indicator is an ammoniacal lead solution, made by mixing together, at the time required, one volume of pure ammonia and four volumes of lead acetate solution (1 : 20). The liquid has an opalescent appearance. To use the indicator, a large drop is spread upon a white porcelain plate, and one or two drops of the liquid under titration added; if the reddish-yellow colour of lead chromate is produced, there is an excess of chromate, which can be cautiously reduced by adding more barium until the exact balance occurs.

Precht (*Z. a. C.* 1879, 521) modifies this process by precipitating the $SO^3$ with excess of standard baric chloride, which excess is removed by standard potassic chromate also in excess, which latter is in turn estimated by weak standard ferrous sulphate, the end of the reaction being found by spotting the liquid on a white plate with potassic ferricyanide.

I can see no advantage in this modification, and in many cases it would be totally inadmissible, owing to the presence of substances affecting the ferrous re-agent.

### 3. Direct Precipitation with Normal Baric Chloride.

Very good results may be obtained by this method when carefully performed.

The substance in solution is to be acidified with hydrochloric acid, heated to boiling, and the baric solution allowed to flow cautiously in from the burette until no further precipitation occurs. The end of the process can only be determined by filtering a portion of the liquid, and testing with a drop of the baric solution. Beale's filter (shown in fig. 16) is a good aid in this case. A few drops of clear liquid are poured into a test tube and a drop of baric solution added from the burette; if a cloudiness occurs, the contents of the tubes must be emptied back again, washed out into the liquid, and more baric solution added until all the $SO^3$ is precipitated. It is advisable to use $\frac{N}{10}$ solution towards the end of the process.

Instead of the test tube for finding whether barium or sulphuric acid is in excess, a plate of black glass may be used, on which a drop of the clear solution is placed and tested by either a drop of baric chloride or sodic sulphate,—these testing solutions are preferably kept in two small bottles with elongated stoppers. A still better plan is to spot the liquids on a small mirror, as suggested by Haddock (*C. N.* xxxix. 156); the faintest reaction can then be seen, although the liquid may be highly coloured.

Wildenstein has arranged another method for direct precipitation, especially useful where a constant series of estimations have to be made. The apparatus is shown in fig. 38. A is a bottle of 900 or 1000 c.c. capacity, with the bottom removed, and made of well-annealed glass so as to stand heating; B a thistle funnel bent round, as in the figure, and this syphon filter is put into action by opening the pinch-cock below the cork. The mouth of the funnel is first tied over with a piece of fine cotton cloth, then two thicknesses of Swedish filter paper, and again with a piece of cotton cloth, the whole being securely tied with waxed thread.

Fig. 38.

In precipitating $SO^3$ by baric chloride, there occurs a point similar to the so-called neutral point in silver assay, when in one and the same solution both barium and sulphuric acid after a minute or two produce a cloudiness. Owing to this circumstance, the barium solution must not be reckoned exactly by its amount of $BaCl^2$, but by its working effect; that is to say, the ending of the process must be, that when the addition of a drop or two of barium solution gives no cloudiness after the lapse of two minutes.

*The Analysis:* The solution containing the $SO^3$ being prepared, and preferably in HCl, the vessel A is filled with warm distilled water, and the pinch-cock opened so as to fill the filter to the bend C; the cock is then opened and shut a few times so as to bring the water further down into the tube, but not to fill it entirely; the water is then emptied out of A, and about 400 c.c. of boiled distilled water poured in together with the $SO^3$ solution, then, if necessary, a small quantity of HCl added, and the baric chloride added in moderate quantity from a burette. After mixing well, and waiting a few minutes, a portion is drawn off into a small beaker, and poured back without loss into A; a small quantity is then drawn off into a test tube, and two drops of baric chloride added. So long as a precipitate occurs, the liquid is returned to A, and more barium added until a test is taken which shows no distinct cloudiness; the few drops added to produce this effect are deducted. If a distinct excess has been used, the analysis must be corrected with a solution of $SO^3$ corresponding in strength to the barium solution.

A simpler and even more serviceable arrangement of apparatus on the above plan may be made, by using as the boiling and precipitating vessel an ordinary beaker standing on wire gauze or hot plate. The filter is made by taking a small thistle funnel, tied over as described, with about two inches of its tube, over which is tightly slipped about four or five inches of elastic tubing, terminating with a short piece of glass tube drawn out to a small orifice like a pipette; a small pinch-cock is placed across the elastic tube just above the pipette end, so that when hung over the edge of the beaker with the funnel below the surface of the liquid, the apparatus will act as a syphon. It may readily be filled with warm distilled water by gentle suction, then transferred to the liquid under titration. By its means much smaller and more concentrated liquids may be used for the analysis, and consequently a more distinct evidence of the reaction obtained.

## SULPHURETTED HYDROGEN.

$$H^2S = 34.$$

$$1 \text{ c.c. } \tfrac{N}{10} \text{ arsenious solution} = 0{\cdot}00255 \text{ gm. } H^2S.$$

### 1. By Arsenious Acid (Mohr).

§ 74. This residual process is far preferable to the direct titration of sulphuretted hydrogen by iodine. The principle is based on the fact, that when $H^2S$ is brought into contact with an excess of arsenious acid in hydrochloric acid solution, arsenic sulphide is formed; 1 eq. of arsenious acid and 3 eq. of sulphuretted hydrogen produce 1 eq. of arsenic sulphide and 3 eq. of water,

$$As^2O^3 + 3H^2S = As^2S^3 + 3H^2O.$$

The excess of arsenious acid used is found by $\frac{N}{10}$ iodine and starch, as in § 36. In estimating the strength of sulphuretted hydrogen water, the following plan may be pursued.

A measured quantity, say 10 c.c., of $\frac{N}{10}$ arsenious solution is put into a 300 c.c. flask, and 20 c.c. of sulphuretted hydrogen water added, well mixed, and sufficient HCl added to produce a distinct acid reaction; this produces a precipitate of arsenic sulphide, and the liquid itself is colourless. The whole is then diluted to 300 c.c., filtered through a dry filter into a dry vessel, 100 c.c. of the filtrate taken out and neutralized with sodic bicarbonate, then titrated with $\frac{N}{10}$ iodine and starch. The quantity of arsenious acid so found is deducted from the original 10 c.c., and the remainder multiplied by the requisite factor for $H^2S$.

The estimation of $H^2S$ contained in coal gas, may by this method be made very accurately by leading the gas very slowly through the arsenious solution, or still better, through a dilute solution of caustic alkali, then adding arsenious solution, and titrating as before described. The apparatus devised by Mohr for this purpose is arranged as follows:—

The gas from a common burner is led by means of a vulcanized tube into two successive small wash bottles, containing the alkaline solution; from the last of these it is led into a large Woulf's bottle filled with water. The bottle has two necks, and a tap at the bottom; one of the necks contains the cork through which the tube carrying the gas is passed; the other, a cork through which a good-sized funnel with a tube reaching to the bottom of the bottle is passed. When the gas begins to bubble through the flask, the tap is opened so as to allow the water to drop rapidly; if the pressure of gas is strong, the funnel tube acts as a safety valve, and allows the water to rise up into the cup of the funnel. When a sufficient quantity of gas has passed into the bottle, say six or eight pints, the water which has issued from the tap into some convenient vessel is measured into cubic inches or liters, and gives the quantity of gas which has displaced it. In order to insure accurate measurement, all parts of the apparatus must be tight.

The flasks are then separated, and into the second 5 c.c. of arsenious solution placed, and acidified slightly with HCl. If any traces of a precipitate occur it is set aside for titration with the contents of the first flask, into which 10 c.c. or so of arsenious solution are put, acidified as before, both mixed together, diluted to a given measure, filtered, and a measured quantity titrated as before described.

This method does not answer for very crude gas containing large quantities of $H^2S$ unless the absorbing surface is largely increased.

### 2. By Permanganate (Mohr).

If a solution of $H^2S$ is added to a dilute solution of ferric sulphate, the ferric salt is reduced to the ferrous state, and free sulphur separates. The ferrous salt so produced may be measured accurately by permanganate without removing the separated sulphur. Ferric sulphate, free from ferrous compounds, in sulphuric acid solution, is placed in a stoppered flask, and the solution of $H^2S$ added to it with a pipette; the mixture is allowed to stand half an hour or so, then diluted considerably, and permanganate added until the rose colour appears.

$$56\ Fe = 17\ H^2S$$

or each c.c. of $\frac{N}{10}$ permanganate represents 0·0017 gm. of $H^2S$. The process is considerably hastened by placing the stoppered flask containing the acid ferric liquid into hot water previous to the addition of $H^2S$, and excluding air as much as possible.

### 3. By Iodine.

Sulphuretted hydrogen in mineral waters may be accurately estimated by iodine in the following manner:—

10 c.c. or any other necessary volume of $\frac{N}{100}$ iodine solution are measured into a 500 c.c. flask, and the water to be examined added until the colour disappears. 5 c.c. of starch liquor are then added, and $\frac{N}{100}$ iodine until the blue colour appears; the flask is then filled to the mark with pure distilled water. The respective volumes of iodine and starch solution, together with the added water, deducted from the 500 c.c., will show the volume of water actually titrated by the iodine. A correction should be made for the excess of iodine necessary to produce the blue colour.

Fresenius examined the sulphur water of the Grindbrunnen, in Frankfurt a. M. (*Z. a. C.* xiv. 321), both volumetrically and by weight for $H^2S$ with very concordant results. 361·44 gm. of water (correction for blue colour being allowed) required 20·14 c.c. of iodine, 20·52 c.c. of which contained 0·02527 of free iodine $= H^2S$ 0·009194 gm. per million. 444·65 gm. of the same water required, under the same conditions, 25·05 c.c. of the same iodine solution $= H^2S$ 0·009244 gm. per million. By weight the $H^2S$ was found to be 0·009377 gm. per million.

## TANNIC ACID.

§ 75. THE estimation of tannin in the materials used for tanning is by no means of the most satisfactory character. Many methods have been proposed, and given up as practically useless. In the previous edition of this book Löwenthal's method (originated by Estcourt) as then perfected was given; but it is still deficient in accuracy or constancy of results, although much ingenuity and intelligence have been expended on it.

One difficulty is still unsurmounted, and that is, the preparation of a pure tannic acid to serve as standard. The various tannins in existence are still very imperfectly understood,* but so far as the

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* Von Schröder, whose suggestions have been adopted by the German Association of Tanners, selects a commercial pure tannic acid for use as a standard by dissolving 2 gm. in a liter of water. 10 c.c. of this is titrated with permanganate as described. 50 c.c. are then digested twenty hours with 3 gm. moistened hide powder. 10 c.c. of the filtrate from this is then titrated, and if the permanganate consumed amounts to less than 10 per cent. of the total consumed by the tannin, it is suitable for a standard. 1000 parts being considered equivalent in reducing power to 1048 parts of tannin precipitable by hide, according to Hammer's experiments, therefore Von Schröder, after titrating as described, calculates the dry matter, and multiplies by the round number 1·05 to obtain the value in actual tannin precipitable by hide.

comparative analysis of tanning materials among themselves is concerned, the method in question is theoretically the best.

The principle of the method depends on the oxidation of the tannic acid, together with other glucosides and easily oxidizable substances, by permanganate, regulated by the presence of soluble indigo-carmine, which also acts as an indicator to the end of the reaction. The total amount of such substances being found and expressed by a known volume of permanganate, the actual available tannin is then removed by gelatine, and the second titration is made upon the solution so obtained in order to find the amount of oxidizable matters other than tannin.

The volume of permanganate so used, deducted from the volume used originally, shows the amount of tannin actually available for tanning purposes expressed in terms of permanganate.

It will be at once seen that this method is essentially a practical one, because it is only the particular tannin capable of combining with organic tissue which is estimated. It has been critically examined with approbation by good authorities, among whom may be mentioned, Procter (*C. N.* xxxvi. 59; *ibid*, xxxvii. 256), Kathreiner (*Z. a C.* xviii. 112), (Dingler's *Polyt. Jour.* cxxvii. 481), and Hewitt (*Tanner's Jour.*, May, 1877, 93). My own experiments have shown that for all materials containing tannin, even catechu, it is the best process yet discovered, but requires patient practice to ensure concordant results. Löwenthal's description of the method is given in *Z. a. C.* xvi. 33.

The extraction of the tannic acid from the raw material is best performed by boiling it in a large flask with about a liter of distilled water for half an hour, then straining, and diluting when cold to 1 liter. Portions are filtered if necessary. Concentrated extracts are dissolved before titration by adding them to boiling water, then cooling and diluting to the measure. In the case of strong materials such as sumach or valonia 10 gm., or oak-bark 20 gm., are used.

The quantity of these extracts to be used for titration must be regulated to some extent by the amount of permanganate required to oxidize the tannic and gallic acids present. Practice and experience will enable the operator to judge of the proper proportions to use in dealing with the various materials, bearing in mind that volumetric processes are largely dependent upon identity of conditions for securing concordant results.

Procter, who is probably one of the best authorities on this subject, has modified to some extent the details of this process (*J. S. C. I.* iii. 82, and *ibid.* v. 79), and these modifications are embodied here.

### Standard Solutions and Re-agents.

*Standard Potassic Permanganate.*—Kathreiner recommends that this solution should contain not more than 1·333 gm. of the pure salt per liter (better only about 1 gm.); therefore, if the operator is accustomed to use the decinormal solution, a very convenient strength is made by diluting one volume of it with two of water, thus obtaining a solution of $\frac{N}{30}$ strength (=1·052 gm. per liter).

This standard is the more advisable because it enables the operator to calculate its value into oxalic acid, and so arrive at the theoretical standards adopted by Neubauer and Oser; namely, that 0·063 gm. of oxalic acid represents 0·04157 gm. of gallo-tannic acid (gall-nut tannin), or 0·062355 gm. of querci-tannic acid (oak bark tannin). These coefficients for calculation are now largely adopted, and are certainly preferable to standardizing the permanganate upon any specimen of so-called pure tannin.

30 c.c. of $\frac{N}{30}$ permanganate will therefore represent 0·063 gm. of oxalic acid or the weights of tannin above mentioned.

*Solution of Indigo-Carmine.*—This should be a clear solution of about 5 gm. to the liter with about 50 c.c. of pure $H^2SO^4$.

*Solution of Gelatine.*—This solution is used to precipitate the available tannin in any given solution after its total oxidizable matters have been determined by the indigo and permanganate. It should be made fresh for each series of titrations, by dissolving 2 gm. of Nelson's gelatine in 100 c.c. of water and filtering.

*Dilute Sulphuric Acid.*—1 : 10.

*Processes of Titration:* The first thing to be done is to ascertain the relationship between the permanganate and indigo solutions (it is assumed that the permanganate is correct as regards its relation to oxalic acid), and therefore 10 or 20 c.c. of the indigo are measured into a white porcelain basin, and diluted to $\frac{3}{4}$ of a liter with distilled water, or good ordinary water free from organic matter or other substances capable of reducing permanganate. 10 c.c. of the dilute acid are measured in, and the permanganate delivered in with a hand-pipette in drops, with constant stirring, until the colour is just discharged, leaving a clear faint yellow tint, with just a shade of pink at the rim.

This experiment will act as a guide to the final adjustment of the indigo with an accurate 30 c.c. burette in $\frac{1}{10}$, which should be of such dilution that about 20 c.c. correspond to about 15 c.c. of permanganate.

*Titration of the Tanning Material:* It is very important, in order to avoid uncertainty in the end-point of the reaction, that only so much material shall be used as shall consume about 7 or 8 c.c. of permanganate of $\frac{N}{30}$ strength above that point which is required for the indigo.

Procter and Kathreiner both insist upon these proportions, and the general method adopted by them is to add 20 c.c. of indigo with 10 c.c. of dilute acid to about $\frac{3}{4}$ of a liter of water, in a porcelain dish, followed by 5 c.c. of tannin solution. The permanganate is then delivered in very slowly, with constant stirring, until a faint rose colour appears round the edges of the liquid. The time allowed for the titration is also very important.

Von Schröder, representing the Association of German Tanners, prefers to add the permanganate 1 c.c. at a time with vigorous stirring, until the colour of the liquid indicates that a few drops only are required to end the titration. Procter, on the other hand, prefers the rapid drop method for the commencement, and until near the end. He also finds that the method of stirring influences the result in no very slight degree. Whatever plan the operator adopts, it is advisable to keep consistently to it in order that the results may be comparatively the same.

It must be remembered that neither by this nor any other method is it possible to accurately estimate the tannin, but only as a means of comparing two samples of the same material.

*Precipitation of the Tannin, and subsequent Titration of Substances other than Tannin.*—Procter's procedure is to take 50 c.c. of the tannin infusion (5 c.c. of which has been titrated), and add to it 28·6 c.c. of gelatine solution in a flask holding about 150 c.c. The mixture is well shaken, then saturated with clean table salt, and 10 c.c. of the dilute acid added, together with a teaspoonful of kaolin: the whole is vigorously shaken, then filtered, and made up to exactly 100 c.c. 10 c.c. of this liquid, representing 5 c.c. of the tannin decoction, is then titrated in precisely the same manner as before. The calculation of percentage is then made as follows: Let the first titration (two of which should be made for security) be called $a$; the second, also in duplicate, $b$. If further, $c$ be the quantity of permanganate required to oxidize 10 c.c. of $\frac{N}{10}$ oxalic acid, and 10 gm. of substance have been employed for 1 liter of decoction, then $c : (a-b) :: 6·3 : x$, where $x$ is the percentage of tannin expressed in terms of oxalic acid.

Hunt, who is also an undoubted authority on tannin estimation, differs from Procter on the question of saturating the liquid for final titration with salt (*J. C. S. I.* iv. 263), on the ground that, in the case of material containing much gallic acid, some of it is precipitated with the tannin, thus leading to higher results. This he has proved by experiment, and therefore prefers to act as follows:—

50 c.c. of the tannin solution are run into a small dry flask, to this 25 c.c. of the fresh filtered gelatine solution are added, and the flask shaken. 25 c.c. of a saturated solution of salt, containing 50 c.c. of strong $H^2SO^4$ per liter, are now added, and about a teaspoonful of kaolin or baric sulphate. The flask is thoroughly shaken for a few minutes, after which a clear bright filtrate may be obtained.

For materials containing over 45 per cent. tannin, it is advisable to take 25 c.c. instead of 50, and to use 50 c.c. of salt, the amount of gelatine solution being the same. The same authority also states that, for gambier and its allies, the method of titration as above described does not give accurate results, inasmuch as the gelatine and salt do not remove all the substances of tanning value from the liquid. In such case it is necessary to digest the liquid for at least twelve hours with pure dry skin shavings in powder. The mixture is then filtered and titrated in the usual way.

It is impossible to give here the opinions held by various authorities on this subject, therefore the reader who desires fuller information should consult the papers to which reference has been made.

The following table given by Hunt is however appended, as the result of careful working, and as a guide to the nature of various tanning materials:—

The "total extract" in the table was determined by evaporating a portion of the tannin solution to dryness in a small porcelain basin and drying the residue at 110° C. The "insoluble matter" was also dried at 110° C.

| NAME OF MATERIAL. | Total matters oxidized by Permanganate, as Oxalic Ac. | Tannin, as Oxalic Ac. (Procter) | Tannin, as Oxalic Ac, (Hunt) | Total Extract. | Insoluble. |
|---|---|---|---|---|---|
| | per cent. | per cent. | per cent. | per cent. | per cent. |
| English Oak Bark ... | 15·70 | 13·54 | 11·97 | 18·38 | 66·15 |
| Canadian Hemlock Bark | 9·03 | 7·46 | 7·08 | 13·96 | 75·25 |
| Larch Bark ... ... | 8·20 | 7·17 | 6·15 | 20·64 | 60·80 |
| Mangrove Bark ... ... | 31·35 | 29·71 | 28·48 | 26·60 | 49·70 |
| Alder Bark ... ... | 8·27 | 6·15 | 5·73 | 19·36 | 68·00 |
| Blue Gum Bark ... | 10·18 | 8·91 | 8·91 | 11·76 | 74·65 |
| Valonia ... ... ... | 37·41 | 35·24 | 30·50 | 38·50 | 46·05 |
| Myrabolans ... ... | 48·23 | 38·43 | 38·00 | 42·80 | — |
| Sumach ... ... ... | 42·53 | 34·30 | 31·46 | 44·10 | 47·77 |
| Betel Nut ... ... ... | 15·91 | 13·87 | 13·79 | 17·94 | 67·00 |
| Turkish Blue Galls ... | 73·38 | 65·83 | 59·96 | 48·40 | 36·35 |
| Aleppo Galls ... ... | 98·85 | 87·82 | 83·05 | 68·80 | 14·32 |
| Wild Galls ... ... ... | 26·21 | 18·75 | 16·56 | 31·70 | 54·17 |
| Divi-Divi ... ... ... | 66·98 | 62·62 | 61·22 | 54·38 | 29·90 |
| Balsamocarpon (poor and old sample) ... | 50·49 | 37·76 | 32·88 | 57·14 | 28·25 |
| Pomegranate Rind ... | 27·58 | 24·18 | 23·12 | 41·00 | 49·50 |
| Tormentil Root ... ... | 22·27 | 20·98 | 20·68 | 19·70 | 67·95 |
| Rhatany Root ... ... | 22·27 | 20·15 | 19·30 | 18·80 | 66·00 |
| Pure Indian Tea ... | 23·06 | 18·65 | 17·40 | 34·46 | 53·40 |
| Pure China Tea ... | 18·03 | 14·21 | 14·09 | 24·50 | 62·60 |
| Cutch ... ... ... ... | 57·65 | 51·95 | 44·24 | 61·60 | 4·75 |
| Gum Kino ... ... ... | 66·39 | 59·55 | 51·55 | 79·30 | 1·00 |
| Hemlock Extract ... | 35·16 | 33·17 | 30·98 | 48·78 | — |
| Oakwood Extract ... | 33·49 | 26·90 | 23·86 | 37·78 | — |
| Chestnut Extract ... | 39·77 | 32·63 | 28·88 | 50·28 | — |
| Quebracho Extract ... | 48·22 | 44·45 | 40·84 | 49·00 | — |
| "Pure Tannin" ... | 135·76 | 122·44 | 121·93 | — | — |
| Tan Liquor, sp. gr. 1·030 | 4·84 | 3·14 | 2·10 | 6·01 | — |
| Spent Tan Liquor, sp. gr. 1·0165 ... ... | 1·40 | 0·37 | 0·25 | 3·10 | — |
| | | | Absorbed by Dry Pure Skin. | | |
| Gambier, Cube ... ... | 70·12 | — | 51·07 | 74·40 | 5·31 |
| „ Sarawak ... | 63·13 | — | 47·09 | 70·70 | 3·67 |
| „ Bale ... ... | 56·00 | — | 43·70 | 63·54 | 1·40 |

### Other Methods of Estimating Tannin.

*Direct Precipitation by Gelatine.*—The difficulty existing with this method is that of getting the precipitate to settle, so that it may be clearly seen when enough gelatine has been added.

Tolerably good results may sometimes be obtained by using a strong solution of sal ammoniac or chrome alum as an adjunct. The best aid is probably barium sulphate, 2 or 3 gm. of which should be added to each portion of liquid used for titration.

*The Standard Solution of Gelatine* should contain 1·33 gm. of dry gelatine per liter, in which is also mixed 100 c.c. of cherry laurel water to preserve it. 45 c.c. = 0·05 gm. tannin (Carles). This method is adapted only for rough technical purposes, as also the following.

*Direct Precipitation by Antimony.*—This method is still in favour with some operators; but, like the gelatine process, is beset with the difficulty of getting the precipitate to settle.

*The Standard Antimony Solution* is made by dissolving 2·611 gm. of crystals of emetic tartar dried at 100° C. in a liter. 1 c.c. = 0·005 gm. tannin. 50 c.c. of the tannin solution may be taken for titration, to which is added 1 or 2 gm. of sal ammoniac, and the antimonial solution run in until no further cloudiness is produced.

In both the above methods the final tests must either be made by repeatedly filtering small portions to ascertain whether the precipitation is complete, or by bringing drops of each liquid together on black glass or a small mirror.

## TIN.

Sn = 118.

| | | |
|---|---|---|
| Metallic iron | × | 1·0536 = Tin. |
| Double iron salt | × | 0·1505 = „ |
| Factor for $\frac{N}{10}$ iodine or permanganate solution | | 0·0059 |

§ 76. The method, originally devised by Streng, for the direct estimation of tin by potassic bichromate, or other oxidizing agents in acid solution, has been found most unsatisfactory, from the fact that variable quantities of water or acid seriously interfere with the accuracy of the results. The cause is not fully understood, but that it is owing partly to the oxygen mechanically contained in the water reacting on the very sensitive stannous chloride, there can be very little doubt, as the variations are considerably lessened by the use of water recently boiled and cooled in closed vessels. These difficulties are set aside by the processes of Lenssen, Löwenthal, Stromeyer, and others, now to be described, and which are found fairly satisfactory.

### 1. Direct Titration by Iodine in Alkaline Solution (Lenssen).

Metallic tin or its protosalt, if not already in solution, is dissolved in hydrochloric acid, and a tolerable quantity of Rochelle salt added, together with sodic bicarbonate in excess. If enough tartrate be present, the solution will be clear; starch is then added, and the mixture titrated with $\frac{N}{10}$ iodine. Metallic tin is best dissolved in HCl by placing a platinum crucible or cover in contact with it, so as to form a galvanic circuit.

Benas (*Chem. Centr-blatt.* li. 957) points out that the chief error in the estimation as above arises from oxygen dissolved in the liquid, or absorbed during the operation. In order to obtain constant results, it is necessary to dissolve the tin compound in HCl, dilute with oxygen free water, and add at once excess of standard iodine, which excess is found by residual titration with standard thiosulphate.

### 2. Indirect Titration by Ferric Chloride and Permanganate (Lowenthal, Stromeyer, etc.).

This method owes its value to the fact, that when stannous chloride is brought into contact with ferric or cupric chloride, it acts as a reducing agent, in the most exact manner, upon these compounds, stannic chloride being formed, together with a proportionate quantity of ferrous or cuprous salt, as the case may be. If either of the latter be then titrated with permanganate, the original quantity of tin may be found, the reaction being, in the case of iron,—

$$SnCl^2 + Fe^2Cl^6 = SnCl^4 + 2FeCl^2.$$

56 iron = 59 tin. If decinormal permanganate, or the factor necessary to convert it to that strength, be used, the calculation by means of iron is not necessary.

*The Analysis:* The solution of stannous chloride, or other protosalt of tin in HCl, or the granulated metal, is mixed with pure ferric chloride, which, if tolerably concentrated, dissolves metallic tin readily, and without evolution of hydrogen, then diluted with distilled water, and titrated with permanganate as usual. To obtain the most exact results, it is necessary to make an experiment with the same permanganate upon a like quantity of water, to which ferric chloride is added; the quantity required to produce the same rose colour is deducted from the total permanganate, and the remainder calculated as tin.

Stannic salts, also tin compounds containing iron, are dissolved in water, HCl added, and a plate of clean zinc introduced for ten or twelve hours; the tin so precipitated is carefully collected and washed, then dissolved in HCl, and titrated as above; or the finely divided metal may at once be mixed with an excess of ferric chloride, a little HCl added, and when solution is complete, titrated with permanganate. 4 eq. of iron (=224) occurring in the form of ferrous chloride represent 1 eq. (=118) of tin.

Tin may also be precipitated from slightly acid peroxide solution as sulphide by $H^2S$, the sulphide well washed, and mixed with ferric chloride, the mixture gently warmed, the sulphur filtered off, and the filtrate then titrated with permanganate as above. 4 eq. of iron = 1 eq. of tin.

*Tin Ore.*—In the case of analysis of cassiterite, Arnold (*C. N.* xxxvi. 238) recommends that 1 gm. of the very finely powdered mineral be heated to low redness for two hours in a porcelain boat in a glass tube with a brisk current of dry and pure hydrogen gas, by which means the metal is reduced to the metallic state. It is then dissolved in acid ferric chloride, and titrated with permanganate or bichromate in the usual way.

## URANIUM.

Ur=240.

§ 77. The estimation of uranium may be conducted with great accuracy by permanganate, in precisely the same way as ferrous salts (§ 59). The metal must be in solution either as acetate, sulphate, or chloride, but not nitrate. In the latter case it is necessary to evaporate to dryness with excess of sulphuric or hydrochloric acid, or to precipitate with alkali, wash and redissolve in acetic acid.

The reduction to the uranous state is made with zinc, but as the end of reduction cannot, like iron, be known by the colour, it is necessary to continue the action for a certain time; in the case of small quantities a quarter, larger half an hour, at a temperature of 50° to 60° C., and in the presence of excess of sulphuric acid; all the zinc must be dissolved before titration. The solution is then freely diluted with boiled water, sulphuric acid added if necessary, and then permanganate until the rose colour is faintly permanent. The ending is distinct if the solution be well diluted, and the reaction is precisely the same as in the case of ferrous salts; namely, 2 eq. of uranium existing in the uranous state require 1 eq. of oxygen to convert them to the uranic state; hence 56 Fe=120 Ur, consequently the strength of any permanganate solution in relation to iron being known, it is easy to find the amount of uranium.

## ZINC.

Zn = 65.

1 c.c. $\frac{N}{10}$ solution=0·00325 gm. Zinc.
Metallic iron × 0·5809 = Zinc.
" × 0·724 = Zinc oxide.
Double iron salt × 0·08298 = Zinc.
" " × 0·1034 = Zinc oxide.

### 1. Indirect Method (Mann).

§ 78. This process gives exceedingly good results, and consists in precipitating the zinc as hydrated sulphide, decomposing the sulphide with moist silver chloride, then estimating the zinc chloride so formed with ammonic sulphocyanate as in Volhard's method (§ 39).

The requisite materials are—

*Silver Chloride.*—Well washed and preserved from the light under water.

*Standard Silver Nitrate.*—33·18 gm. of pure silver, dissolved in nitric acid and made up to 1 liter, or 52·3 gm. silver nitrate per liter. If made direct from silver, the solution must be well boiled to dissipate nitrous acid. 1 c.c. = 0·01 gm. of zinc.

*Ammonic Sulphocyanate.*—Of such strength that exactly 3 c.c. suffice to precipitate 1 c.c. of the silver solution.

*Ferric Indicator* and *Pure Nitric Acid* (see § 39.3 and 4).

*The Analysis:* 0·5 to 1 gm. of the zinc ore is dissolved in nitric acid. Heavy metals removed by $H^2S$, iron and alumina by double precipitation with ammonia. The united filtrates are acidified with acetic acid, and $H^2S$ passed into the liquid until all zinc is precipitated as sulphide. Excess of $H^2S$ is removed by rapid boiling, so that a drop or two of the filtered liquid gives no further stain on lead paper. The precipitate is then allowed to settle, decanted while hot, the precipitate brought in a filter with a little hot water, and without further washing, the filter with its contents is transferred to a small beaker, 30—50 c.c. of hot water added, well stirred, and so much moist silver chloride added as is judged necessary to decompose the sulphide, leaving an excess of silver. The mixture is now boiled till it shows signs of settling clear; 5 or 6 drops of dilute sulphuric acid (1 : 5) are added to the hot mixture, and in a few minutes the whole of the zinc sulphide will be converted into zinc chloride. The free sulphur and excess of silver chloride are now filtered off, washed, and the chloride in the mixed filtrate and washings estimated as follows:—

To the cool liquid, measuring 200 or 300 c.c., are added 5 c.c. of ferric indicator, and so much pure nitric acid as is necessary to remove the yellow colour of the iron. A measured excess of the standard silver solution is then delivered in with the pipette, and without filtering off the silver chloride, or much agitation, so as to clot the precipitate, the sulphocyanate is cautiously added, with a gentle movement after each addition, until a permanent light brown colour appears.

The volume of silver solution represented by the sulphocyanate being deducted from that originally used, will give the volume to be calculated to zinc, each c.c. being equal to 0·01 gm. Zn.

### 2. Precipitation as Sulphide and subsequent titration with Ferric Salts and Permanganate (Schwarz).

The principle of this method is based on the fact, that when zinc sulphide is mixed with ferric chloride and hydrochloric acid, or better still, with ferric sulphate and sulphuric acid, ferrous or zinc chloride, or sulphates respectively, and free sulphur are produced. If the ferrous salt so produced is estimated with permanganate or bichromate, the proportional quantity of zinc present is ascertained. 2 eq. Fe represent 1 eq. Zn.

*Preparation of the Ammoniacal Zinc Solution.*—In the case of rich ores 1 gm., and poorer qualities 2 gm., of the finely powdered material are placed into a small wide-mouthed flask, and treated with HCl, to which a little nitric acid is added, the mixture is warmed to promote solution, and when this has occurred the excess of acid is evaporated by continued heat. If lead is present, a few drops of concentrated sulphuric acid are added previous to complete dryness, in order to render the lead insoluble; the residue is then extracted with water and filtered. Should metals of the fifth or sixth group be present, they must be removed by $H^2S$ previous to the following treatment. The solution will contain iron, and in some cases manganese. If the iron is not already fully oxidized, the solution must be boiled with nitric acid; if only traces of manganese are present, a few drops of bromized HCl should be added. When cold, the solution may be further diluted if necessary, and then supersaturated with ammonia to precipitate the iron; if the proportion of this metal is small, it will suffice to filter off and wash the oxide with ammoniacal warm water, till the washings give no precipitate of zinc on adding ammonic sulphide. Owing to the fact that this iron precipitate tenaciously holds about a fifth of its weight of zinc, it will be necessary when the proportion is large to redissolve the partly washed precipitate in HCl, and reprecipitate (best as basic acetate); the filtrate from this second precipitate is added to the original zinc filtrate, and the whole made up to a liter.

*The Analysis:* The ammoniacal zinc solution (prepared as described above) is heated, and the zinc precipitated in a tall beaker, with a slight excess of sodic or ammonic sulphide, then covered closely with a glass plate, and set aside in a warm place for a few hours. The clear liquid is removed by a syphon, and hot water containing some ammonia again poured over the precipitate, allowed to settle, and again removed, and the washing by decantation repeated three or four times; finally, the precipitate is brought upon a tolerably large and porous filter, and well washed with warm water containing ammonia, till the washings no longer discolour an alkaline lead solution. The filter pump may be used here with great advantage.

The filter with its contents is then pushed through the funnel into a large flask containing a sufficient quantity of ferric sulphate mixed with sulphuric acid, immediately well stopped or corked, gently shaken, and put into a warm place; after some time it should be again well shaken, and set aside quietly for about ten minutes. After the action is all over the mixture should possess a yellow colour from the presence of undecomposed ferric salt; when the cork or stopper is lifted there should be no odour of $H^2S$. The flask is then nearly filled with cold distilled water, if necessary some dilute sulphuric acid added, and the contents of the flask titrated with permanganate or bichromate as usual.

The free sulphur and filter will have no reducing effect upon the permanganate if the solution be cool and very dilute.

### 3. Precipitation by Standard Sodic Sulphide, with Alkaline Lead Solution as Indicator (applicable to most Zinc Ores and Products).

*The Ammoniacal Solution of Zinc* is prepared just as previously described in Schwarz's method.

*The Standard Sodic Sulphide* is made by saturating a portion of caustic soda solution with $H^2S$, then adding sufficient soda to remove the odour of the free gas, and diluting the whole to a convenient strength for titrating. Pure crystals of $Na^2S$ dissolved in water answer equally well.

*The Standard Zinc Solution* is best made by dissolving 44·12 gm. of pure zinc sulphate to the liter. 1 c.c. will then contain 0·010 gm. of metallic zinc, and upon this solution, or one prepared from pure metallic zinc of the same strength, the sulphide solution must be titrated.

*The Alkaline Lead Solution* used as indicator is made by heating together acetate of lead, tartaric acid, and caustic soda solution in excess, until a clear solution is produced. It is preferable to mix the tartaric acid and soda solution first, so as to produce sodic tartrate; or if the latter salt is at hand, it may be used instead of tartaric acid. Some operators use sodic nitroprusside instead of lead.

*The Analysis:* 50 c.c. of zinc solution (=0·5 gm. Zn) are put into a beaker, a mixture of solutions of ammonia and ammonic carbonate (3 of the former to about 1 of the latter) added in sufficient quantity to redissolve the precipitate which first forms. A few drops of the lead solution are then, by means of a glass rod, placed at some distance from each other, on filtering paper, laid upon a slab or plate.

The solution of sodic sulphide contained in an ordinary Mohr's burette is then suffered to flow into the zinc solution until, on bringing a drop from the mixture and placing it upon the filtering paper, so that it may expand and run into the drop of lead solution, a black line occurs at the point of contact; the reaction is very delicate. At first it will be difficult, probably, to hit the exact point, but a second trial with 25 or 50 c.c. of zinc solution will enable the operator to be certain of the corresponding strength of the sulphide solution. As this latter is always undergoing a slight change, it is necessary to titrate occasionally.

Direct titration with pure zinc solution gave 99·6 and 100·2, instead of 100.

Groll recommends the use of protochloride of nickel as indicator, instead of sodic nitroprusside or lead. The drops are allowed to flow together on a porcelain plate; while the point of contact shows a blue or green colour the zinc is not all precipitated by the sodic sulphide, therefore the latter must be added until a greyish black colour appears at contact.

Another indicator is paper soaked in a nearly neutral dilute solution of cobaltous chloride, which when dry and cold is colourless. When touched with a drop of liquid containing sodic sulphide it turns to a green tint, rapidly becoming brown when warmed.

### 4. Precipitation as Sulphide with Ferric Indicator (Schaffner).

Schaffner's modification of this process, and which is used constantly at the laboratory of the Vieille Montagne and the

Rhenish Zinc Works, is conducted as follows:—For ores containing over 35 per cent. zinc, 0·5 gm. is taken; for poorer ones, 1 gm. to 2 gm. Silicates, carbonates, or oxides, are treated with hydrochloric acid, adding a small proportion of nitric acid at boiling heat to peroxidize the iron. Sulphur ores are treated with *aqua regia*, evaporated to dryness, and the zinc afterwards extracted by hydrochloric acid; the final ammoniacal solution is then prepared as described on page 289.

*The Analysis:* The titration is made with a solution of sodic sulphide, 1 c.c. of which should equal about 0·01 gm. Zn. The Vieille Montagne laboratory uses ferric chloride as an indicator, according to Schaffner's method. For this purpose a single drop or some few drops of this chloride are let fall into the ammoniacal solution of zinc. The iron which has been added is at once converted into red flakes of hydrated ferric oxide, which float at the bottom of the flask. If sodic sulphide be dropped from a burette into the solution of zinc, a white precipitate of zinc sulphide is at once thrown down, and the change in the colour of the flakes of iron from red to black shows the moment when all the zinc is sulphuretted, and the titration is ended. It is advisable to keep the solution for titration at from 40 to 60° C. Titration carried out under exactly equal conditions, with a known and carefully weighed proportion of zinc, gives comparative data for calculation, and thus for the determination of the contents of any zinc solution by means of a simple equation. If, for example, 30·45 c.c. of sodic sulphide have been used to precipitate 0·25 gm. of zinc, 1 c.c. of it will precipitate 8·21 m.gm. of zinc ($30{\cdot}45 : 0{\cdot}25 = 1 : x$, and therefore $x = 0{\cdot}00821$).

Practice has pointed out the following concentrations and proportions as best suited for the successful execution of these titrations.

The sodic sulphide solution which is used for titration must be such that 1 c.c. precipitates 8 to 10 m.gm. of zinc. The solution which contains the zinc which has to be estimated will comply with the best conditions, if its volume varies between the limits of 175 and 225 c.c. It is advisable that all solutions of zinc should be pretty equally saturated with ammonia, so that the ferric chloride added as an indicator may be precipitated in the same manner in all samples, and so that the flakes of iron may be always clean and clear.

The essential point of the volumetric process practised at the Vieille Montagne is the perfect uniformity of working adopted in the assays with reference to the volume of the solutions and re-agents used and the colour of the indicator. In titrating, the same quantities of ferric chloride, hydrochloric acid and ammonia are steadily used. Work is done always at one temperature and in the same time, particularly at the end of the operation, when the iron begins to take on that characteristic colour which the flakes take at the edges—points which should not be overlooked. As a further precaution, the titrating apparatus is provided in duplicate, two assays being always made. It permits the execution of several titrations without the necessity of a too frequent renewal of sodic sulphide which is stored in a yellow flask of large capacity supplying two Mohr's burettes, under which the beakers can be placed and warmed. A mirror shows by reflection the iron flakes which settle down after shaking the liquid.

Lunge uses for the indicator paper soaked with basic ferric chloride, strips of which are so suspended during titration that about half the strip dips into the liquid.

Too much stress cannot be laid upon the necessity of standardizing the sodic sulphide under the same conditions as to volume of fluid, proportions of $NH^3$ and HCl, and colour of the indicator, as will actually occur in the analysis.

### 5. Estimation as Ferrocyanide.

*In Acetic Acid Solution* (Galetti). When ores containing zinc and iron are dissolved in acid, and the iron precipitated with ammonia, the ferric oxide invariably carries down with it a portion of zinc, and it is only by repeated precipitation that the complete separation can be made. In this process the zinc is converted into soluble acetate, and titrated by a standard solution of potassic ferrocyanide in the presence of insoluble ferric acetate.

*The Standard Solution of Potassic Ferrocyanide*, as used by Galetti, contains 41·250 gm. per liter. 1 c.c. = 0·01 gm. Zn, but its actual working power must be fixed by experiment.

*Standard Zinc Solution*, 10 gm. of pure metallic zinc per liter dissolved in hydrochloric acid.

The process is available in the presence of moderate quantities of iron and lead, but copper, manganese, nickel, and cobalt must be absent, or previously removed.

The adjustment of the ferrocyanide solution (which should be freshly prepared at short intervals) must be made in precisely the same way, and with the same volume of liquid as the actual analysis of ores, and is best done as follows:—

25 c.c. of zinc solution are measured into a beaker, 15 c.c. of liquid ammonia of sp. gr. 0·900 added to render the solution alkaline, then very cautiously acidified with acetic acid, and 50 c.c. of acid ammonic acetate (made by adding together 20 c.c. of ammonia of sp. gr. 0·900, 15 c.c. of concentrated acetic acid and 65 c.c. of distilled water), which is poured into the mixture, then diluted to 250 c.c., and warmed to about 50° C. The titration is then made with the ferrocyanide solution by adding it from a burette until the whole of the zinc is precipitated. Galetti judges the ending of the process from the first change of colour from white to ash grey, which occurs when the ferrocyanide is in excess; but I prefer to ascertain the ending by taking drops from the solution, and bringing them in contact with solution of uranic acetate on a white plate until a faint brown colour appears. The ferrocyanide solution should be of such strength that measure for measure it agrees with the standard zinc solution. In the present case 25 c.c. would be required.

In examining ores of zinc, such as calamine and blende, Galetti takes 0·5 gm. for the analysis, and makes the solution up to 500 c.c. Calamine is at once treated with HCl in sufficient quantity to bring it into solution. Blende is treated with *aqua regia*, and evaporated with excess of HCl to remove nitric acid. The solutions of zinc so obtained invariably contain iron, which together with the zinc is kept in solution by the HCl, but to insure the peroxidation of the iron, it is always advisable to add a little potassic chlorate at a boiling heat during the extraction of the ore. The hydrochloric solution is then diluted to about 100 c.c., 30 c.c. of ammonia added, heated to boiling, exactly neutralized with acetic acid, 100 c.c. of the acid ammonic acetate poured in, and diluted to about 500 c.c. The mixture as prepared will contain all the zinc in solution, and the iron will be precipitated as acetate. The titration may at once be proceeded with at a temperature of about 50° to 60° C. by adding the ferrocyanide until the necessary reaction with uranium is obtained. As before mentioned, Galetti takes the change of colour as the ending of the process, and when iron is present this is quite distinguishable, but it requires considerable practice to rely upon, and it is therefore safer to use the uranium indicator. When using the uranium, however, I prefer to dilute the zinc solution less, both in the adjustment of the standard ferrocyanide and the analysis of ores. The dilution is necessary with Galetti's method of ending the process, but half the volume of liquid, or even less, is better with the external indicator.

*In Hydrochloric Acid Solution* (Fahlberg and Maxwell Lyte). This method is not available in the presence of iron, copper, nickel, cobalt, or manganese.

*The Standard Solution of Ferrocyanide* is made of such strength, that 1 c.c. = 0·01 gm. of zinc. Lyte finds that this is obtained by dissolving 43·2 gm. of pure potassic ferrocyanide and diluting to 1 liter. This corresponds volume for volume with a solution of 10 gm. of pure zinc in excess of hydrochloric acid diluted to 1 liter. My experiments confirm this, but each operator is advised to adjust his solutions by experiment, always using the same quantities of re-agents and volume of liquid. The end of the reaction between the zinc and ferrocyanide is found by uranium.

*The Analysis:* If a solution of zinc freely acidified with HCl is heated to nearly boiling point, two or three drops of uranic solution added, and the ferrocyanide delivered into the mixture from a burette, white zinc ferrocyanide immediately precipitates, and as the drops of ferrocyanide fall into the mixture, a brown spot of uranic ferrocyanide appears, but disappears again on stirring so long as free zinc exists in solution. The moment all the zinc is converted into ferrocyanide, the addition of test solution tinges the whole liquid brown. This addition of uranium to the liquid may be used as a guide to the final testing on a porcelain plate, since as the precipitation approaches completion, the tinge of brown disappears more slowly. The actual ending, however, is always ascertained by spreading a drop or two of the liquid upon the plate, bringing into contact with it a glass rod moistened with uranic solution; when the same shade of colour is produced as occurred in the original titration of the ferrocyanide solution, the process is ended.

Lyte gives the following method of treating a blende containing lead, copper, and iron (*C. N.* xxi. 222):—

2 gm. of finely powdered ore were boiled with strong HCl and a little $KClO^3$, the insoluble matter again treated in like manner, the solutions mixed and evaporated somewhat, washed into a beaker, cooled, and moist baric carbonate added to precipitate iron, allowed to stand a few hours, then filtered into a 200 c.c. flask containing 10 c.c. of strong HCl, and washed until the exact measure was obtained. 20 c.c. (=0·2 gm.) of blende were measured into a small beaker, diluted with the same quantity of water, 3 drops of uranic solution added, and the ferrocyanide delivered in from a burette. When 70 c.c. were added the brown tinge disappeared slowly; the testing on a white plate was then resorted to, and the ferrocyanide added drop by drop until the proper effect occurred at 73 c.c. As a slight excess of ferrocyanide was necessary to produce the brown colour, 0·2 c.c. was deducted, leaving 72·8 c.c. as the quantity necessary to precipitate all the zinc. The 0·2 gm. of blende therefore contained 0·0728 gm. of Zn or 36·4 per cent.

The sample in question contained about 2·7 per cent. of copper, but this was precipitated with the iron by the baric carbonate; had it contained a larger quantity, the process would not have been available unless the copper was removed by other means.

Fahlberg (*Z. a. C.* 1874, 379) estimates the zinc in hydrochloric solution with ferrocyanide and uranic indicator, but recommends the addition of ammonic chloride to the extent of about five times the weight of zinc present. With the well-known retarding effect of ammonia salts on the uranium re-action, the operator must be careful to carry out his analysis precisely in the same way as the original titration.

Ores containing galena or copper are treated with *aqua regia*, then boiled with excess of HCl, the heavy metals precipitated with $H^2S$ and filtered off, the iron peroxidized with $HNO^3$ or $KClO^3$, cooled, precipitated with ammonia, dissolved and re-precipitated twice, to remove all zinc. The ammoniacal solutions are then mixed, neutralized with HCl, 10 or 15 c.c. of concentrated HCl added, then titrated with ferrocyanide.

Fahlberg stated in his original paper that the process yields good results with ores containing lead, copper, manganese, and iron; but this is certainly not true as to manganese, and he has since acknowledged the fact. He states, however, that if moist brown lead dioxide is shaken up with the sulphuric solution of Zn, the whole of the Fe and Mn are precipitated.

The liquid is filtered off, precipitate washed, then filtrate and washings titrated with ferrocyanide.

Mahon (*Amer. Chem. Journ.* iv. 53) uses the ferrocyanide method much in the same way as above described, but finds that Mn must be absent to ensure good results. In the presence of Mn he separates the Zn from a strong acetic solution with $H^2S$. The sulphide is then dissolved in HCl and titrated as before.

### 6. Estimation of Zinc as Oxalate.

This method is based on the fact that all the metals of the magnesia group are precipitated in the absence of alkaline salts by oxalic acid, with the addition of alcohol. The cases are very few in which such a method can be made available, but the process as described by W. G. Leison (*Silliman's Journ.*, Sept. 1870) is here given.

The zinc compound is obtained, preferably as sulphate, in neutral solution, and strong solution of oxalic acid and a tolerable quantity of strong alcohol are added. Zinc oxalate quickly separates in a fine crystalline powder, which when washed by alcohol from excess of oxalic acid and dried, can be dissolved in hot dilute sulphuric acid, and titrated with permanganate; the amount of zinc is calculated from the weight of oxalic acid so found. If the zinc oxalate be washed on a paper filter, it cannot be separated from the paper without contamination with fibres of that material, which would of course affect to some extent the permanganate solution. Hence it is advisable to filter through very clean sand, best done by a special funnel ground conical at the throat; into this is dropped a pear-shaped stopper with a long stem, the pear-shaped stopper fitting the funnel throat tightly enough to prevent sand but not liquids from passing; a layer of sand being placed upon the globular end of the stopper and packed closely, the liquid containing the oxalate is brought upon it and so washed; finally the stopper is lifted, the sand and oxalate washed through with dilute acid into a clean flask, and the titration completed.

## VANADIUM.

$V=51{\cdot}2$.

§ 79. VANADIUM salts, or the oxides of this element, may be very satisfactorily titrated by reduction with a standard ferrous solution; thus—

$$2FeO+VO^5=Fe^2O^3+VO^4.$$

1 gm. of Fe represents 1·630357 gm. of vanadic pentoxide.

Lindemann (*Z. a. C.* xviii. 99) recommends the use of a solution of ferrous ammonio-sulphate (double iron salt) standardized by $\frac{N}{10}$ potassic bichromate.

Of course it is necessary that the vanadium compound should be in the highest state of oxidation, preferably in pure sulphuric acid solution. The blue colour of the tetroxide in the dilute liquid has no misleading effect in testing with ferridcyanide.

With hydrochloric acid great care must be taken to insure absence of free Cl or other impurities. The end-point in the case of this acid is different from that with sulphuric acid, owing to the colour of the ferric chloride, the mixture becoming clear green.

The accuracy of the reaction is not interfered with by ferric or chromic salts, alumina, fixed alkalies, or salts of ammonia.

Vanadic solutions being exceedingly sensitive to the action of reducing agents (see § 31.2*f*), great care must be exercised to exclude dust or other carbonaceous matters, alcohol, etc.

## APPENDIX TO PART V.

### BORIC ACID AND BORATES.

Boric Anhydride $B^2O^3=70$.

§ 80. THE soda in borax may, according to Thompson, be very accurately estimated by titrating the salt with standard $H^2SO^4$ and methyl orange or lacmoid paper. Litmus and phenacetolin give very doubtful end-reactions: phenolphthalein is utterly useless.

*Example:* 1·683 gm. sodic pyroborate in 50 c.c. of water required in one case 16·7 c.c. normal acid, and in a second 16·65 c.c. The mean of the two represents 0·517 gm. $Na^2O$. Theory requires 0·516 gm.

Since borates are now much used as preservative agents, a method which may be relied upon for technical purposes will be of considerable service, and such is described by E. F. Smith (*Amer. Chem. Journ.* 1882). The process depends on the fact, that if a solution of manganese sulphate is added to one of borax, then alcohol in equal volume, a white flocculent precipitate of $MnB^4O^7$ separates, which is insoluble in the alcoholic liquid. The excess of manganese sulphate is then determined after expulsion of the alcohol by permanganate, according to Guyard's or Volhard's method (§ 64.2).

*Example:* 10 c.c. of borax solution containing 0·1 gm.; to this were added 10 c.c. of solution of manganese sulphate containing 0·06 gm. $MnSO^4$ and 20 c.c. of strong alcohol. The mixture was well stirred, covered up, and allowed to stand for half an hour; then filtered (best with suction pump) and well washed with alcohol. Filtrate and washings then evaporated to dryness in a platinum or porcelain basin.

The residual Mn was then dissolved in water, some strong solution of zinc sulphate added, heated near to boiling, and permanganate delivered in from a burette until a permanent pink colour was produced. The strength of the permanganate was such that 18·5 c.c.=10 c.c. of $MnSO^4$ solution by the same method of titration. The amount of $MnSO^4$ so found deducted from that originally added gave the amount combined with the boracic acid.

In this instance 6·4 c.c. of permanganate were required=0·0207 gm., showing 0·0393 gm. to be combined=36·44 per cent. $B^2O^3$. Theory requires 36·6 per cent.

A mean of eighteen determinations gave 36·5 per cent. of $B^2O^3$ in the sample of pure borax. The method is therefore very fairly accurate for soluble borates.

In estimating the boracic acid in insoluble borates, as tourmaline, the following course was pursued:—

The finely pulverized substance was fused with a weighed quantity of pure sodic carbonate, the fused mass exhausted with water, and to the filtrate containing all the sodic borate, together with some silicate and aluminate, was added an amount of pure ammonic sulphate molecularly equivalent to the sodic carbonate. The solution was then digested until all the ammonia was expelled and the volume of the liquid largely reduced. Any silica or alumina which had separated was now filtered off, and the precipitate thoroughly washed with hot water. The solution, again reduced in volume and containing only the borate and sulphates of sodium and ammonium, was mixed with a definite amount of a manganese sulphate solution (strength previously determined), alcohol added, and after standing one half-hour the borate was removed by filtration, the filtrate evaporated to dryness, and the residue carefully ignited to expel the ammonium salt. The manganese sulphate left was dissolved in water, and the titration carried out as before described.

In a specimen of tourmaline from New York the boracic acid found by this method was 9·70 per cent. Another portion of the same material with Marignac's method yielded 10 per cent. $B^2O^3$. In another tourmaline (locality unknown) two determinations by this method gave 6·55 and 6·32 per cent. $B^2O^3$, while with Marignac's method the amount obtained was 6·80 per cent. $B^2O^3$.

In some instances upon evaporating the alcoholic solution preparatory to determining the excess of manganese sulphate, brownish flocks separated. These were always dissolved in a little sulphuric acid and then evaporated to dryness.

It is perhaps hardly necessary to say that some delicacy of manipulation is necessary in carrying out this process, especially if very small quantities are dealt with.

## OILS AND FATS.

§ 81. The examination of fatty matters by titration of their soluble or volatile and total fatty acids has of late assumed some considerable importance, in view of furnishing results which may aid in determining the amount of adulteration to which they are subject. It has been found especially serviceable in the case of butter, and two methods are in vogue, both of which give good technical results. The same methods are more or less available for the examination of fats other than butter; but further experiments are required to render the methods of value for differentiating various fatty bodies. The titration methods have been originated by Koetstorfer (*Z. a. C.* xix. 199) and Reichert (*Z. a. C.* xviii. 68), both being based on suggestions originating with the veteran chemist Chevreul, and by Hehner and Angell in their well-known treatise on Butter Analysis.

The same may be said to a great extent of another novel and interesting method of examining the nature and composition of various fats, by the power they possess of absorbing bromine or iodine. This method, as regards bromine, has been worked out with considerable diligence and ability by Mills and Snodgrass (*J. S. C. I.* ii. 435 and *ibid* iii. 366), also by Allen (*ibid* v. 68), also in his well-known treatise on Organic Analysis. The iodine method of Hubl is described in *J. S. C. I.* iii. 641. These various methods have been most voluminously discussed in their chemical and practical aspects, so that it must suffice here to give shortly the methods of analysis.

### Butter.

*Reichert's Method.*—This consists in saponifying the fat to be examined by an alkali, separating the fixed acids by neutralizing the alkali, and distilling off the volatile acids (chiefly butyric) for titration with standard acid.

**2·5** gm. of the sample, after melting on the water-bath, allowing the water to settle and filtering through a dry filter, are weighed into a flask holding about 160 c.c. and to it is added a sufficiency of alcoholic solution of potash to saponify the fat on heating in the water-bath. 25 c.c. of solution of about $\frac{N}{2}$ strength is generally sufficient. Close the flask with a cork, and continue the heating in the water-bath until perfect solution is obtained, then transfer the liquid to a porcelain or glass basin, and heat in the bath till the alcohol is evaporated. The residue is then dissolved in about 50 c.c. of water, transferred back to the flask, dilute $H^2SO^4$ added in moderate excess, then diluted with water to about 75 c.c. Some small pieces of pumice strung together with intervening small spirals of thin platinum wire are then placed in the liquid, the flask connected with a small condenser, and the liquid distilled on a small sand-bath until at least two-thirds of its volume have been collected. The distillate is then carefully titrated with $\frac{N}{10}$ soda or potash, using phenolphthalein as indicator.

The distillate from 2·5 gm. of a genuine butter requires, according to all experience, not less than 12·5 c.c. of $\frac{N}{10}$ alkali, when the method is conducted as above described. Higher figures may doubtless be obtained by carrying the distillation still further. Reichert himself obtained an average of 14 c.c. in the case of pure butters; but his paper describes the details of the process so imperfectly, that a doubt is left as to how far the distillation was carried. If the number of c.c. of acid used is to be expressed in terms of butyric acid the factor 0·312 may be used (Allen), and in the case of requiring 12·5 c.c. of acid with 2·5 gm. of butter the resulting figure is 3·9. The results of many operators reduced in this way show from 3·9 to 4·96, but none of them fell below the former number, which may therefore be taken as the inferior limit. Butter from goats' and ewes' milk gave practically the same results, while butterine or oleomargarine gave in no case higher than 0·5, and generally much less. Cocoanut oil, among the possible adulterants of butter, gave the highest figure, viz., 1·15 (Moore); but this is so far below the figure for butter, that even a very large admixture could at once be detected. It may be remarked that the exact weighing of 2·5 gm. of butter into a flask, especially if not solidified, is a difficult operation; it is therefore advisable to operate with about this quantity, noting the exact weight, and arriving at a comparative result by calculation.

*Koetstorfer's Method.*—This is a simpler operation than the foregoing, but is allowed on all hands to be less satisfactory in discriminating mixtures of other fats with butter, although extremely useful. In this method the whole of the acids existing in the fat are estimated. The solutions required are the following:—

*Standard Hydrochloric Acid* of semi-normal strength, *i.e.*, 18·185 gm. per liter.

*Standard Solution of Pure Caustic Potash* in alcohol of 80 per cent., of same strength, *i.e.*, 28 gm. per liter. If not of precise strength it should be near it, and the necessary factor found for calculation.

*The Indicator* is phenolphthalein.

The adjustment of the two solutions should take place under the same conditions as the actual analysis, and this must be done at short intervals, because the strength of the potash solution will vary from oxidation of alcohol. In doing this, 25 c.c. of potash should be heated for a few minutes on the water bath in the same way as when saponifying a fat, then tinted with not too small a quantity of the indicator (it is always advisable to use a definite measure), and while still hot the standard acid run in from a burette till the red colour is just discharged.

*The Analysis:* From 1 to 2 gm. of the fat, previously purified by melting and filtration, are weighed into a tall beaker holding about 70 c.c. 25 c.c. of standard potash are then added, the mixture covered with a watch-glass, and heated on the water bath to gentle boiling, with occasional agitation, until a perfectly clear solution is obtained (if a stirring rod is used, it must be carefully washed into the mixture with alcohol before titration). Koetstorfer recommends heating for fifteen minutes; but in the case of butters this is generally more than sufficient. At the end of the saponification the beaker is removed from the bath, the indicator added, and the titration carried out precisely as in the case of standardizing the solutions.

I prefer a small flask closed loosely with a cork to the beaker for the saponification, as also does Wigner. There is less chance of loss by spirting, and the use of a stirrer is obviated. He also dilutes the liquid with hot water before titration; but in this case there is greater risk of absorbing $CO^2$, which somewhat affects the indicator, and it is not really necessary, beside which a larger excess of KHO is then required. Whatever modification may be adopted by the operator, it is essential, in order to obtain concordant results, that all titrations should be carried out in the same way.

The method of calculation adopted by Koetstorfer is to ascertain the number of milligrams of KHO required to saturate the acids contained in 1 gm. of fat, or, in other words, parts per 1000. He found that, operating in this way, pure butters required from 221·5 to 232·4 m.gm. of KHO for 1 gm., whereas the fats usually mixed with butter, such as beef, mutton, and pork fat, required a maximum of 197 m.gm. for 1 gm., and other oils and fats much less.

Practically this means that the amount of KHO required for genuine butters ranges from 23·24 to 22·15 per cent., the latter being the inferior limit. If caustic soda is used instead of potash, other numbers must of course be used.

My experience, and, I believe, also that of others, shows that the method cannot be depended upon in the case of old re-melted butters, although perfectly genuine.

The following list shows the parts of KHO required per 1000 of fat; the first four being calculated from their known equivalents, the rest obtained experimentally by Koetstorfer, Allen, Stoddart, or Archbutt:—

| | | | |
|---|---|---|---|
| Tripalmitin | 208·8 | Linseed | 189—195 |
| Tristearin | 189·1 | Cotton Seed | 191—196 |
| Triolein | 190·4 | Whale | 190—191 |
| Tributyrin | 557·3 | Seal | 191—196 |
| Cocoanut Oil | 270·0 | Colza and Rape | 175—179 |
| Dripping | 197·0 | Cod Oil | 182—187 |
| Lard | 195·6 | Pilchard | 186—187 |
| Horse Fat | 199·4 | Castor | 176—178 |
| Lard Oil | 191—196 | Sperm | 130—134 |
| Olive Oil | 191—196 | Shark | 84·5 |
| Niger Oil | 189—191 | | |

### Titration of Miscellaneous Oils and Fats with Bromine or Iodine.

The newest and best method of carrying out this examination appears to be that of Mills and Snodgrass, to which reference has previously been made. The idea of using bromine is by no means new. Cailletet in 1857 adopted such a method; but the difficulty then, and up to the time when the task was undertaken by the operators mentioned, was the accurate measurement of the excess of bromine used, and the adaptation of such a solvent for both the fats and the bromine as would exclude the presence of water, and the tendency to form substitution products of variable and unknown character in preference to merely additive products.

Our knowledge of the exact composition of the great family of fats and oils is at present limited, and it is not possible to make this reaction possess any strict chemical valency; but experiment has shown that there are certain well-defined fats which absorb within a very narrow limit the same amount of the halogen under the same conditions, and hence the method may be made highly suggestive as to mixtures of various fats whose absorption powers have been observed.

In the first instance the common solvent used for the fat and the bromine was carbon disulphide; but although very good results were obtained, compared with solvents previously tried by other operators, there were the drawbacks of its offensive smell, and the solutions of bromine in it did not possess much stability. Finally, Dr. Mills adopted carbon tetrachloride as the medium with the happiest effects; and it was found that the bromide solution could be preserved for at least three months without diminution of standard. On the other hand, by using this medium, there is the necessity of working with greater delicacy, since the presence of the merest trace of water has more effect in producing substitution compounds than in the case of the disulphide. The accurate estimation of the excess of bromine, after the absorption is complete, is necessarily a matter of great importance; and this can be done either by comparison of colour with bromine solution of known strength (the least effective method); by titration with thiosulphate, using starch and potassic iodide as the indicator, which is better. But, best of all, the operators after long research found that by using $\beta$ naphthol (a substance which is readily and cheaply obtainable, and which forms in the presence of carbon tetrachloride a mono-bromo derivative) they could construct a solution of corresponding strength to the standard bromine, and thus titrate back in the same way as is commonly practised in alkalimetry. Very fair results were obtained colorimetrically by adopting the device of interposing a stratum of chromate solution (page 117), so as to neutralize the yellow colour produced with some of the fish oils, and which tended to mask the red colour of the bromine. Experiments showed that, using a bromine solution having a mean standard of 0·00644 gm. per c.c., the average probable error per cent. in a single result, when adopting the colour method or the thiosulphate and iodine was 0·62, whereas with $\beta$ naphthol it was reduced to 0·46. But it is hardly necessary to say that, using such a small portion of material as is absolutely necessary in order to avoid secondary results, considerable care and practice are required. The sample of oil or fat must be dried as completely as possible, by heating and subsequent filtering through dry scraps of bibulous paper, or through dry double filters before being weighed.

*The Analysis:* 0·1 to 0·2 gm. of the fat is dissolved in 50 c.c. of the tetrachloride and standard bromine added, until at the end of 15 minutes there is a permanent red colour. If the colorimetric method is used, 50 c.c. of tetrachloride is tinted with standard bromine to correspond. If the iodine re-action, the solution of brominated material is added to potassic iodide and starch, and $\frac{N}{10}$ sodic thiosulphate delivered in from a burette till the colour is discharged. If, on the other hand, the standard naphthol solution is used, it is also cautiously added from a burette until the colour is removed. It is imperative that the operations in all cases be carried on out of direct sunlight. If the operator is unable to use carbon tetrachloride, the disulphide may be used; but the solution of bromine in this medium is less stable, and must be checked more frequently. Somewhat larger portions of oil or fat may however be used for the analysis.

It may be of service to give some few of the results obtained by Mills and Snodgrass.

**Absorption per cent.—**

| OILS. | | FATS. | | WAXES. | |
|---|---|---|---|---|---|
| Almond (from bitter fruit) | 26·27 | Beef | 35·01 | Beeswax | 0·00 |
| Do. (from sweet) | 53·74 | Butter (fresh) | 27·93 | Carnauba | 33·50 |
| Cod | 83·00 | Do. (commercial) | 25·0 | Japan (1) | 2·33 |
| Nut | 30·24 | Butterine Scotch | 36·32 | Do. (2) | 1·53 |
| Ling Liver | 82·44 | Do. (French) | 39·71 | Myrtle | 6·34 |
| Mustard | 46·15 | Cocoanut | 5·70 | | |
| Neatsfoot | 38·33 | Vaseline | 5·55 | | |
| Olive | 60·61 | Stearic Acid | 0·00 | | |
| Palm | 35·00 | Lard | 37·29 | | |
| Seal | 57·34 | | | | |
| Whale | 30·92 | | | | |
| Linseed | 76·09 | | | | |
| Mineral Oil | 30·31 | | | | |
| Shale Oil according to sp. gr. | 22to12 | | | | |
| Aniline | 169·8 | | | | |
| Turpentine (dry) | 236·0 | | | | |

The same operators determined the percentage absorption by pure anhydrous turpentine, aniline and olive oil purified by filtration after long deposition at low temperature. The calculated values are based on the known ratios—

$$C^{10}H^{16} : Br^{4},\ C^{6}H^{7}N : Br^{2} \text{ and } (C^{3}H^{5})\,(C^{18}H^{33}O^{2})^{3} : Br^{6}.$$

The mean of three estimations each in turpentine and aniline were 236·0 and 169·8 per cent., five estimations in olive oil (triolein) 54 per cent. The percentage by calculation is respectively 235·3, 172, and 54·3. The iodine method has been worked out by Baron Hubl, but is not nearly so expeditious as the method just described. The standard iodine solution is made by dissolving respectively 25 gm. iodine and 30 gm. mercuric chloride in separate portions of strongest alcohol, say 500 c.c., then mixing the two liquids, and allowing to stand for some hours before taking the standard with thiosulphate and starch. This solution must always be standardized before use.

*The Analysis:* 0·2 to 0·5 gm. of the fat or oil is dissolved in 10 c.c. of purest chloroform, and 20 c.c. of the iodine solution added. The amount must finally be regulated, so that after not less than two hours digestion the mixture possesses a dark brown tint. Some KI solution is then added, the whole diluted with 150 c.c. water, and $\frac{N}{10}$ thiosulphate delivered in till the colour is nearly discharged. Starch is then added, and the titration finished in the usual way.

The numbers obtained by Hubl are given in *J. S. C. I.* iii. 642.

Allen states that, in both of these methods of titration, the amount of halogen taken up may be considered as a measure of the unsaturated fatty acids (or their glycerides) present. Thus, the acids of the acetic or stearic series exhibit no tendency to combine with bromine or iodine under the conditions of the experiments, while the acids of the acrylic or oleic series assimilate two, and the acids of the linoleic series four atoms of the halogen.

## GLYCERIN (GLYCEROL).

$C^3H^8O^3=92$.

§ 82. Up to a very recent time no satisfactory method of determining glycerin had been devised, but the problem has now been solved in a tolerably satisfactory manner. The method appears to have been originally suggested by Wanklyn, improved by him and Fox, and further elaborated by Benedikt and Zsigmondy (*Chem. Zeit.* ix. 975). The method in the case of fatty matters depends on the saponification of the fat, and oxidation of the resultant glycerin by permanganate in alkaline solution, with formation of oxalic acid, carbon dioxide, and water, thus,

$$C^3H^8O^3+3O^2=C^2H^2O^4+CO^2+3H^2O.$$

Aqueous solutions of glycerin may of course be submitted to the method very easily.

The excess of permanganate is destroyed by a sulphite, the liquid filtered from the manganese precipitate, the oxalic acid then precipitated by a soluble calcium salt in acetic solution, and the precipitate of calcic oxalate, after ignition to convert it into carbonate, titrated with standard acid in the usual way, or the oxalic precipitate titrated with permanganate. The oxalic solution may be titrated direct after addition of $H^2SO^4$ with permanganate; but Allen and Belcher have found this method faulty, probably from the formation of a dithionate, due to the sulphite. On the other hand, these operators have obtained very satisfactory results by the alkalimetric or the permanganate titration, on known weights of pure oxalic acid and glycerin.

These operators have also shown that, in the case of dealing with fats, where it has been recommended by Wanklyn and Fox to use ordinary alcohol as the solvent, and by Benedikt methyl alcohol, both these media, especially ethylic alcohol, produce in themselves a variable quantity of oxalic acid when treated with alkaline permanganate, and hence vitiate the process. Again, if it be attempted to avoid this by boiling off the alcohols, there is a danger of losing glycerin.

Allen's method with oils and fats is as follows:—

10 gm. of the fat or oil are placed in a strong small bottle, together with 4 gm. of pure KHO dissolved in 25 c.c. of water. A solid rubber stopper is then used to close the bottle, and tied down firmly with wire. It is then placed in boiling water, or in a water oven, and heated, with occasional shaking, from 6 to 10 hours, or until the contents are homogeneous. When saponification is complete, the bottle is emptied into a beaker, the fatty acids separated by dilute acid, filtered, the filtrate made up to a given volume, and half of it rendered alkaline with potash, then powdered permanganate or a strong solution added in excess at ordinary temperature, or until the mixture is of very dark colour; it is then heated to boiling, the excess of permanganate cautiously destroyed by a sulphite, and the thick mixture transferred to a 500 c.c. flask. When cold, the measure is made up to 502 c.c. to allow for the space occupied by the manganese precipitate, well shaken, and allowed to stand until clear. 300 or 400 c.c. are then removed, acidified with acetic acid, and calcium acetate added in excess, warmed to aggregate the precipitate, which is then filtered off, washed, redissolved in dilute $H^2SO^4$, and titrated with permanganate as in § 48; or it may be dried, ignited, and titrated with standard acid and methyl orange.

## PHENOL (CARBOLIC ACID).

$C^6H^5OH=94$.

§ 83. The only method claiming accuracy for the estimation of this substance volumetrically was originated by Koppeschaar (*Z. a. C.* xvi. 233), and consists in precipitating the phenol from its aqueous or dilute alcoholic solution with bromine water in the form of tribromphenol.

The strength of the bromine water was established by Koppeschaar, by titration with thiosulphate and potassic iodide with starch.

Allen modifies the process as follows:—

A certain weight of the sample is dissolved in water; as much as corresponds to 0·1 gm. of phenol is taken out and put into a stoppered bottle holding 250 c.c. Further, to 7 c.c. of normal soda solution (=0·040 gm. NaOH per c.c.) bromine is gradually added till a yellow colour appears and remains; the liquid is then boiled till it has become colourless again. It now contains 5 molecules of sodic bromide and 1 of sodic bromate. When completely cooled, it is put into the phenol solution, after which 5 c.c. concentrated hydrochloric acid is at once added, and the bottle stoppered and shaken for some time. The reactions are :—

I. $5NaBr+NaBrO^3+6HCl=6NaCl+6Br+3H^2O$.

II. $C^6H^6O+6Br=C^6H^3Br^3O+3HBr$.

The bromine set free in the first, and not fixed by phenol in the second reaction, must be still free, and is estimated by adding potassic iodide and titrating the iodine liberated, by $\frac{N}{10}$ thiosulphate :—

III. $2KI+Br^2=2KBr+2I$.

IV. $I^2+2Na^2S^2O^3=Na^2S^4O^6+2NaI$.

For this purpose the bottle is allowed to stand for 15 or 20 minutes; a solution of about 1·25 gm. potassic iodide (free from iodate) is added, the bottle is stoppered, shaken up, and allowed to rest. Its contents are now poured into a beaker; the bottle is rinsed out, a little starch-solution is added, and thiosulphate is run in from a burette till the blue colour is gone. (It will be best not to add the starch till the colour of the liquid has diminished to light yellow.) The calculation is made as follows:—7 c.c. of normal soda solution neutralize 0·560 gm. of bromine, all of which is liberated by HCl. 0·1 gm. phenol would require 0·4068 and leave a surplus of 0·1532 gm.; the latter would liberate enough iodine to saturate 19·5 c.c. of $\frac{N}{10}$ thiosulphate. Every c.c. of thiosulphate used over and above this indicates 0·00197 gm. impurities in 0·1 gm. of the sample—that is, 1·97 per cent.

If a number of estimations have to be made at one time, it would seem decidedly preferable to adopt Koppeschaar's original method, rather than to prepare special bromine solution as above. For the estimation of phenol in raw products, Töth (*Z. a. C.* xxv. 160) modifies the bromine process as follows:—

20 c.c. of the impure carbolic acid are placed in a beaker with 20 c.c. of caustic potash solution of 1·3 sp. gr., well shaken, and allowed to stand for half an hour, then diluted to about ¼ liter with water. By this treatment the foreign impurities are set free, and may mostly be removed by filtration; the filter is washed with warm water until all alkali is removed. The filtrate and washings are acidulated slightly with HCl, and diluted to 3 liters. 50 c.c. are then mixed with 150 c.c. of standard bromine solution, and then 5 c.c. concentrated HCl. After twenty minutes, with frequent shaking, 10 c.c. of iodide solution are added, mixed, and allowed to rest three to five minutes, then starch, and the titration with thiosulphate carried out as usual.

*Example:* 20 c.c. raw carbolic oil were treated as above described. 50 c.c. of the solution, with 150 c.c. bromine solution (made by dissolving 2·04 gm. sodic bromate and 6·959 gm. sodic bromide to the liter), then 5 c.c. of HCl, required 17·8 c.c. of thiosulphate for titration. The 150 c.c. bromide =0·237 gm. Br. The 17·8 c.c. thiosulphate required for residual titration =0·052 gm. Br, leaving 0·185 gm. Br for combination with the phenol. According to the equation—

$$C^6H^5OH + 3Br^2 = 3HBr + C^6H^2OHBr^3.$$

One mol. phenol=3 mol. Br, hence the percentage of phenol was 10·86.

This operator proved that Koppeschaar used too little of the bromide solution in his method, by taking only 100 c.c. instead of 150 c.c.

Kleinert (*Z. a. C.* xxxiii. 1) suggests, and his experiments appear to prove, that in titrating acid creosote oil by Koppeschaar's method for phenol, a serious error occurs in virtue of such oil containing substances of higher boiling point than phenol, which are soluble in water, and behave with bromine in the same manner as true phenol.

## CARBON DISULPHIDE AND THIOCARBONATES.

$$CS^2 = 76.$$

§ 84. For the purpose of estimating carbon disulphide in the air of soils, gases, or in thiocarbonates, Gastine has devised the following process (*Compt. Rend.* xcviii. 1588):—

The gas or vapour to be tested is carefully dried, and then passed through a concentrated solution of recently fused potassium hydroxide in absolute alcohol. The presence of even traces of water seriously diminishes the delicacy of the reaction. The alcoholic solution is afterwards neutralized with acetic acid, diluted with water, and tested for xanthic acid by adding copper sulphate.

In order to determine the distribution of carbon bisulphide introduced into the soil, 250 c.c. of the air in the soil is drawn by means of an aspirator through sulphuric acid, and then through bulbs containing the alcoholic potash. For quantitative determinations, a larger quantity of air must be used, and the xanthic acid formed is estimated by means of the reaction $2C^3H^6OS^2 + I^2 = 2C^3H^5OS^2 + 2HI$. The alkaline solution is slightly acidified with acetic acid, mixed with excess of sodic bicarbonate, and titrated in the usual way with a solution of iodine containing 1·68 gm. per liter, 1 c.c. of which is equivalent to 1 m.gm. of carbon bisulphide.

To apply this method to thiocarbonates, about 1 gm. of the substance, together with about 10 c.c. of water, is introduced into a small flask and decomposed by a solution of zinc or copper sulphate, the flask being heated on a water-bath, and the evolved carbon bisulphide passed, first through sulphuric acid, and then into alcoholic potash. In the case of gaseous mixtures of carbon bisulphide, nitrogen, hydrogen sulphide, carbonic anhydride, carbonic oxide, and water-vapour, the gas is passed through a strong aqueous solution of potash, then into sulphuric acid, and finally into alcoholic potash. The thiocarbonate formed in the first flask is decomposed by treatment with copper or zinc sulphate as above, and the xanthic acid obtained is added to that formed in the third flask, and the whole titrated with iodine.

Another method available for technical purposes, such as the comparative estimation of $CS^2$ in coal gas, or in comparing samples of thiocarbonates, is as follows :—

The liquid, or other substance, containing the disulphide, is added to strong alcoholic potash or gas containing the $CS^2$, is passed slowly through the alkaline absorbent. The disulphide unites with the potassic ethylate to form potassic xanthate. The liquid is neutralized with acetic acid and the xanthate is then estimated by titrating with a standard solution of cupric sulphate (12·47 gm. per liter), until an excess of copper is found by potassic ferrocyanide used as an external indicator. Each c.c. of copper solution represents 0·0076 gm. $CS^2$.

## MOLYBDENUM AND TUNGSTEN.

Mo=95·8. W=184.

§ 85. VOLUMETRIC methods are probably of very limited use in the case of these substances, but cases may arise in which their estimation is more simply accomplished by volumetric than by gravimetric means.

Von d. Pfordten (*C. N.* l. 18) gives the following processes :—

The solution of the salt is mixed, for molybdenum, with 50—60 c.c., and for tungsten with 70—80 c.c. of HCl of 27 per cent. There are then added for molybdenum, 8—10 gm., and for tungsten 14—15 gm. zinc in the form of rods, and in as large pieces as possible. The solution may contain 0·3 gm. molybdic oxide, or 0·1 gm. of tungstic oxide; in the latter case, the solution is previously heated on the water-bath, and the HCl and zinc are then added; the deposition of tungstic oxide in a solid state is thus avoided. Towards the end of the reduction, a little heat may sometimes be applied to the molybdenum solution with advantage. When the molybdenum solution has become yellow, and that of tungsten red, the flask is cooled—in the case of tungsten with especial care. The remainder of the procedure is different. The molybdenum solution is poured into a porcelain capsule containing 40 c.c. dilute sulphuric acid, and 20 c.c. of manganous sulphate solution free from ferrous salt, and containing 200 gm. per liter. An equal volume of water is added, and a dilute solution of standard permanganate is run in. The results are accurate:

$$1 \text{ c.c. } KMnO^4 = 0{\cdot}0007521850 = 0{\cdot}00451311 MoO^3.$$

The reduced tungsten solution is rinsed quickly into a capsule in which there is an excess of permanganate, 70—100 c.c. dilute sulphuric acid, 40 c.c. manganous sulphate solution, but otherwise no water. Not until the flask has been rinsed out is the liquid diluted to 1 liter. In presence of such large quantities of HCl the manganous sulphate exerts its power of transferring oxygen only in concentrated solutions. Quick working is essential. An excess of ferrous sulphate is now run in, and the solution is finally titrated with permanganate.

# PART VI.

# SPECIAL APPLICATIONS OF THE VOLUMETRIC SYSTEM TO THE ANALYSIS OF URINE, POTABLE WATERS, SEWAGE, ETC.

## ANALYSIS OF URINE.

§ 86. THE complete and accurate determination of the normal and abnormal constituents of urine presents more than ordinary difficulty to even experienced chemists, and is a hopeless task in the hands of any other than such. Fortunately, however, the most important matters, such as urea, sugar, phosphates, sulphates, and chlorides, can all be determined volumetrically with accuracy by ordinary operators, or by medical men who cannot devote much time to practical chemistry. The researches of Liebig, Neubauer, Bence Jones, Vogel, Beale, Hassall, Pavy, and others, during the last few years, have resulted in a truer knowledge of this important secretion; and to the two first mentioned chemists we are mainly indebted for the simplest and most accurate methods of estimating its constituents. With the relation which the proportion of these constituents bear to health or disease the present treatise has nothing to do, its aim being simply to point out the readiest and most useful methods of determining them quantitatively. Their pathological importance is very fully treated by some of the authorities just mentioned, among the works of which Neubauer and Vogel's *Analyse des Harns*, Beale's *Urine, Urinary Deposits, and Calculi*, and Mehu's *Traité de Chimie Medicale*, are most prominent and exhaustive; and we now have the collected experience of all the best authorities in the world in *The Pathological Handbook* of Drs. Lauder Brunton, Klein, Foster, and Burdon Sanderson (Churchill).

The gram system of weights and measures will be adopted throughout this section, while those who desire to use the grain system will have no difficulty in working, when once the simple relation between them is understood* (see § 9, p. 21). The question of weights and measures is, however, of very little consequence, if the analyst considers that he is dealing with relative parts or pro-

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* In a word, whenever c.c. occurs, dm. may be substituted; and in case of using grains for grams, move the decimal point one place to the right—thus 7·0 grams would be changed to 70 grains. Of course it is understood that where grams are taken, c.c. must be measured, and with grains dm.; the standard solution being the same for both systems.

portions only; and as urine is generally described as containing so many parts of urea, chlorides, or phosphates, per 1000, the absolute weight may be left out of the question. The grain system is more readily calculated into English ounces and pints, and therefore is generally more familiar to the medical profession of this country.

One thing, however, is necessary as a preliminary to the examination of urine, and which has not generally been sufficiently considered; that is to say, the relation between the quantity of secretion passed in a given time, and the amount of solid matters found in it by analysis. In a medical point of view it is a mere waste of time, generally speaking, to estimate the constituents in half-a-pint or so of urine passed at any particular hour of the day or night, without ascertaining the relation which that quantity, with its constituents, bears to the whole quantity passed during say, 24 hours; and this is the more necessary, as the amount of fluid secreted varies very considerably in healthy persons; besides this, the analyst should register the colour, peculiarity of smell (if any), consistence, presence or absence of a deposit (if the former, it should be collected for separate analysis, filtered urine only being used in such cases for examination), and lastly its reaction to litmus should be observed.

### 1. Specific Gravity.

This may be taken by measuring 10 c.c. with an accurate pipette into a tared beaker or flask. The observed weight say is 10·265 gm.; therefore 1026·5 will be the specific gravity, water being 1000. Where an accurate balance, pipette, or weights are not at hand, a good urinometer may be used. These instruments are now to be had with enclosed thermometer and of accurate graduation.

### 2. Estimation of Chlorides (calculated as Sodic Chloride).

This may be done in several ways, and I have placed the methods in the order in which I consider they ought to be ranked as regards accuracy. Liebig's method is by far the simplest, but the end-point is generally so obscure that the liability to error is very great. Mohr's method I have modified by the use of ammonic in place of potassic nitrate, owing to the solvent effect which the latter has been found to produce on silver chromate. By ignition the ammonia salt is destroyed.

(*a*) *By Silver Nitrate with Chromate Indicator* (Mohr). 10 c.c. of the urine are measured into a thin porcelain capsule, and 1 gm. of pure ammonic nitrate in powder added; the whole is then evaporated to dryness, and gradually heated over a small spirit lamp to low redness till all vapours are dissipated and the residue becomes white; it is then dissolved in a small quantity of water, and the carbonates produced by the combustion of the organic matter neutralized by dilute acetic acid; a few grains of pure calcic carbonate to remove all free acid are then added, and one or two drops of solution of potassic chromate.

The mixture is then titrated with $\frac{N}{10}$ silver, as in § 37.2 (*b*).

Each c.c. of silver solution represents 0·005837 gm. of salt, consequently if 12·5 c.c. have been used, the weight of salt in the 10 c.c. of urine is 0·07296 gm., and as 10 c.c. only were taken, the weight multiplied by 10, or what amounts to the same thing, the decimal point moved one place to the right, gives 7·296 gm. of salt for 1000 of urine.

If 5·9 c.c. of the urine are taken for titration, the number of c.c. of $\frac{N}{10}$ silver used will represent the number of parts of salt in 1000 parts of urine.

Pibram (*Vierteljahrsh, f. pract. Heilk*, cvi. 101) obviates the necessity for evaporating the urine with a nitrate previous to titration by heating the urine with permanganate. 10 c.c. of urine are mixed with about 5 c.c. of $\frac{N}{10}$ permanganate, and 40 c.c. of water then brought nearly to boiling; by this means a brown flocculent precipitate is produced, consisting of organic matter and manganous salt, which is filtered away, leaving the clear liquor colourless, so that an excess of permanganate shows the rose tint at once. Enough permanganate must be used to give this tint, which is then removed by a drop or two of dilute oxalic acid solution, a little calcic carbonate added, and the fluid titrated with $\frac{N}{10}$ silver solution and chromate as before described. This method gives very good results with normal urines.

(*b*) *By Volhard's Method.*—This is a direct estimation of Cl by excess of silver and the excess found by ammonic sulphocyanate (§ 39), which gives very good results in the absence of much organic matter, and is carried out as follows:—

10 c.c. of urine are placed in a 100 c.c. flask and diluted to about 60 c.c. 2 c.c. of pure nitric acid and 15 c.c. of standard silver solution (1 c.c.=0·01 gm. NaCl) are then added; the closed flask is well shaken, and the measure made up to 100 c.c. with distilled water.

The mixture is then passed through a dry filter, and about 70 or 80 c.c. of the clear fluid titrated with standard ammonic sulphocyanate for the excess of silver, using the ferric indicator described on page 116. The relative strength of the silver and sulphocyanate being known, the measure of the former required to combine with the chlorine in the 7 or 8 c.c. of urine is found and calculated into NaCl.

Arnold (*Pflüger's Archiv.* xxxv. 541) carries out this process as follows:—

10 c.c. of urine are mixed with 10 to 20 drops of nitric acid sp. gr. 1·2, 2 c.c. of ferric indicator, and 10 to 15 drops of solution of permanganate to oxidize organic matter. The liquid is then titrated according to Volhard's directions.

Another variation of Mohr's method is proposed by Zuelzer (*Berichte*, xviii. 320).

10 c.c. of urine are acidulated with nitric acid, and precipitated with silver nitrate; the silver chloride is filtered off and washed, then dissolved in ammonia: from this solution the silver is precipitated with fresh $NH^4S$. The excess of sulphide is then removed by cadmium nitrate, the liquid diluted to a definite volume, and an aliquot part filtered off, acidulated with nitric acid, neutralized with calcic carbonate, then titrated with $\frac{N}{10}$ silver and chromate. This method is cumbrous, and, if the reagents are not extremely pure, liable to great inaccuracy.

(*c*) *By Mercuric Nitrate* (Liebig).—The principle of this method is as follows:—If a solution of mercuric nitrate, free from any excess of acid, is added to a solution of urea, a white gelatinous precipitate is produced, containing urea and mercuric oxide in the proportion of 1 eq. of the former to 4 eq. of the latter ($4HgO + Ur$). When sodic chloride, however, is present in the solution, this precipitate does not occur, until all the sodic chloride is converted by double decomposition into mercuric chloride (sublimate) and sodic nitrate, the solution remaining clear; if the exact point be overstepped, the excess of mercury immediately produces the precipitate above described, so that the urea present acts as an indicator of the end of the process. It is therefore possible to ascertain the proportion of chlorides in any given sample of urine by this method, if the strength of the mercurial solution is known, since 1 eq. of mercuric oxide converts 1 eq. of sodic chloride into 1 eq. each of corrosive sublimate and sodic nitrate.

*Standard Solution of Mercuric Nitrate.*—It is of great importance that the solution be pure, for if the mercury from which it is made be contaminated with traces of other metals, such as bismuth, silver, or lead, they will produce a cloudiness in the liquid while under titration, which may possibly hinder the exact ending of the reaction; therefore 18·42 gm. of the purest precipitated mercuric oxide are put into a beaker, with a sufficiency of pure nitric acid of about 1·20 spec. grav. to dissolve it by the aid of a gentle heat; the clear solution so obtained is evaporated on the water bath to remove any excess of free acid. When the liquid is dense and sirupy in consistence, it may be transferred to the graduated cylinder or flask and diluted to a liter. 1 c.c. of the solution so prepared is equal to 0·01 gm. of sodic chloride, or 0·006059 gm. of chlorine.

If pure mercuric oxide is not at hand, the solution is best made by weighing 25 gm. of mercuric chloride, which is dissolved in about a liter of water and the oxide precipitated with a slight excess of caustic potash or soda. The precipitate of yellow oxide is allowed to settle clear and the liquor decanted. It is repeatedly washed in this manner with warm distilled water until the washings show no amount of alkali or alkaline chloride; the precipitate is then dissolved in the smallest quantity of pure nitric acid, and diluted to about 950 c.c. If any great excess of nitric acid is present, it may be cautiously neutralized by pure sodic hydrate or carbonate.

*Verification of the Mercuric Solution.*—This is carried out by the help of the following solutions:—

*Pure Sodic Chloride.*—20 gm. per liter.

*Solution of Urea.*—4 gm. of pure urea in 100 c.c.

*Solution of pure Sodic Sulphate.*—Saturated at ordinary temperatures. This is used to regulate the action of the free acid which is liberated in the reaction. In the case of natural urine it is not necessary.

*Process of Titration:* 10 c.c. of the standard sodic chloride (=0·2 gm. NaCl) are placed in a small beaker, together with 3 c.c. of the urea solution, and 5 c.c. of sodic sulphate. The mercuric solution is then delivered in from the burette, with constant stirring, until a decided permanent white precipitate is seen to form. A mere opalescence may occur even at the beginning, arising from slight impurities in the mercury, but this may be disregarded. If the mercuric solution has been made from weighed pure oxide, exactly 20 c.c. should be required; if, on the contrary, it has been made from the fresh unweighed oxide, somewhat less than 20 c.c. should be required. Say that 18·5 c.c. have been found to give the necessary reaction, then the solution must be diluted with distilled water in the proportion of 1·5 c.c. to every 18·5, or 925 c.c. made up to a liter.

It may happen that the solution, when made from weighed dry mercuric oxide, is not correct, owing to the difficulty of obtaining perfectly pure material; in such case a factor must be used to bring the volume used to the correct standard.

(*d*) **Baryta Solution for removing Phosphoric and Sulphuric Acids.**—Before urine can be submitted to titration by the mercurial solution, it is necessary to remove the phosphoric acid, and the proper agent for this purpose is a mixture composed of 1 volume of cold saturated solution of pure baric nitrate and 2 volumes ditto baric hydrate; the same agent is used previous to the estimation of urea, and may be simply designated *Baryta Solution.*

*The Analysis of Urine:* 40 c.c. of the clear urine are mixed with 20 c.c. of baryta solution, and the thick mixture poured upon a small dry filter; when sufficient clear liquid has passed through, 15 c.c. (=10 c.c. of urine) are taken with a pipette and just neutralized, if necessary, with a drop or two of nitric acid. If not alkaline, the probability is that sufficient baryta solution has not been added to precipitate all the phosphoric and sulphuric acids. This may be known by adding a drop or so of the baryta solution to the filtrate; if any precipitate is produced, it will be necessary to mix off a fresh quantity of urine with three-fourths or an equal quantity of baryta, in which case 17½ or 20 c.c. must be taken to represent 10 c.c. of urine; the excess in either case of baryta must be *cautiously* neutralized with nitric acid. The vessel containing the fluid is then brought under a Mohr's burette containing the mercurial solution, and small portions delivered in with stirring, until a distinct permanent precipitate is produced. The volume of solution used is then read off and calculated for 1000 parts of urine.

*Example:* 15 c.c. of the liquid prepared with a sample of urine, as described above (=10 c.c. of urine), required 6·2 c.c. of mercurial solution: the quantity of salt present was therefore 0·062 gm., or 6·2 parts in 1000 parts of urine.

### 3. Estimation of Urea (Liebig).

The combination between urea and mercuric oxide in neutral or alkaline solutions has been alluded to in the foregoing article on chlorides; it will therefore probably be only necessary to say that the determination of urea in urine is based on that reaction; and as the precipitate so produced is insoluble in water or weak alkaline solutions, it is only necessary to prepare a standard solution of mercury of convenient strength, and to find an indicator by which to detect the point when all the urea has entered into combination with the mercury, and the latter slightly predominates. This indicator is sodic carbonate. Liebig's instructions are, that when in the course of adding the mercurial solution from the burette to the urine, a drop of the mixture be taken from time to time and brought in contact with a few drops of solution of sodic carbonate on a glass plate or in a watch-glass, no change of colour should be produced at the point of contact until the free urea is all removed; when this is the case, and the mercury is slightly in excess, a yellow colour is produced, owing to the formation of hydrated mercuric oxide.

The compound of urea and mercury consists, according to Liebig's analysis, of 1 eq. of the former to 4 eq. of the latter; that is to say, if the nitric acid set free by the mixture is neutralized from time to time with sodic carbonate or other suitable alkali. If this be not done, the precipitate first formed alters in character, and eventually consists only of 3 eq. of mercury with 1 of urea. In order to produce the yellow colour with sodic carbonate, there must be an excess of mercurial solution. Theoretically, 100 parts of urea should require 720 parts of mercuric oxide; but practically, 772 parts of the latter are necessary to remove all the urea, and at the same time show the yellow colour with alkali; consequently the solution of mercuric nitrate must be of empirical strength, in order to give accurate results.

*Preparation of the Mercuric Solution.*—77·2 gm. of red mercuric oxide, or 71·5 gm. of the metal itself, are treated with nitric acid, as described in the previous article on chlorides, and in either case diluted to 1 liter: 1 c.c. of the solution is then equal to 0·01 gm. of urea. (The extreme care required to remove traces of foreign metals from the mercury is not so necessary here as in the foregoing instance, but no large amount of free acid must be present.) Dragendorff prefers to use mercuric chloride in the preparation of the standard solution, by weighing 96·855 gm. of the pure salt, which is dissolved in water, then precipitated with dilute caustic soda, the precipitate well washed by decantation until free from chlorine, then dissolved in a slight excess of nitric acid, and the solution diluted to 1 liter.

*The Analysis:* Two volumes of the urine are mixed with one of baryta solution, as before described in the case of chlorides (reserving the precipitate for the determination of phosphoric acid, if necessary), and 15 c.c. (=10 c.c. of urine) taken in a small beaker for titration; it is brought under the burette containing the mercurial solution (without neutralizing the excess of baryta, as in the case of chlorides), and the solution added in small quantities so long as a distinct precipitate is seen to form. A plate of glass laid over dark paper is previously sprinkled with a few drops of solution of sodic carbonate, and a drop of the mixture must be brought from time to time, by means of a small glass rod, in contact with the soda. So long as the colour remains white, free urea is present in the mixture; when the yellow colour is distinctly apparent, the addition of mercury is discontinued, and the quantity used calculated for the amount of urea. It is always advisable to repeat the analysis, taking the first titration as a guide for a more accurate estimation by the second.

*Example:* 15 c.c. of urine deprived of phosphates (=10 c.c. of the original urine) were titrated as described, and required 17·6 c.c. of mercurial solution; consequently there was 0·176 gm. of urea present in the 10 c.c., or 17·6 parts in the 1000 of urine.

The experiments of Rautenberg (*Ann. d. Chem. u. Pharm.* cxxxiii. 55) and Pflüger (*Z. a. C.* xix. 375) show, however, that the method, as devised by Liebig, is open to serious errors, due to the uncertainty in the point of neutralization.

Pflüger's researches are very complete, and lead to the following modification of the process.

A solution of pure urea is prepared containing 2 gm. in 100 c.c. 10 c.c. of this solution is placed in a beaker, and 20 c.c. of the mercury solution ran into it in a continuous stream; the mixture is then immediately brought under a burette containing normal sodic carbonate, and this solution is added with constant agitation until a permanent yellow colour appears. The volume of soda solution so used is noted as that which is necessary to neutralize the acidity produced by 20 c.c. of the mercury solution in the presence of urea. Pflüger found that by titrating 10 c.c. of the urea solution by small additions of the mercury, and occasional neutralization, the end of the reaction occurred generally at from 17·2 to 17·8 c.c. of mercury; but when he ran in boldly 19·7 c.c. of mercury, followed immediately by normal sodic carbonate to near neutrality, then alternately a drop or two of first mercury, then soda, the exact point was reached at 20 c.c. of mercury; and when 10 c.c. of the mercury solution which gave this reaction were analyzed as sulphide by weight, a mean of several determinations gave 0·7726 gm. of HgO, which agrees very closely with Liebig's number.

In the case of titrating urine, the following method is adopted:—

A plate of colourless glass is laid upon black cloth, and some drops of a thick mixture of sodic bicarbonate (free from carbonate) and water placed upon it at convenient distances. The mercury solution is added to the urine in such volume as is judged appropriate, and from time to time a drop of the white mixture is placed beside the bicarbonate so as to touch, but not mix completely. At first the urine mixture remains snow-white, but with further additions of mercury a point at last occurs when the white gives place to yellow. When the colour has developed itself, both drops are rubbed quickly together with a glass rod: the colour should disappear. Further addition of mercury is made cautiously until a faint yellow is permanent. Now is the time to neutralize by the addition of the normal soda to near the volume which has been found necessary to completely neutralize a given volume of mercury solution. If the time has not been too long in reaching this point, it will be found that a few tenths of a c.c. will suffice to complete the reaction. If, however, much time has been consumed, it may occur that, notwithstanding the mixture is distinctly acid, the addition of soda produces a more or less yellow colour: in this case, nothing is left but to go over the analysis again, taking the first trial as a guide for the quantities of mercury and soda solutions, which should be delivered in one after the other as speedily as possible until the exact end is reached.

It is absolutely necessary, with this modified process, to render the urine perfectly neutral, after it is freed from phosphates and sulphates, by baryta solution.

*Corrections and Modifications* (Liebig).—In certain cases the results obtained by the above methods are not strictly correct, owing to the variable state of dilution of the liquid, or the presence of matters which affect the mercury solution. The errors are, however, generally so slight as not to need correction. Without entering into a full description of their origin, I shall simply record the facts, and give the modifications necessary to be made where thought desirable.

The Urine contains more than 2 per cent. of Urea, *i.e.*, more than 20 parts per 1000. This quantity of urea would necessitate 20 c.c. of mercurial solution for 10 c.c. of urine. All that is necessary to be done when the first titration has shown that over 2 per cent. is present, is to add half as much water to the urine in the second titration as has been needed of the mercurial solution above 20 c.c. Suppose that 28 c.c. have been used at first, the excess is 8 c.c., therefore 4 c.c. of water are added to the fluid before the second experiment is made.

The Urine contains less than 2 per cent. of Urea. In this case, for every 4 c.c. of mercurial solution less than 20, 0·1 c.c. must be deducted, before calculating the quantity of urea; so that if 16 c.c. have been required to produce the yellow colour with 10 c.c. urine, 15·9 is to be considered the correct quantity.

The Urine contains more than 1 per cent. of Sodic Chloride, *i.e.*, more than 10 parts per 1000. In this case 2 c.c. must be deducted from the quantity of mercurial solution actually required to produce the yellow colour, with 10 c.c. of urine.

The Urine contains Albumen. In this case 50 c.c. of the urine are boiled with 2 drops of strong acetic acid to coagulate the albumen, the precipitate allowed to settle thoroughly, and 30 c.c. of the clear liquid mixed with 15 c.c. of baryta solution, filtered, and titrated for both chlorides and urea, as previously described.

The Urine contains Ammonic Carbonate. The presence of this substance is brought about by the decomposition of urea, and it may sometimes be of interest to know the quantity thus produced, so as to calculate it into urea.

As its presence interferes with the correct estimation of urea direct, by mercurial solution, a portion of the urine is precipitated with baryta as usual, and a quantity, representing 10 c.c. of urine, evaporated to dryness in the water bath to expel the ammonia, the residue then dissolved in a little water, and the urea estimated in the ordinary way. On the other hand, 50 or 100 c.c. of the urine, not precipitated with baryta, are titrated with normal sulphuric acid and litmus paper, each c c. of acid representing 0·017 gm. of ammonia, or 0·030 gm. of urea.

Pflüger's correction for concentration of the urea differs from Liebig's, his rule being as follows :—

Given the volume of urea solution + the volume of $NaCO^3$ required + the volume of any other fluid free from urea which may be added, and call this $V^1$; the volume of mercury solution is $V^2$; the correction, C, is then

$$C = -(V^1 - V^2) \times 0{\cdot}08.$$

This formula holds good for cases where the total mixture is less than three times the volume of mercury used.

With more concentrated solutions this formula gives results too high.

Pfeiffer (*Zeit. f. Biol.* xx. 540) has made a careful comparison of Liebig's (as modified by Pflüger) and Rautenberg's methods of estimating urea. The essential difference of Rautenberg's method consists in maintaining the urea solution neutral throughout by successive additions of calcic carbonate; under these conditions, the composition of the precipitate differs from that formed when the titration is made according to Pflüger's process, a fact which accounts for the diminished consumption of mercuric nitrate in the former method. The general conclusions from his observations may be summarized as follows :— (1) In estimating the correction for sodic chloride, the amount of free acid should be as small as possible, and 0·1 c.c. should be subtracted from every c.c. of mercuric nitrate used, but in human urine it is preferable to precipitate the chlorine with silver nitrate, as a slight excess of the latter does not influence the result. (2) The coefficient for dilution should be determined afresh for every new standard solution.

### 4. Estimation of Urea by its conversion into Nitrogen Gas.

If a solution of urea is mingled with an alkaline solution of hypochlorite or hypobromite, the urea is rapidly decomposed and nitrogen evolved, which can be collected and measured in any of the usual forms of gas apparatus described in the section on analysis of gases.

Test experiments with pure urea have shown, that the whole of the nitrogen contained in it are eliminated in this process, with the exception of a constant deficit of 8 per cent. In the case of urine there are other nitrogenous constituents present, such as uric acid, hippuric acid, and creatinine, which render up a small proportion of their nitrogen in the process, but the quantity so obtained is insignificant, and may be disregarded. Consequently, for all medical purposes, this method of estimating urea in urine is sufficiently exact.

In the case of diabetic urines, however, Mehú and others have pointed out that this deficiency is diminished, and if, in addition to the glucose present, cane sugar be also added, it will almost entirely disappear. Mehú therefore recommends that in the analysis of saccharine urines cane sugar be added to ten times the amount of urea present, when the difference between the actual and theoretical yield of nitrogen will not exceed 1 per cent (*Bull. Soc. Chim.* [2] xxxiii. 410).

Russell and West (*J. C. S.* [2] xii. 749) have described a very convenient apparatus for working the process, and which gives very good results in a short space of time. This method has given rise to endless forms of apparatus devised by various operators, including Mehú, Yvon, Dupré, Apjohn, Maxwell Simpson, O'Keefe, etc., etc.: the principles of construction are all, however, the same. Those who may wish to construct simple forms of apparatus from ordinary laboratory appliances, will do well to refer to the arrangements of Dupré (*J. C. S.* 1877, 534) or Maxwell Simpson (*ibid.* 538).

The apparatus devised by Russell and West is shown in fig. 39, and may be described as follows:—

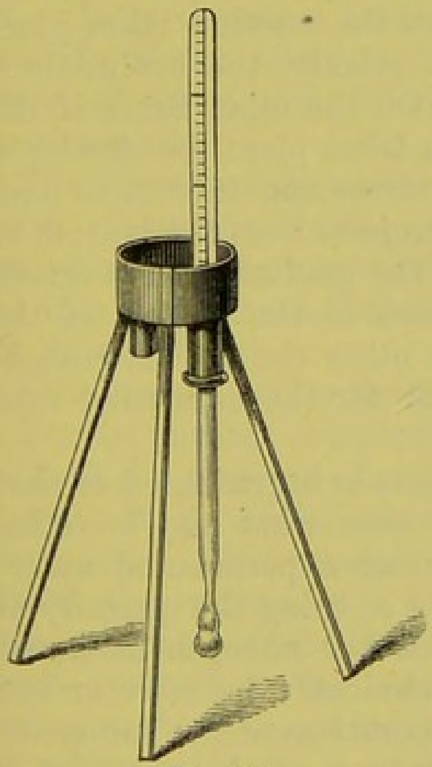
Fig. 39.

The tube for decomposing the urine is about 9 inches long, and about half an inch inside diameter. At 2 inches from its closed end an elongated bulb is blown, leaving an orifice at its neck of $\frac{3}{8}$ of an inch in diameter; the bulb should hold about 12 c.c. The mouth of this tube is fixed into the bottom of a tin tray about $1\frac{3}{4}$ inch deep, which acts as a pneumatic trough; the tray is supported on legs long enough to allow of a small spirit lamp being held under the bulb tube. The measuring tube for collecting the nitrogen is graduated into cubic centimeters, and of such size as to fit over the mouth of the decomposing tube; one holding about 40 c.c. is a convenient size. Russell and West have fixed by experiment the proportions, so as to obviate the necessity for correction of pressure and temperature, namely, 37·1 c.c.$=$0·1 gm. of urea, since they found that 5 c.c. of a 2 per cent. solution of urea constantly gave 37·1 c.c. of nitrogen at ordinary temperatures and pressures. The entire apparatus can be purchased of most operative chemists for a moderate sum.

*Hypobromite Solution.*—This is best prepared by dissolving 100 gm. of caustic soda in 250 c.c. of water and adding 25 c.c. of bromine; this mixture gives a rapid and complete decomposition of the urea. It is always best prepared in small quantities as required.

*The Analysis:* 5 c.c. of the urine are measured into the bulb-tube, fixed in its proper position, and the sides of the tube washed down with distilled water so that the bulb is filled up to its constriction. A glass rod, having a thin band of india-rubber on its end, is then passed down into the tube so as to plug up the narrow opening of the bulb. The hypobromite solution is then poured into the upper part of the tube until it is full, and the trough is afterwards half filled with water.

The graduated tube is filled with water, the thumb placed on the open end, and the tube is inverted in the trough. The glass rod is then pulled out, and the graduated tube slipped over the mouth of the bulb-tube.

The reaction commences immediately, and a torrent of gas rises into the measuring tube. To prevent any of the gas being forced out by the reaction, the upper part of the bulb-tube is slightly narrowed, so that the gas is directed to the centre of the tube. With the strength of hypobromite solution above described, the reaction is complete in the cold in about ten or fifteen minutes; but in order to expedite it, the bulb is slightly warmed. This causes the mixing to take place more rapidly, and the reaction is then complete in five minutes. The reaction will be rapid and complete only when there is considerable excess of the hypobromite present. After the reaction the liquid should still have the characteristic colour of the hypobromite solution.

The amount of constriction in the tube is by no means a matter of indifference, as the rapidity with which the reaction takes place depends upon it. If the liquids mix too quickly, the evolution of the gas is so rapid that loss may occur. On the other hand, if the tube is too much constricted, the reaction takes place too slowly.

The simplest means of supporting the measuring tube is to have the bulb-tube corked into a well, which projects from the bottom of the trough about one inch downwards. The graduated tube stands over the bulb-tube, and rests upon the cork in the bottom of the well. It is convenient to have, at the other end of the trough, another well, which will form a support for the measuring tube when not in use.

To avoid all calculations, the measuring tube is graduated so that the amount of gas read off expresses at once what may be called the percentage amount of urea in the urine experimented upon; *i.e.* the number of grams in 100 c.c., 5 c.c. being the quantity of urine taken in each case. The gas collected is nitrogen saturated with aqueous vapour, and the bulk will obviously be more or less affected by temperature and pressure. Alterations of the barometer produce so small an alteration in the volume of the gas, that it may be generally neglected; *e.g.* if there are 30 c.c. of nitrogen, the quantity preferred, an alteration of one inch in the height of barometer would produce an error in the amount of urea of about 0·003; but for more exact experiments, the correction for pressure should be introduced.

In the wards of hospitals, and in rooms where the experiments are most likely to be made, the temperature will not vary much from 65° F., and a fortunate compensation of errors occurs with this form of apparatus under these circumstances. The tension of the aqueous vapour, together with the expansion of the gas at this temperature, almost exactly counterbalances the loss of nitrogen in the reaction.

The authors found from experience that 5 c.c. of urine is the most advantageous quantity to employ, as it usually evolves a convenient bulk of gas to experiment with, *i.e.* about 30 c.c. They have shown that 5 c.c. of a standard solution containing 2 per cent. of urea evolve 37·1 c.c. of nitrogen, and have consequently taken this as the basis of the graduation of the measuring tube. This bulk of gas is read off at once as 2 per cent. of urea, and in the same way the other graduations on the tube represent percentage amounts of urea.

If the urine experimented with is very rich in urea, so that the 5 c.c. evolve a much larger volume of gas than 30 c.c., then it is best at once to dilute the urine with its own bulk of water ; take 5 c.c. of this diluted urine, and multiply the volume of gas obtained by two.

If the urine contains much albumen, this interferes with the process so far that it takes a long time for the bubbles of gas to subside, before the volume of gas obtained can be accurately read off. It is therefore better in such cases to remove as much as possible of the albumen by heating the urine with two or three drops of acetic acid, filtering, and then using the filtrate in the usual manner.

The hypobromite method of estimating urea has given rise to much discussion during the last few years, and among other contributions, there occurs one from Dr. Wormley, which negatives the idea that there is necessarily a loss of nitrogen by this process (*C. N.* xlv. 27).

This operator gives the result of his experiments as follows :—

For the purpose of examining the accuracy of this process for urea, without the presence of cane sugar or glucose, the form of apparatus, at least in principle, advised by Apjohn (*C. N.* xxxi. 37), was employed. This consists of a wide-mouthed bottle in which is placed the reagent, and also a small test-tube, for containing the urea solution, of about 10 c.c. capacity and of such length as to stand inclined in the bottle. The mouth of the bottle is closed with a rubber stopper carrying a glass tube, by which it is connected by rubber tubing to a graduated burette divided into 0·1 c.c. and suspended in a long cylinder of water from an adjustable arm.

The urea solution is placed in the small tube within the charged bottle, the apparatus closed, and when there is no longer any change in the height of the column of liquid within the graduated tube, this is so adjusted that the surface of the contained liquid exactly coincides with that in the cylinder. This point, the temperature, and in exact experiments the barometric pressure, being noted, the urea solution is mixed with the reagent by inclining the bottle and gently shaking the mixture. As the evolved nitrogen collects in the burette, the latter is gradually raised to relieve the contained gas from the increased pressure. When the evolution of gas has entirely ceased and there is no longer any change in the volume of gas, the tube is finally adjusted and the exact volume noted. The hypobromite employed was the same as described p. 318. In applying the reagent it was diluted with a volume and a half of pure water.

With this arrangement a series of experiments was performed employing 1 c.c. of a standard solution of pure urea varying in strength from 1 to 6 per cent., variously diluted, and added to varying quantities of the reagent. These experiments gave different results, in some only about 90 per cent., and even less, of the nitrogen being evolved, while in others a larger proportion was obtained, and in still others the *whole* of the nitrogen was set free. It was finally observed that under certain conditions the whole of the nitrogen is uniformly eliminated. These conditions are :—

1. The reagent should be freshly prepared.
2. The urea solution should be wholly added to the reagent, none of the latter being allowed to mix with the urea solution in the containing tube.
3. The amount of urea operated upon should not exceed one part to about twelve hundred parts of the diluted reagent.

Moreover, the diluted urea solution should be added in small portions at a time to the reagent, thoroughly mixed, and the effervescence allowed to cease before any further addition of urea. So, also, it would appear, at least when comparatively large quantities of urea are present, that the surrounding temperature should not be less than about 20° C. (68° F.).

In the practical application of the test, if a 2 per cent. solution of urea is under examination, 1 c.c. of the solution, diluted with from 5 to 10 c.c. water, is placed in the containing tube, and the mixing bottle charged with 10 c.c. of the reagent diluted with 15 c.c. of water; whereas, for 1 c.c. of a 4 per cent. solution of urea, similarly diluted, not less than about 50 c.c. of the diluted reagent should be employed.

In a final series of experiments, in which the above conditions were observed, the temperature being noted to $\frac{1}{10}$ of a degree, and the results reduced to the standard temperature and pressure, the following average results were obtained :—

| Urea employed. | Nitrogen evolved= |
|---|---|
| 10 milligrams | 9·98 m.gm. urea. |
| 20 ,, | 20·07 ,, |
| 30 ,, | 29·95 ,, |
| 40 ,, | 39·88 ,, |

In these experiments it was assumed that 1 gm. of urea contains 372 c.c. of nitrogen, measured at 0° C. and 760 m.m. barometric pressure; or, that each c.c. of nitrogen evolved, measured under the conditions stated, represented 0·002688 gm. urea.

During these investigations it was observed, in cases in which the whole of the nitrogen was not evolved, that so long as the conditions remained the same, the relative proportion of the nitrogen eliminated was pretty uniform. Hence, if the volume of nitrogen evolved from a known quantity of urea under certain conditions, or by a given form of apparatus, be determined, the result may be taken as the basis for the determination of the urea in the urine with sufficient accuracy for clinical purposes.

Hamburger (*Zeit. f. Biol.* xx. 286) refers to Pflüger's modification of Liebig's method, which although an improvement leaves much to be desired; his own method is founded on Quinquand's (*Monit. Scien.* 1882, 2), in which the decomposition of urea by sodic hypobromite is supposed to take place thus:—

$$CO(NH^2)^2 + 3NaBrO = 3NaBr + 2H^2O + CO^2 + N^2.$$

This reaction requires the proportion of bromine, sodic hydrate, and water to be exactly balanced or incorrect results will be obtained. The author claims for his method that it will yield correct results, no matter in what proportions these reagents are present. It consists essentially in adding an excess of an alkaline solution of sodic hypobromite of known strength to the liquid containing urea, then destroying the excess of hypobromite with an excess of standard sodic arsenite (=19·8 gm. $As^2O^3$ per liter), and finally determining the amount of arsenite remaining unoxidized, by titration with standard iodine solution, the amount of urea then being readily calculated from the amount of sodic arsenite remaining unoxidized. The author's experiments as to the accuracy of the method, show that a certain quantity of urea always requires the same amount of hypobromite, and that the dilution of the solution of urea has no effect on the quantity of hypobromite employed.

To decide on the applicability of the method to natural urine, great pains were taken, the urea being determined as described, the effect of its dilution with water studied, pure urea added, and the whole estimated, and lastly sodic hypobromite of various degrees of concentration employed; the results of the experiments are given very fully and tabulated. On the whole, they are very satisfactory, the differences falling well within the limits of errors of observation and manipulation: the method is therefore considered applicable to the determination of urea in urine.

### 5. Estimation of Phosphoric Acid (see also § 69).

The principle of this method is fully described at page 241.

The following solutions are required:—

(1) *Standard Uranic Acetate or Nitrate.* 1 c.c.=0·005 gm. $P^2O^5$ (see p. 243).

(2) *Standard Phosphoric Acid* (see p. 243).

(3) *Solution of Sodic Acetate* (see p. 242).

(4) *A Solution of Potassic Ferrocyanide.*—About 1 part to 20 of water, freshly prepared, or some of the finely powdered salt.

*The Analysis:* 50 c.c. of the clear urine are measured into a small beaker, together with 5 c.c. of the solution of sodic acetate (if uranic nitrate is used). The mixture is then warmed in the water bath, or otherwise, and the uranium solution delivered in from the burette, with constant stirring, as long as a precipitate is seen to occur. A small portion of the mixture is then removed with a glass rod and tested as described (p. 243); so long as no brown colour is produced, the addition of uranium may be continued; when the faintest indication of this reaction is seen, the process must be stopped, and the amount of colour observed. If it coincides with the original testing of the uranium solution with a similar quantity of fluid, the result is satisfactory, and the quantity of solution used may be calculated for the total phosphoric acid contained in the 50 c.c. of urine; if the uranium has been used accidentally in too great quantity, 10 or 20 c.c. of the same urine may be added, and the testing concluded more cautiously. Suppose, for example, that the solution has been added in the right proportion, and 19·2 c.c. used, the 50 c.c. will have contained 0·096 gm. phosphoric acid (=1·92 per 100). With care and some little practice the results are very satisfactory.

*Earthy Phosphates:* The above determination gives the total amount of phosphoric acid, but it may sometimes be of interest to know how much of it is combined with lime and magnesia. To this end 100 or 200 c.c. of the urine are measured into a beaker, and rendered freely alkaline with ammonia; the vessel is then set aside for ten or twelve hours, for the precipitate of earthy phosphates to settle: the clear fluid is then decanted through a filter, the precipitate brought upon it and washed with ammoniacal water; a hole is then made in the filter and the precipitate washed through; the paper moistened with a little acetic acid, and washed into the vessel containing the precipitate, which latter is dissolved in acetic acid, some sodic acetate added, and the mixture diluted to about 50 c.c. and titrated as before described; the quantity of phosphoric acid so found is deducted from the total previously estimated, and the remainder gives the quantity existing in combination with alkalies.

### 6. Estimation of the Sulphuric Acid.

*Standard Baric Chloride.*—A quantity of crystallized baric chloride is to be powdered, and dried between folds of blotting-paper. Of this, 30·5 gm. are dissolved in distilled water, and the liquid made up to a liter. 1 c.c. = 0·01 gm. of $SO^3$.

*Solution of Sodic Sulphate.*—1 part to 10 of water.

*The Analysis:* 100 c.c. of the urine are poured into a beaker, a little hydrochloric acid added, and the whole placed on a small sand-bath, to which heat is applied. When the solution boils, the baric chloride is allowed to flow in very gradually as long as the precipitate is seen distinctly to increase. The heat is removed, and the vessel allowed to stand still, so that the precipitate may subside. Another drop or two is then added, and so on, until the whole of the $SO^3$ is precipitated. Much time, however, is saved by using Beale's filter, represented in fig. 16. A little of the fluid is thus filtered clear, poured into a test-tube, and tested with a drop from the burette; this is afterwards returned to the beaker, and more of the test solution added, if necessary. The operation is repeated until the precipitation is complete. In order to be sure that too much of the baryta solution has not been added, a drop of the clear fluid is added to the solution of sodic sulphate placed in a test-tube or upon a small mirror (see § 73.3). If no precipitate occurs, more baryta must be added; if a slight cloudiness takes place, the analysis is finished; but if much precipitate is produced, too large a quantity of the test has been used, and the analysis must be repeated.

For instance, suppose that 18·5 c.c. have been added, and there is still a slight cloudiness produced which no longer increases after the addition of another ½ c.c., we know that between 18½ and 19 c.c. of solution have been required to precipitate the whole of the sulphuric acid present, and that accordingly the 100 c.c. of urine contain between 0·185 and 0·19 gm. of $SO^3$.

### 7. Estimation of Sugar.

Fehling's original method is precisely the same as described in § 71, but if the urine has decomposed so as to contain ammonia or ammonic carbonate, this method must be discarded and Pavy's solution used.

*The Analysis:* 10 c.c. of the clear urine are diluted by means of a measuring flask to 200 c.c. with water, and a large burette filled with the fluid; 10 c.c. of the copper solution (=0·05 gm. of sugar) are then measured into a white porcelain capsule, 40 c.c. of distilled water added, the vessel arranged over a spirit or gas lamp under the burette, and brought to boiling; the diluted urine is then delivered in cautiously from the burette until the bluish colour has nearly disappeared. The addition of the urine must then be continued more carefully, allowing the red precipitate to subside after each addition by removing the heat, when by gently sloping the capsule, the clear liquid allows the white sides of the capsule to be seen, so that the faintest shade of blue would be at once perceptible. When the colour is all removed, the burette is read off, and the quantity of sugar in the urine calculated as follows:—

Suppose that 40 c.c. of the diluted urine have been required to reduce the 10 c.c. of copper solution, that quantity will have contained 0·05 gm. of sugar; but, the urine being diluted 20 times, the 40 c.c. represent only 2 c.c. of the original urine; therefore 2 c.c. of it contain 0·05 gm. of sugar, or 25 parts per 1000.

The Pavy-Fehling solution is much more generally adapted to urine, and is prepared and used precisely as described in § 71.

*The Analysis:* 10 c.c. of clear urine are diluted as just described, and delivered cautiously from the burette into 50 or 100 c.c. of the Pavy-Fehling liquid (previously heated to boiling) until the colour is discharged. The calculation is the same as before. 100 c.c. of Pavy-Fehling solution =0·05 gm. glucose.

The ammoniacal fumes are best absorbed by leading an elastic tube from the reduction flask into a beaker of water ; the end of the tube should be plugged with a piece of solid glass rod, and a transverse slit made in the elastic tube just above the plug. This valve allows the vapours to escape, but prevents the return of the liquid in case of a vacuum.

Knapp's method, which is equally applicable to urine, is described in § 71.

### 8. Estimation of Uric Acid.

The determination of uric acid in urine is not often considered of much consequence ; there are, however, circumstances under which it is desirable, especially in urinary deposits. As the quantity present in urine is very small, it is necessary to take, say, from 200 to 500 c.c. for the estimation.

The urine being measured into a beaker, from 5 to 8 c.c. of pure hydrochloric acid are added, the whole well mixed, covered with a glass plate, and set aside in a cellar for 24 or 30 hours ;[*] at the end of that time the uric acid will be precipitated in small crystals upon the bottom and sides of the beaker. The supernatant liquid is decanted, washed once with cold distilled water, then dissolved in a small quantity of pure solution of potash diluted to 150 c.c. or so with distilled water, acidified strongly with sulphuric acid, and titrated precisely as oxalic acid (§ 30.2 *c*), with $\frac{N}{10}$ permanganate, each c.c. of which is equal to 0·0075 gm. of uric acid. This method is not absolutely correct, owing to the fact that with the uric acid there is always precipitated a certain amount of colouring matter of the urine, which destroys the permanganate equally with the uric acid. The method by weighing is, however, open to the same objection, beside being very troublesome, so that no advantage is gained by the latter plan. Hassall states that the normal quantity of uric acid in urine has hitherto been considerably under-estimated, and that if the urine is concentrated by evaporation before precipitating with hydrochloric acid, a much larger quantity will be obtained (see *Lancet*, Feb. 1865).

Haycraft (*Z. a. C.* xxv. 165) has devised a method of estimating uric acid, which although it cannot be said to be absolutely accurate, is capable of giving very good results in the hands of a careful operator. The method is based on the fact that uric acid combines with silver as silver urate, which is practically insoluble in water, ammonia, or acetic acid, but perfectly soluble in nitric acid. The chief drawback to the method is the peculiar nature of the precipitate of silver urate, which is slimy and difficult to wash ; this, however, is overcome by collecting the precipitate on an asbestos filter attached to a filter pump. The filter is easily made by half filling a small funnel with broken glass, upon which small asbestos fibres suspended in water are poured to the depth of ¼ inch and evenly distributed. Such a filter may be used repeatedly for the same operation. The estimation of the uric acid depends upon the titration of the silver with which it is combined, by Volhard's method (§ 39). The necessary solutions are—

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[*] If 200 c.c. of urine are violently agitated for 5 minutes with 5 c.c. of fuming HCl, the separation will be complete in an hour.

$\frac{N}{100}$ *Ammonic Thiocyanate* standardized by a silver solution of known strength. 1 c.c. of this = 0·00168 gm. uric acid.

*Ammoniacal Silver Solution.*—5 gm. silver nitrate in about 100 c.c. of water, precipitated and re-dissolved in ammonia to a clear solution.

*Ferric Indicator* and *Pure Nitric Acid.*—The same as described in § 39.

*The Analysis:* 25 c.c. of urine are placed in a small beaker, together with about 1 gm. of sodic bicarbonate and 2 or 3 drops of strong ammonia. This precipitates ammonio-magnesic phosphate and prevents reduction of silver. 1—2 c.c. of ammoniacal silver solution are then added, which at once precipitates the silver as urate. The mixture is now placed on the filter, and washed until the washings show no trace of silver by testing with salt. The precipitate is then dissolved in a few c.c. of nitric acid, washed into a flask, and the titration carried out precisely as described in § 39. The number of c.c. of thiocyanate used multiplied by 0·00168 gives the uric acid.

If the urine to be examined contains albumen, it must be first removed by acidifying slightly with acetic acid, heating, and filtering.

### 9. Estimation of Lime and Magnesia.

100 c.c. of the urine are precipitated with ammonia, the precipitate redissolved in acetic acid, and sufficient ammonic oxalate added to precipitate all the lime present as oxalate. The precipitate is allowed to settle in a warm place, then the clear liquid passed through a small filter, the precipitate brought upon it, washed with hot water, the filtrate and washings set aside, then the precipitate, together with the filter, pushed through the funnel into a flask, some sulphuric acid added, the liquid freely diluted, and titrated with permanganate, precisely as in § 48; each c.c. of $\frac{N}{10}$ permanganate required represents 0·0028 gm. of CaO.

Instead of the above method the following may be adopted :—

The precipitate of calcic oxalate, after being washed, is dried and, together with the filter, ignited in a platinum or porcelain crucible, by which means it is converted into a mixture of calcic oxide and carbonate. It is then transferred to a flask by the aid of the washing bottle, and an excess of $\frac{N}{10}$ nitric acid delivered in with a pipette. The amount of acid, over and above what is required to saturate the lime, is found by $\frac{N}{10}$ caustic alkali, each c.c. of acid being equal to 0·0028 gm. of CaO.

In examining urinary sediment or calculi for calcic oxalate, it is first treated with caustic potash to remove uric acid and organic matter, then dissolved in sulphuric acid, freely diluted, and titrated with permanganate ; each c.c. of $\frac{N}{10}$ solution represents 0·0054 gm. of calcic oxalate.

*Magnesia.*—The filtrate and washings from the precipitate of calcic oxalate are evaporated on the water bath to a small bulk, then made alkaline with ammonia, sodic phosphate added, and set aside for 8 or 10 hours in a slightly warm place, that the magnesia may separate as ammonio-magnesic phosphate. The supernatant liquid is then passed through a small filter, the precipitate brought upon it, washed with ammoniacal water in the cold, and dissolved in acetic acid, then titrated with uranium solution, as in § 69; each c.c. of solution required represents 0·002815 gm. of magnesia.

### 10. Ammonia.

The only method hitherto applied to the determination of ammonia in urine is that of Schlösing, which consists in placing a measured quantity of the urine, to which milk of lime is previously added, under an air-tight bell-glass, together with an open vessel containing a measured quantity of titrated acid. In the course of from 24 to 36 hours all the ammonia will have passed out of the urine into the acid, which is then titrated with standard alkali to find the amount of ammonia absorbed.

One great objection to this method is the length of time required, since no heating must be allowed, urea being decomposed into free ammonia, when heated with alkali. There is also the uncertainty as to the completion of the process; and if the vessel be opened before the absorption is perfect, the analysis is spoiled. The following plan is recommended as in most cases suitable:—When a solution containing salts of ammonia is mixed with a measured quantity of free fixed alkali of known strength, and boiled until ammoniacal gas ceases to be evolved, it is found that the resulting liquid has lost so much of the free alkali as corresponds to the ammonia evolved (§ 18); that is to say, the acid which existed in combination with the ammonia in the original liquid has simply changed places, taking so much of the fixed alkali (potash or soda) as is equivalent to the ammonia it has left to go free. In the case of urine being treated in this way, the urea will also be decomposed into free ammonia, but happily in such a way as not to interfere with the estimation of the original amount of ammoniacal salts. The decomposition is such that, while free ammonia is evolved from the splitting up of the urea, carbonate of fixed alkali (say potash) is formed in the boiling liquid, and as this reacts equally as alkaline as though it were free potash, it does not interfere in the slightest degree with the estimation of the original ammonia.

The following is the best method of procedure:—

100 c.c. of the urine are exactly neutralized with $\frac{N}{10}$ soda or potash, as for the estimation of free acid; it is then put into a flask capable of holding five or six times the quantity, 10 c.c. of normal alkali added, and the whole brought to boiling, taking care that the bladders of froth which at first form do not boil over. After a few minutes these subside, and the boiling proceeds quietly. When all ammoniacal fumes are dissipated, the lamp is removed, and the flask allowed to cool slightly; the contents then emptied into a tall beaker, and normal nitric acid delivered in from the burette with constant stirring, until a fine glass rod or small feather dipped in the mixture and brought in contact with violet-coloured litmus paper produces neither

a blue nor a red spot. The number of c.c. of normal acid are deducted from the 10 c.c. of alkali, and the rest calculated as ammonia. 1 c.c. of alkali = 0·017 gm. of ammonia.

*Example:* 100 c.c. of urine were taken, and required 7 c.c. of $\frac{N}{10}$ alkali to saturate its free acid; 10 c.c. of normal alkali were then added, and the mixture boiled until a piece of moistened red litmus paper was not turned blue when held in the steam; 4·5 c.c. of normal acid were afterwards required to saturate the free alkali; the quantity of ammonia was therefore equal to 5·5 c.c., which, multiplied by 0·017, gave 0·0935 gm. in 1000 of urine.

It must be borne in mind, that the plan just described is not applicable to urine which has already suffered decomposition by age or other circumstances so as to contain carbonate of ammonia; in this case it would be preferable to adopt Schlösing's method; or where no other free alkali is present, direct titration with normal acid may be adopted.

### 11. Estimation of Free Acid.

The acidity of urine is doubtless owing to variable substances, among the most prominent of which appear to be acid sodic phosphate and lactic acid. Other free organic acids are probably in many cases present. Under these circumstances, the degree of acidity cannot be placed to the account of any particular body; nevertheless, it is frequently desirable to ascertain its amount, which is best done as follows:—

100 c.c. of urine are measured into a beaker, and $\frac{N}{10}$ alkali delivered in from a small burette, until a thin glass rod or feather, moistened with the mixture and streaked across some well-prepared violet litmus paper, produces no change of colour; the degree of acidity is then registered as being equal to the quantity of $\frac{N}{10}$ alkali used.

### 12. Estimation of Albumen.

(*a*) *By Weight:* 100 c.c. of the clear urine (or less than that quantity if much albumen is present, the 100 c.c. being made up with water) are introduced into a good-sized beaker, and heated in the water bath for half an hour. If the urine is sufficiently acid, the albumen will be separated in flocks. Should this not be the case at the end of the half-hour's heating, and the fluid merely appears turbid, one or two drops (not more, unless the urine is alkaline) of acetic acid are added, and the heating continued until the albumen separates in flocks; the beaker is then put aside till the precipitate has settled, and the clear liquid passed through a small filter (previously dried at 212°, then cooled between two watch-glasses held together with a spring clip, and weighed); the precipitate is then washed with a little hot water, and brought upon the filter without loss, the beaker washed out with hot distilled water, and the last traces of precipitate loosened from the sides with a feather. The filter, with its contents, is then repeatedly washed with hot water, until a drop of the filtrate evaporated on a piece of glass leaves no residue. The funnel containing the filter is then put into a warm place to dry gradually; lastly, the filter removed into one of the watch-glasses and dried thoroughly in the air-bath at 110° C., or 220° Fahr.; another watch-glass is then covered over that containing the filter, the spring clip passed over to hold them together, the whole cooled under the exsiccator and weighed. The weight of the glasses, filter, and clip, deducted from the total, gives the weight of albumen in 100 c.c. of urine.

(*b*) *By Measure:* In order to avoid the tedious process of estimating the albumen as just described, **Bödeker** devised a method of titration which gives approximate results when the quantity of albumen is not too small, say not less than 2 per cent. The principle is based on the fact that, potassic ferrocyanide completely precipitates albumen from an acetic acid solution in the atomic proportions of 211 ferrocyanide to 1612 albumen.

*Standard Solution of Ferrocyanide.*—Made by dissolving 1·309 gm. of the pure salt in a liter of distilled water. 1 c.c. of the solution precipitates 0·01 gm. of albumen. It must be freshly prepared.

*The Analysis:* 50 c.c. of the clear filtered urine are mixed with 50 c.c. of ordinary commercial acetic acid, and the fluid put into a burette. Five or six small filters are then chosen, of close texture, and put into as many funnels, then moistened with a few drops of acetic acid, and filled up with boiling water; by this means the subsequent clear filtration of the mixture is considerably facilitated. 10 c.c. of the ferrocyanide solution are then measured into a beaker, and 10 c.c. of the urinary fluid from the burette added, well shaken, and poured upon filter No. 1. If the fluid which passes through is bright and clear with yellowish colour, the ferrocyanide will be in excess, and a drop of the urine added to it will produce a cloudiness. On the other hand, if not enough ferrocyanide has been added, the filtrate will be turbid, and pass through very slowly; in this case, frequently both the ferrocyanide and the urine will produce a turbidity when added. In testing the filtrate for excess of ferrocyanide, care must be taken not to add too much of the urine, lest the precipitate of hydroferrocyanide of albumen should dissolve in the excess of albumen.

According to the results obtained from the first filter, a second trial is made, increasing the quantity of urine or ferrocyanide half or as much again, and so on until it is found that the solution first shown to be in excess is reversed. A trial of the mean between this quantity and the previous one will bring the estimation closer, so that a final test may be decisive.

*Example:* 50 c.c. of urine passed by a patient suffering from **Bright's** disease were mixed with the like quantity of acetic acid, and tested as follows:—

| | Urine. | Ferrocyanide. | In filtrate<br>Urine gave | <br>Ferrocyanide gave |
|---|---|---|---|---|
| 1. | 10 c.c. | 10 c.c. | 0 | prec. |
| 2. | 10 ,, | 20 ,, | prec. | 0 |
| 3. | 10 ,, | 15 ,, | 0 | prec. |
| 4. | 10 ,, | 17·5 ,, | 0 | faint prec. |
| 5. | 10 ,, | 18 ,, | 0 | 0 |

Therefore the 10 c.c. of diluted urine (=5 c.c. of the original secretion) contained 0·18 gm. albumen, or 36 parts per 1000.

### 13. Estimation of Soda and Potash.

50 c.c. of urine are mixed with the same quantity of baryta solution, allowed to stand a short time, and filtered; then 80 c.c. (=40 c.c. urine) measured into a platinum dish and evaporated to dryness in the water bath; the residue is then ignited to destroy all organic matter, and when cold dissolved in a small quantity of hot water, ammonic carbonate added so long

as a precipitate occurs, filtered through a small filter, the precipitate washed, the filtrate acidified with hydrochloric acid and evaporated to dryness, then cautiously heated to expel all ammoniacal salts. The residue is then treated with a little water and a few drops each of ammonia and ammonic carbonate, filtered, the filter thoroughly washed, the filtrate and washings received into a tared platinum dish, then evaporated to dryness, ignited, cooled, and weighed.

By this means the total amount of mixed sodic and potassic chlorides is obtained. The proportion of each is found by titrating for the chlorine as in § 38, and calculating as directed on page 115.

### 14. Estimation of Total Nitrogen.

This can now be easily accomplished by Kjeldahl's method (§ 18.5) and is especially serviceable, since it has been found that the results of the titration method for urea by Liebig's process, either in its original way or by subsequent modifications, cannot give the true data for calculating the nitrogen in any given specimen of urine.

*The Analysis:* 5 c.c. of urine of average concentration are measured into a flask holding about 300 c.c., together with 20 c.c. of the mixed acids described on page 69 (§ 18), then heated to boiling, and the heat continued until all vapour and gases are given off and the fluid possesses a clear yellow tint. 25 to 30 minutes generally suffices. The flask is then suffered to cool, diluted, and the liquid distilled with caustic soda and zinc as described on page 69.

## ANALYSIS OF NATURAL WATERS AND SEWAGE.

§ 87. The analysis of natural waters and sewage has for a long period received the attention of chemists, but until lately no methods of examination have been produced which could be said to satisfy the demands of those who have been interested in the subject from various points of view. The researches of Clark, Frankland, Miller, Wanklyn, Tidy, Bischof, Warington, and others, have, however, now brought the whole subject into a more satisfactory form, so that it may fairly be said that, as regards accuracy of chemical processes, or interpretation of results from a sanitary point of view, very little addition is required. Considerable space will be devoted to the matter here; and as most of the processes are now volumetric, and admit of ready and accurate results, the general subject naturally falls within the scope of this work. Considerable pains have been taken to render the treatment of the matter practical and trustworthy.

Since the various processes necessitate the use of peculiar materials and apparatus, the preparation and arrangement of these will be described at some length previous to the introduction of the general subject.

## THE PREPARATION OF RE-AGENTS.

### A. Re-agents required for the Estimation of Nitrogen present as Ammonia.

(α) *Nessler's Solution.*—Dissolve 62·5 gm. of potassic iodide in about 250 c.c. of distilled water, set aside a few c.c., and add gradually to the larger part a cold saturated solution of corrosive sublimate until the mercuric iodide precipitated ceases to be redissolved on stirring. When a permanent precipitate is obtained, restore the reserved potassic iodide so as to redissolve it, and continue adding corrosive sublimate very gradually until a slight precipitate remains undissolved. (The small quantity of potassic iodide is set aside merely to enable the mixture to be made rapidly without danger of adding an excess of corrosive sublimate.)

Next dissolve 150 gm. of solid potassic hydrate (that usually sold in sticks or cakes) in 150 c.c. of distilled water, allow the solution to cool, add it gradually to the above solution, and make up with distilled water to one liter.

On standing, a brown precipitate is deposited, and the solution becomes clear, and of a pale greenish-yellow colour. It is ready for use as soon as it is perfectly clear, and should be decanted into a smaller bottle as required.

(β) *Standard Solution of Ammonic Chloride.*—Dissolve 1·9107 gm. of pure dry ammonic chloride in a liter of distilled water; of this take 100 c.c., and make up to a liter with distilled water. The latter solution will contain ammonic chloride corresponding to 0·00005 gm. of nitrogen in each c.c. In use it should be measured from a narrow burette of 10 c.c. capacity divided into tenths.

[If it is desired to estimate "*ammonia*" rather than "*nitrogen as ammonia,*" take 1·5735 gm. of ammonic chloride instead of 1·9107 gm. 1 c.c. will then correspond to 0·00005 gm. of ammonia ($NH^3$).]

(γ) *Sodic Carbonate.*—Heat anhydrous sodic carbonate to redness in a platinum crucible for about an hour, taking care not to fuse it. Whilst still warm rub it in a clean mortar so as to break any lumps which may have been formed, and transfer to a clean dry wide-mouthed stoppered bottle.

(δ) *Water free from Ammonia.*—If, when 1 c.c. of Nessler's solution (**A.** α) is added to 100 c.c. of distilled water in a glass cylinder, standing on a white surface (*see* Estimation of Ammonia), no trace of a yellow tint is visible after five minutes, the water is sufficiently pure for use. As, however, this is rarely the case, the following process must usually be adopted. Distil from a large glass retort (or better, from a copper or tin vessel holding 15—20 liters) ordinary distilled water which has been rendered distinctly alkaline by addition of sodic carbonate. A glass Liebig's condenser, or a clean tin worm should be used to condense the vapour; it should be connected to the still by a short india-rubber joint. Test the distillate from time to time with Nessler's solution, as above described, and when free from ammonia collect the remainder for use. The distillation must not be carried to dryness. Ordinary water may be used instead of distilled water, but it occasionally continues for some time to give off traces of ammonia by the slow decomposition of the organic matter present in it.

### B. Re-agents required for the Estimation of Organic Carbon and Nitrogen.

(α) *Water free from Ammonia and Organic Matter.*—Distilled water, to which 1 gm. of potassic hydrate and 0·2 gm. of potassic permanganate per liter have been added, is boiled gently for about twenty-four hours in a similar vessel to that used in preparing water free from ammonia (A. δ), an inverted condenser being so arranged as to return the condensed water. At the end of that time the condenser is adjusted in the usual way, and the water carefully distilled, the distillate being tested at intervals for ammonia, as in preparing A. δ. When ammonia is no longer found, the remainder of the distillate may be collected, taking care to stop short of dryness. The neck of the retort or still should point slightly upwards, so that the joint which connects it with the condenser is the highest point. Any particles carried up mechanically will then run back to the still, and not contaminate the distillate. The water thus obtained should then be rendered slightly acid with sulphuric acid, and re-distilled from a clean vessel for use, again stopping short of dryness.

(β) *Solution of Sulphurous Acid.*—Sulphurous anhydride is prepared by the action of pure sulphuric acid upon cuttings of clean metallic copper which have been digested in the cold with concentrated sulphuric acid for twenty-four hours, and then washed with water. The gas is made to bubble through water to remove mechanical impurities, and then conducted into water free from ammonia and organic matter (B. α) until a saturated solution is obtained.

(γ) *Solution of Hydric Sodic Sulphite.*—Sulphurous anhydride, prepared and washed as above, is passed into a solution of sodic carbonate made by dissolving ignited sodic carbonate (A. γ) in water free from ammonia and organic matter (B. α). The gas is passed until carbonic anhydride ceases to be evolved.

(δ) *Solution of Ferrous Chloride.*—Pure crystallized ferrous sulphate is dissolved in water, precipitated by sodic hydrate, the precipitate well washed (using pure water B. α for the last washings), and dissolved in the smallest possible quantity of pure hydrochloric acid. Two or three drops must not contain an appreciable quantity of ammonia. It is convenient to keep the solution in a bottle with a ground glass cap instead of a stopper, so that a small dropping tube may be kept in it always ready for use.

($\epsilon$) *Cupric Oxide* is prepared by heating to redness with free access of air, on the hearth of a reverberatory furnace, or in a muffle, copper wire cut into short pieces, or copper sheets cut into strips. That which has been made by calcining the nitrate cannot be used, as it appears to be impossible to expel the last traces of nitrogen. After use, the oxide should be extracted by breaking the combustion tube, rejecting the portion which was mixed with the substance examined. As soon as a sufficient quantity has been recovered, it should be recalcined. This is most conveniently done in an iron tube about 30 m.m. in internal diameter, and about the same length as the combustion furnace. One end should be closed with a cork, the cupric oxide poured in, the tube placed in the combustion furnace (which is tilted at an angle of about 15°, so as to produce a current of air), the cork removed, and the tube kept at a red heat for about two hours. In a Hofmann's gas furnace, with five rows of burners, two such tubes may be heated at the same time if long clay burners are placed in the outer rows, and short ones in the three inner rows. If the furnace has but three rows of burners, a rather smaller iron tube must be used. When cold, the oxide can easily be extracted, if the heat has not been excessive, by means of a stout iron wire, and should be kept in a clean dry stoppered bottle. Each parcel thus calcined should invariably be assayed by filling with it a combustion tube of the usual size, and treating it in every respect as an ordinary combustion. It should yield only a very minute bubble of gas, which should be almost wholly absorbed by potassic hydrate. (The quantity of $CO^2$ found should not correspond to more than 0·00005 gm. of C.) The finer portions of the oxide should, after calcining, be sifted out by means of a sieve of clean copper gauze, and reserved for use as described hereafter.

New cupric oxide as obtained from the reverberatory furnace should be assayed, and if not sufficiently pure, as is most likely the case, calcined as above described, and assayed again.

($\zeta$) *Metallic Copper.*—Fine copper gauze is cut into strips about 80 m.m. wide, and rolled up as tightly as possible on a copper wire so as to form a compact cylinder 80 m.m. long. This is next covered with a tight case of moderately thin sheet copper, the edges of which meet without overlapping. The length of the strip of gauze, and the consequent diameter of the cylinder, must be regulated so that it will fit easily, but not too loosely in the combustion tubes. A sufficient number of these cylinders being prepared, a piece of combustion tube is filled with them, and they are heated to redness in the furnace, a current of atmospheric air being passed through them for a few minutes in order to burn off organic impurity, and coat the copper gauze superficially with oxide. A current of hydrogen, dried by passing through strong sulphuric acid, is then substituted for the air, and a red heat maintained until hydrogen issues freely from the end of the tube. It is then allowed to cool, the current of hydrogen being continued, and when cold the copper cylinders are removed, and kept in a stoppered bottle. After being used several times they must be heated in a stream of hydrogen as before, and are then again ready for use. The heating in air need not be repeated.

($\eta$) *Solution of Potassic Bichromate* is used as a test for and to absorb sulphurous anhydride which may be present in the gas obtained by combustion of the water residue. It should be saturated, and does not require any special attention. The yellow neutral chromate may also be used, but must be rendered slightly acid, lest it should absorb carbonic as well as sulphurous anhydride.

($\theta$) *Solution of Potassic Hydrate.*—A cold saturated solution made by dissolving solid potassic hydrate in distilled water.

($\iota$) *Solution of Pyrogallic Acid.*—A cold saturated solution, made by dissolving in distilled water solid pyrogallic acid obtained by sublimation.

($\kappa$) *Solution of Cuprous Chloride.*—A saturated solution of cupric chloride is rendered strongly acid with hydrochloric acid, a quantity of metallic copper introduced in the form of wire or turnings, and the whole allowed to stand in a closely stoppered bottle until the solution becomes colourless.

($\lambda$) *Oxygen.*—Blow a bulb of about 30 c.c. capacity at the end of a piece of combustion tube, and draw out the tube so that its internal diameter for a length of about 300 m.m. is about 3 m.m. This is done in order that the capacity of the apparatus apart from the bulb may be as small as possible. Cut the tube at the wide part about 10 m.m. from the point at which the narrow tube commences, thus leaving a small funnel-shaped mouth. Then introduce, a little at a time, dried, coarsely powdered, potassic chlorate until the bulb is full. Cut off the funnel, and, at a distance of 100 m.m. from the bulb, bend the tube at an angle of 45°, and at 10 m.m. from the end bend it at right angles in the opposite direction. It then forms a retort and delivery tube in one piece, and must be adjusted in a mercury trough in the usual manner, taking care that the end does not dip deeper than about 20 m.m. below the surface, as otherwise the pressure of so great a column of mercury might destroy the bulb when softened by heat. On gently heating, the potassic chlorate fuses and evolves oxygen. The escaping gas is collected in test tubes about 150 m.m. long and 20 m.m. in diameter, rejecting the first 60 or 80 c.c., which contain the nitrogen of the air originally in the bulb retort. Five or more of these tubes, according to the quantity of oxygen required, are collected and removed from the mercury trough, in very small beakers, the mercury in which should be about 10 m.m. above the end of the test tube. Oxygen may be kept in this way for any desired length of time, care being taken, if the temperature falls considerably, that there is sufficient mercury in the beaker to keep the mouth of the test tube covered. About 10 c.c. of the gas in the first tube collected is transferred by decantation in a mercury trough to another tube, and treated with potassic hydrate and pyrogallic acid, when, if after a few minutes it is absorbed, with the exception of a very small bubble, the gas in that and the remaining tubes may be considered pure. If not, the first tube is rejected, and the second tested in the same way, and so on.

($\mu$) *Hydric Metaphosphate.*—The glacial hydric metaphosphate, usually sold in sticks, is generally free from ammonia, or very nearly so. A solution should be made containing about 100 gm. in a liter. It should be so far free from ammonia as that 10 c.c. do not contain an appreciable quantity.

($\nu$) *Calcic Phosphate.*—Prepared by precipitating common disodic phosphate with calcic chloride, washing the precipitate with water by decantation, drying, and heating to redness for an hour.

### C. Re-agents required for the Estimation of Nitrogen present as Nitrates and Nitrites (Crum's process).

($\alpha$) *Concentrated Sulphuric Acid.*—The ordinary colourless acid is usually free from nitrates and nitrites. It should be tested before use by the method described hereafter for the estimation of nitrogen as nitrates (§ 83.6).

($\beta$) *Potassic Permanganate.*—Dissolve about 10 gm. of crystallized potassic permanganate in a liter of distilled water.

($\gamma$) *Sodic Carbonate.*—Dissolve about 10 gm. of dry, or an equivalent quantity of crystallized sodic carbonate free from nitrates, in a liter of distilled water.

### For the Estimation of Nitrogen as Nitrates and Nitrites in Waters containing a very large quantity of Soluble Matter, but little Organic Nitrogen.

($\delta$) *Metallic Aluminium.*—As thin foil.

($\varepsilon$) *Solution of Sodic Hydrate.*—Dissolve 100 gm. of solid sodic hydrate in a liter of distilled water; when cold, put it in a tall glass cylinder, and introduce about 100 sq. cm. of aluminium foil, which must be kept at the bottom of the solution by means of a glass rod. When the aluminium is dissolved, boil the solution briskly in a porcelain basin until about one-third of its volume has been evaporated, allow to cool, and make up to its original volume with water free from ammonia. The absence of nitrates is thus ensured.

(ζ) *Broken Pumice.*—Clean pumice is broken in pieces of the size of small peas, sifted free from dust, heated to redness for about an hour, and kept in a closely stoppered bottle.

(η) *Hydrochloric Acid free from Ammonia.*—If the ordinary pure acid is not free from ammonia, it should be rectified from sulphuric acid. As only two or three drops are used in each experiment, it will be sufficient if that quantity does not contain an appreciable proportion of ammonia.

### For the Estimation of Nitrogen as Nitrates and Nitrites by the Indigo Process.

The necessary solutions for this method have already been fully described on page 218.

### For the Estimation of Nitrites by Griess's Process.

(θ) *Meta-phenylene-diamine.*—A half per cent. solution of the base in very dilute sulphuric or hydrochloric acid. The base alone is not permanent. If too highly coloured, it may be bleached by pure animal charcoal.

(ι) *Dilute Sulphuric Acid.*—One volume of acid to two of water.

(κ) *Standard Potassic* or *Sodic Nitrite.*—Dissolve 0·406 gm. of pure silver nitrite in boiling distilled water, and add pure potassic or sodic chloride till no further precipitate of silver chloride occurs. Make up to a liter; let the silver chloride settle, and dilute 100 c.c. of the clear liquid to a liter. It should be kept in small stoppered bottles completely filled, and in the dark.

$$1 \text{ c.c.} = 0{\cdot}01 \text{ m.gm. } N^2O^3.$$

The colour produced by the reaction of nitrous acid on meta-phenylene-diamine is triamidoazo-benzene, or "Bismarck brown."

### D. Re-agents required for the Estimation of Chlorine present as Chloride.

(α) *Standard Solution of Argentic Nitrate.*—Dissolve 2·3944 gm. of pure recrystallized argentic nitrate in distilled water, and make up to a liter. In use it is convenient to measure it from a burette which holds 10 c.c. and is divided into tenths.

($\beta$) *Solution of Potassic Chromate.*—A strong solution of pure neutral potassic chromate free from chlorine. It is most conveniently kept in a bottle similar to that used for the solution of ferrous chloride (B. $\delta$).

### E. Re-agents required for determination of Hardness.

($\alpha$) *Standard Solution of Calcic Chloride.*—Dissolve in dilute hydric chloride, in a platinum dish, 0·2 gm. of pure crystallized calcite, adding the acid gradually, and having the dish covered with a glass plate, to prevent loss by spirting. When all is dissolved, evaporate to dryness on a water bath, add a little distilled water, and again evaporate to dryness. Repeat the evaporation several times to ensure complete expulsion of hydric chloride. Lastly, dissolve the calcic chloride in distilled water, and make up to one liter.

($\beta$) *Standard Solution of Potassic Soap.*—Rub together in a mortar 150 parts of lead plaster (Emplast. Plumbi of the druggists) and 40 parts of dry potassic carbonate. When they are fairly mixed, add a little methylated spirit, and continue triturating until an uniform creamy mixture is obtained. Allow to stand for some hours, then throw on to a filter, and wash several times with methylated spirit. The strong solution of soap thus obtained must be diluted with a mixture of one volume of distilled water and two volumes of methylated spirit (considering the soap solution as spirit), until exactly 14·25 c.c. are required to form a permanent lather with 50 c.c. of the standard calcic chloride (E. $\alpha$), the experiment being performed precisely as in determining the hardness of a water. A preliminary assay should be made with a small quantity of the strong soap solution to ascertain its strength. After making the solution approximately of the right strength, allow it to stand twenty-four hours; and then, if necessary, filter it, and afterwards adjust its strength accurately. It is better to make the solution a little too strong at first, and dilute it to the exact strength required, as it is easier to add alcohol accurately than strong soap solution.

## THE ANALYTICAL PROCESSES.

§ 88. To form, for sanitary purposes, an opinion of the character of a natural water or sewage, it will in most cases suffice to determine the nitrogen as ammonia, organic carbon, organic nitrogen, total solid matter, nitrogen as nitrates and nitrites, suspended matter, chlorine, and hardness; and in the following pages the estimation of these will be considered in detail, and then, more briefly, that of other impurities.

The method of estimating nitrogen as ammonia is substantially that described by the late W. A. Miller (*J. C. S.* [2] iii. 125), and that for estimating organic carbon and nitrogen was devised by Frankland and Armstrong, and described by them in the same journal ([2] vi. 77 *et seq.*).

### 1. Collection of Samples.

The points to be considered under this head are, the vessel to be used, the quantity of water required, and the method of ensuring a truly representative sample.

Stoneware bottles should be avoided, as they are apt to affect the hardness of the water, and are more difficult to clean than glass. Stoppered glass bottles should be used if possible; those known as "Winchester Quarts," which hold about two and a half liters each, are very convenient and easy to procure. One of these will contain sufficient for the general analysis of sewage and largely polluted rivers, two for well waters and ordinary rivers and streams, and three for lakes and mountain springs. If a more detailed analysis is required, of course a larger quantity must be taken.

If corks must be used, they should be *new*, and well washed with the water at the time of collection.

In collecting from a well, river, or tank, plunge the bottle itself, if possible, below the surface; but if an intermediate vessel must be used, see that it is thoroughly clean and well rinsed with the water. Avoid the surface water and also any deposit at the bottom.

If the sample is taken from a pump or tap, take care to let the water which has been standing in the pump or pipe run off before collecting, then allow the stream to flow directly into the bottle. If it is to represent a town water-supply, take it from the service pipe communicating directly with the street main, and not from a cistern.

In every case, first fill the bottle completely with the water, empty it again, rinse once or twice carefully with the water, and then fill it nearly to the stopper, and tie down tightly.

At the time of collection note the source of the sample, whether from a deep or shallow well, a river or spring, and also its local name so that it may be clearly identified.

If it is from a well, ascertain the nature of the soil, subsoil, and water-bearing stratum; the depth and diameter of the well, its distance from neighbouring cesspools, drains, or other sources of pollution; whether it passes through an impervious stratum before entering the water-bearing stratum, and if so, whether the sides of the well above this are, or are not, water-tight.

If the sample is from a river, ascertain the distance from the source to the point of collection; whether any pollution takes place above that point, and the geological nature of the district through which it flows.

If it is from a spring, take note of the stratum from which it issues.

### 2. Preliminary Observations.

In order to ensure uniformity, the bottle should invariably be well shaken before taking out a portion of the sample for any purpose. The *colour* should be observed as seen in a tall, narrow cylinder standing upon a white surface. It is well to compare it with distilled water in a similar vessel. The *taste and odour* are most easily detected when the water is heated to 30°—35° C.

Before commencing the quantitative analysis, it is necessary to decide whether the water shall be filtered or not before analysis. This must depend on the purpose for which the examination is undertaken. As a general rule, if the suspended matter is to be determined, the water should be filtered before the estimation of organic carbon and nitrogen, nitrogen as ammonia, and total solid residue; if otherwise, it should merely be shaken up. If the suspended matter is *not* determined, the appearance of the water, as whether it is clear or turbid, should be noted. This is conveniently done when measuring out the quantity to be used for the estimation of organic carbon and nitrogen. If the measuring flask be held between the eye and a good source of light, but with an opaque object, such as a window bar, in the line drawn from the eye through the centre of the flask, any suspended particles will be seen well illuminated on a dark ground.

Water derived from a newly sunk well, or which has been rendered turbid by the introduction of innocuous mineral matter from some temporary and exceptional cause should be filtered, but the suspended matter in most cases need not be determined. The introduction of organic matter of any kind would almost always render the sample useless.

### 3. Estimation of Nitrogen as Ammonia.

Place about 50 c.c. of the water in a glass cylinder about 150 m.m. high, and of about 70 c.c. capacity, standing upon a white glazed tile or white paper. Add about 1 c.c. of Nessler's solution (A. $\alpha$), stir with a clean glass rod, and allow to stand for a minute or so. If the colour then seen does not exceed in intensity that produced when 0·1 c.c. of the standard ammonic chloride (A. $\beta$) is added to 50 c.c. of water free from ammonia (A. $\delta$), and treated in the same way, half a liter of the water should be used for the estimation. If the colour be darker, a proportionately smaller quantity should be taken; but it is not convenient to use less than 20 or 25 c.c.

If it has been decided that the water should be filtered before analysis, care must be taken, should it contain only a small quantity of ammonia, that the *filter paper* is free from ammonia. If it is not, it must be steeped in water free from ammonia for a day or so, and when used, the first portion of the filtrate rejected. *Washing* with water, even if many times repeated, is generally ineffectual. When a large quantity of ammonia is present, as in highly polluted water and sewage, any ammonia in the filter paper may be neglected. A moderate quantity of suspended matter may also generally be neglected with safety, even if the water is to be filtered in estimating organic carbon and nitrogen and total solid matter.

The water, filtered or unfiltered as the case may be, should be carefully measured and introduced into a capacious retort, connected by an india-rubber joint with a Liebig's condenser, the volume being, if necessary, made up to about 400 c.c. with water free from ammonia. Add about 1 gm. of sodic carbonate (A. $\gamma$), and distil rapidly, applying the lamp flame directly to the retort, and collect the distillate in a small glass cylinder, such as is described above. When about 50 c.c. have distilled into the first cylinder, put it aside and collect a second 50 c.c., and as soon as that is over remove the lamp, and add to the *second* distillate about 1 c.c. of Nessler's solution, stir with a clean glass rod, and allow to stand on a white tile or sheet of paper for five minutes. To estimate the ammonia present, measure into a similar cylinder as much of the standard ammonic chloride solution as you judge by the colour to be present in the distillate; make it up with water free from ammonia to the same volume, and treat with Nessler's solution in precisely the same way. If, on standing, the intensity of colour in the two cylinders is equal, the quantity of ammonia is also equal, and this is *known* in the trial cylinder. If it is not equal, another trial must be made with a greater or less quantity of ammonic chloride. The ammonic chloride must not be added *after* the Nessler's solution, or a turbidity will be produced which entirely prevents accurate comparison. If the ammonia in the second distillate does not exceed that in 0·2 c.c. of the standard ammonic chloride, the distillation need not be proceeded with any farther, but if otherwise, successive quantities must be distilled and tested until ammonia ceases to be found. If the ammonia in the second distillate corresponds to 0·4 c.c. or less of the ammonic chloride, that in the first may be estimated in the same way; but if the second contains a greater quantity of ammonia, the first must be measured, and an aliquot part taken and diluted to about 50 c.c. with water free from ammonia, as it is likely to contain so much ammonia as to give a colour too intense to admit of easy comparison. A colour produced by more than 2 c.c. of ammonic chloride cannot be conveniently employed. When, as in the case of sewage, a large quantity of ammonia is known to be present, it saves trouble to distil about 100 c.c. at first, and at once take an aliquot part of that, as above described. If the liquid spirts in distilling, arrange the retort so that the joint between the retort and condenser is the highest point; the distillation will proceed rather more slowly, but anything carried up mechanically will be returned to the retort. When the ammonia has been estimated in all the distillates, add together the corresponding volumes of ammonic chloride solution; then, if 500 c.c. have been employed for the experiment, the number of c.c. of ammonic chloride used divided by 100 will give the quantity of nitrogen as ammonia in 100,000 parts of the water; if less than that, say $y$ c.c. have been used, multiply the volume of ammonic chloride by $\frac{500}{y}$ and divide by 100 as before.

Before commencing this operation, ascertain that the retort and condenser are free from ammonia by distilling a little common water or distilled water with sodic carbonate until the distillate is free from ammonia. Remove the residue then, and after each estimation, by means of a glass syphon, without disconnecting the retort. If a small quantity of water is to be distilled, the residue or part of it from a previous experiment may be left in the retort, instead of adding water free from ammonia, care being taken that the previous distillation was continued until ammonia ceased to be evolved.

When urea is present the evolution of ammonia is long continued, owing to the decomposition of the urea. In such cases, collect the distillate in smaller quantities, and as soon as the first rapid diminution in the amount of ammonia has ceased, neglect the remainder, as this would be due almost wholly to decomposition of the urea.

### 4. Estimation of Organic Carbon and Nitrogen.

This should be commenced as soon as the nitrogen as ammonia has been determined. If that is less than 0·05 part per 100,000, a liter should be used; if more than 0·05, and less than 0·2, half a liter; if more than 0·2 and less than 1·0, a quarter of a liter; if more than 1·0, a hundred c.c. or less. These quantities are given as a guide in dealing with ordinary waters and sewage, but subject to variation in exceptional cases. A quantity which is too large should be avoided as entailing needless trouble in evaporation, and an inconveniently bulky residue and resulting gas. If it is to be filtered before analysis, the same precaution as to filter paper must be taken as for estimation of nitrogen as ammonia, the same filter being generally used.

Having measured the quantity to be used, add to it in a capacious flask 15 c.c. of the solution of sulphurous acid (B. $\beta$), and boil briskly for a few seconds, in order to decompose the carbonates present. Evaporate to dryness in a hemispherical glass dish, about a decimeter in diameter, and preferably without a lip, supported in a copper dish with a flange (fig. 40, *d e*). The flange has a diameter of about 14 centimeters, is sloped slightly towards the centre, and has a rim of about 5 m.m. turned up on its edge, except at one point, where a small lip is provided. The concave portion is made to fit the contour of the outside of the glass dishes, and is of such a depth as to allow the edge of the dish to rise about 15 m.m. above the flange. The diameter of the concavity at *f* is about 90 m.m., and the depth at *g* about 30 m.m. A thin glass shade, such as is used to protect statuettes, about 30 centimeters high, stands on the flange of the copper dish, its diameter being such as to fit without difficulty on the flange, and leave a sufficient space between its interior surface and the edge of the glass dish. The copper dish is supported on a steam or water bath, and the water as it evaporates is condensed on the interior of the glass shade, runs down into the copper dish, filling the space between it and the glass dish, and then passes off by the lip at the edge of the flange, a piece of tape held by the edge of the glass shade, and hanging over the lip, guiding it into a vessel placed to receive it.

We are indebted to Bischof for an improved apparatus for evaporation, which by keeping the dish always full by a self-acting contrivance, permits the operation to proceed without attention during the night, and thus greatly reduces the time required. This form of apparatus is shown in fig. 40. The glass dish *d* is supported by a copper dish *e* as described above, and resting on the latter is a stout copper ring *h* which is slightly conical, being 115 m.m. in diameter at the top and 130 at the bottom. At the top is a narrow flange of about 10 m.m. with a vertical rim of about 5 m.m.. The diameter across this flange is the same as the diameter of the dish *e*, so that the glass shade *i* will fit securely either on *h* or *e*. The height of the conical ring is about 80 m.m.

The automatic supply is accomplished on the well-known principle of the bird fountain, by means of a delivery tube *b*, the upper end of which is enlarged to receive the neck of the flask *a* containing the water to be evaporated, the joint being carefully ground so as to be water-tight. The upper vertical part of *b*, including this enlargement, is about 80 m.m. in length, and the sloping part about 260 m.m. with a diameter of 13 m.m. The lower end which goes into the dish is again vertical for about 85 m.m., and carries a side tube *c* of about 3 m.m. internal diameter, by which air enters the delivery tube whenever the level of the water in the dish falls below the point at which the side tube joins the delivery tube. The distance from this point to the end of the tube which rests on the bottom of the dish at *g*, and is there somewhat constricted, is about 30 m.m. The side tube *c* should not be attached on the side next the flask, as if so the inclined part of *b* passes over its mouth and renders it very difficult to clean. Mills prevents circulation of liquid in the sloping part of the tube by bending it into a slightly undulating form, so that permanent bubbles of air are caught and detained at two points in it. The flask *a* should hold about 1200 c.c., and have a rather narrow neck —about 20 m.m.—and a flat bottom. A small slot is cut in the upper edge of the copper ring *h* to accommodate the delivery tube, as shown in fig. 41. Its size and shape should be such that the tube does not touch the edge of the glass shade *i*, lest water running down the inner surface of the shade should find its way down the outside of the delivery tube into the dish. This being avoided, the opening should be as closely adjusted to the size of the delivery tube as can be. The copper dish *e* should rest on a steam or water bath, so that only the spherical part is exposed to the heat.

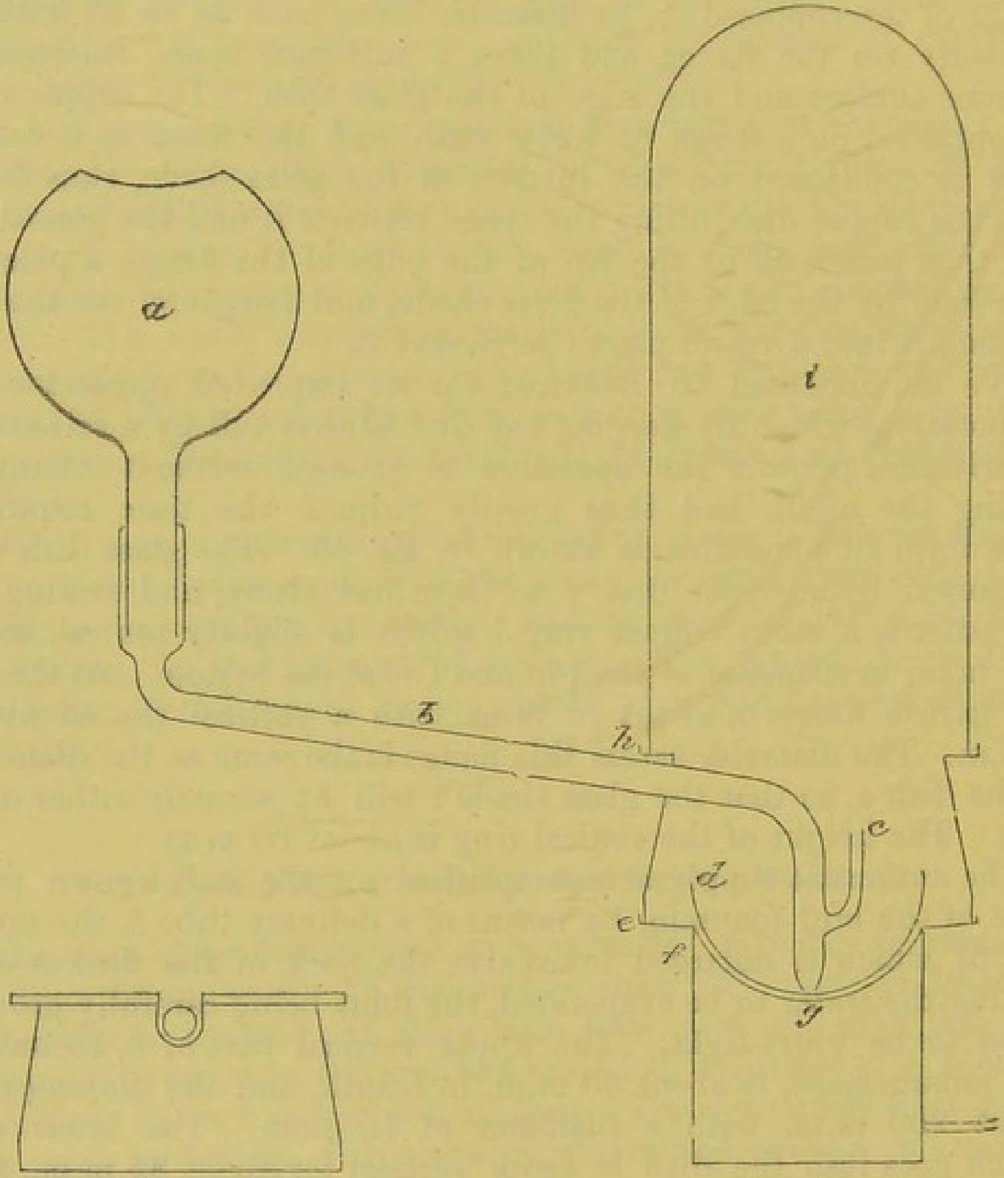

Fig. 41. Fig. 40.

After the addition of the 15 c.c. of sulphuric acid, the water may either be boiled in the flask *a*, or in another more capacious one, and then transferred to *a*. It should be allowed to cool before the delivery tube is adjusted, otherwise the joint between the two is liable to become loose by expansion of the cold socket of the delivery tube, after being placed over the hot neck of the flask.

The glass dish having been placed on the copper dish *e*, the conical ring *h* is fitted on, and the flask with the delivery tube attached inverted, as shown in fig. 40, *a*, *b*. This should not be done too hurriedly, and with a little care there is no risk of loss. The flask is supported either by a large wooden filtering stand, the ring of which has had a slot cut in it to allow the neck of the flask to pass, or by a clamp applied to the upper end of the delivery tube where the neck of the flask fits in. The delivery tube having been placed in the slot made to receive it, the glass shade is fitted on, and the evaporation allowed to proceed. When all the water has passed from the flask into the dish, the flask and delivery tube, and the conical ring *h* may be removed, and the glass shade placed directly on the dish *e* until the evaporation is complete. If the water is expected to contain a large quantity of nitrates, two or three drops of chloride of iron (**B.** $\delta$) should be added to the first dishful; and if it contains little or no carbonate, one or two c.c. of hydric sodic sulphite (**B.** $\gamma$). The former facilitates the destruction of nitrates and nitrites, and the latter furnishes base for the sulphuric acid produced by oxidation of the sulphurous acid, and which would, if free, decompose the organic matter when concentrated by evaporation. An estimate of the quantity of carbonate present, sufficiently accurate for this purpose, may generally be made by observing the quantity of precipitate thrown down on addition of sodic carbonate in the determination of nitrogen as ammonia.

With sewages and very impure waters (containing upwards of 0·1 part of nitrogen as ammonia per 100,000 for example) such great precaution is hardly necessary, and the quantity to evaporate being small, the evaporation may be conducted in a glass dish placed directly over a steam bath, and covered with a drum or disc of filter paper made by stretching the paper by means of two hoops of light split cane, one thrust into the other, the paper being between them, in the way often employed in making dialysers. This protects the contents of the dish from dust, and also, to a great extent, from ammonia which may be in the atmosphere, and which would impair the accuracy of the results. As a glass dish would be in some danger of breaking by the introduction of *cold* water, the flask containing the water being evaporated in this or in the first described manner, must be kept on a hot plate or sand-bath at a temperature of about 60° or 70° C., and should be covered with a watch-glass. This precaution is not necessary when Bischof's apparatus is used. If, at any time, the water in the flask ceases to smell strongly of sulphurous acid, more should be added. The preliminary boiling may be omitted when less than 250 c.c. is used. When the nitrogen as nitrates and nitrites exceeds 0·5 part, the dish, after the evaporation has been carried to dryness, should be filled with distilled water containing ten per cent. of saturated sulphurous acid solution, and the evaporation again carried to dryness. If it exceeds 1·0 part, a quarter of a liter of this solution should be evaporated on the residue; if 2·0 parts, half a liter; and if 5 parts, a liter. If less than a liter has been evaporated, a proportionally smaller volume of this solution may be used. The estimation of nitrogen as nitrates and nitrites will usually be accomplished before this stage of the evaporation is reached.

M. W. Williams proposes to avoid the use of sulphurous acid, with its acknowledged disadvantages and defects, by removing the nitric and nitrous acids with the zinc-copper couple and converting them into ammonia. If the amount is large, it is best distilled from a retort into weak acid; if small, into an empty Nessler tube. The amount so found is calculated into nitrogen as nitrates and nitrites, if the latter are found in the water. The residue, when free from ammonia is further concentrated, the separated carbonates redissolved in phosphoric or sulphurous acid, in just sufficient quantity, then transferred to a glass basin for evaporation to dryness as usual ready for combustion (*J. C. S.* 1881, 144).

In the case of sewage, however, it is advisable to employ hydric metaphosphate in the place of sulphurous acid, as the ammonic phosphate is even less volatile than the sulphite. This can only be employed for sewage and similar liquids, which are free from nitrates and nitrites. To the measured quantity of liquid to be evaporated add, in the glass dish, 10 c.c. of the hydric metaphosphate (B, $\mu$), and, in order to render the residue more convenient to detach from the dish, about half a gram of calcic phosphate (B. $\nu$), and proceed as usual. No chloride of iron, sulphurous acid, or sodic sulphite is required; nor is it necessary to boil before commencing the evaporation.

The next operation is the combustion of the residue. The combustion tube should be of hard, difficultly fusible glass, with an internal diameter of about 10 m.m. Cut it in lengths of about 430 m.m., and heat one end of each in the blowpipe flame to round the edge. Wash well with water, brushing the interior carefully with a tube brush introduced at the end whose edge has been rounded, rinse with distilled water, and dry in an oven. When dry, draw off and close, at the blowpipe, the end whose edge has been left sharp. The tube is then ready for use.

Pour on to the perfectly dry residue in the glass dish, standing on a sheet of white glazed paper, a little of the fine cupric oxide (B. $\varepsilon$), and with the aid of a small elastic steel spatula (about 100 m.m. long and 15 m.m. wide) carefully detach the residue from the glass and rub it down with the cupric oxide. The spatula readily accommodates itself to the curvature of the dish, and effectually scrapes its surface. When the contents of the dish are fairly mixed, fill about 30 m.m. of the length of the combustion tube with granulated cupric oxide (B. $\epsilon$), and transfer the mixture in the dish to the tube. This is done in the usual way by a scooping motion of the end of the tube in the dish, the last portions being transferred by the help of a bent card or a piece of clean and smooth platinum foil. Rinse the dish twice with a little fine cupric oxide, rubbing it well round each time with the spatula, and transfer to the tube as before. Any particles scattered on the paper are also to be put in. Fill up to a distance of 270 m.m. from the closed end with granular cupric oxide, put in a cylinder of metallic copper (B. $\zeta$), and then again 20 m.m. of granular cupric oxide. This last is to oxidize any traces of carbonic oxide which might be formed from carbonic anhydride by the reducing action of iron or other impurity in the metallic copper. Now draw out the end of the tube so as to form a neck about 100 m.m. long and 4 m.m. in diameter, fuse the end of this to avoid injury to the india-rubber connector, and bend it at right angles. It is now ready to be placed in the combustion furnace and attached to the Sprengel pump.

The most convenient form of this instrument for the purpose is shown in fig. 42. The glass funnel *a* is kept supplied with mercury, and is connected by a caoutchouc joint with a long narrow glass tube which passes down nearly to the bottom of a wider tube *d*, 900 m.m. long, and 10 m.m. in internal diameter. The upper end of *d* is cemented into the throat of a glass funnel *c* from which the neck has been removed. A screw clamp *b* regulates the flow of mercury down the narrow tube. A piece of ordinary glass tube *f g*, about 6 m.m. in diameter and 600 m.m. in length, is attached at *g* to a tube *g h k*, about 6 m.m. in diameter, 1500 m.m. long, with a bore of 1 m.m. This is bent sharply on itself at *h*, the part *h k* being 1300 m.m. long, and the two limbs are firmly lashed together with copper wire at two points, the tubes being preserved from injury by short sheaths of caoutchouc tube. The end *k* is recurved for the delivery of gas. At the top of the bend at *h*, a piece of ordinary tube *h l*, about 120 m.m. long, and 5 m.m. in diameter, is sealed on. The whole *l k* is kept in a vertical position by a loose support or guide, near its upper part, the whole of its weight resting on the end *k*, so that it is comparatively free to move. It is connected at *f* with the lower end of *d*, by means of a piece of caoutchouc tube covered with tape, and furnished with a screw clamp *e*. At *l* it is connected with the combustion tube *o*, by the connecting tube *l m n*, which is made of tube similar to that used for *h k*. A cork slides on *h l*, which is fitted into the lower end of a short piece of tube of a width sufficient to pass easily over the caoutchouc joint connecting the tubes at *l*. After the joint has been arranged (the ends of the tubes just touching) and bound with wire, the cork and wide tube are pushed over it and filled with glycerine. The joint at *n* is of exactly the same kind, but as it has to be frequently disconnected, water is used instead of glycerine, and the caoutchouc is not bound on to the combustion tube with wire. It will be seen that the joint at *l* is introduced chiefly to give flexibility to the apparatus. At *m* is a small bulb blown on the tube

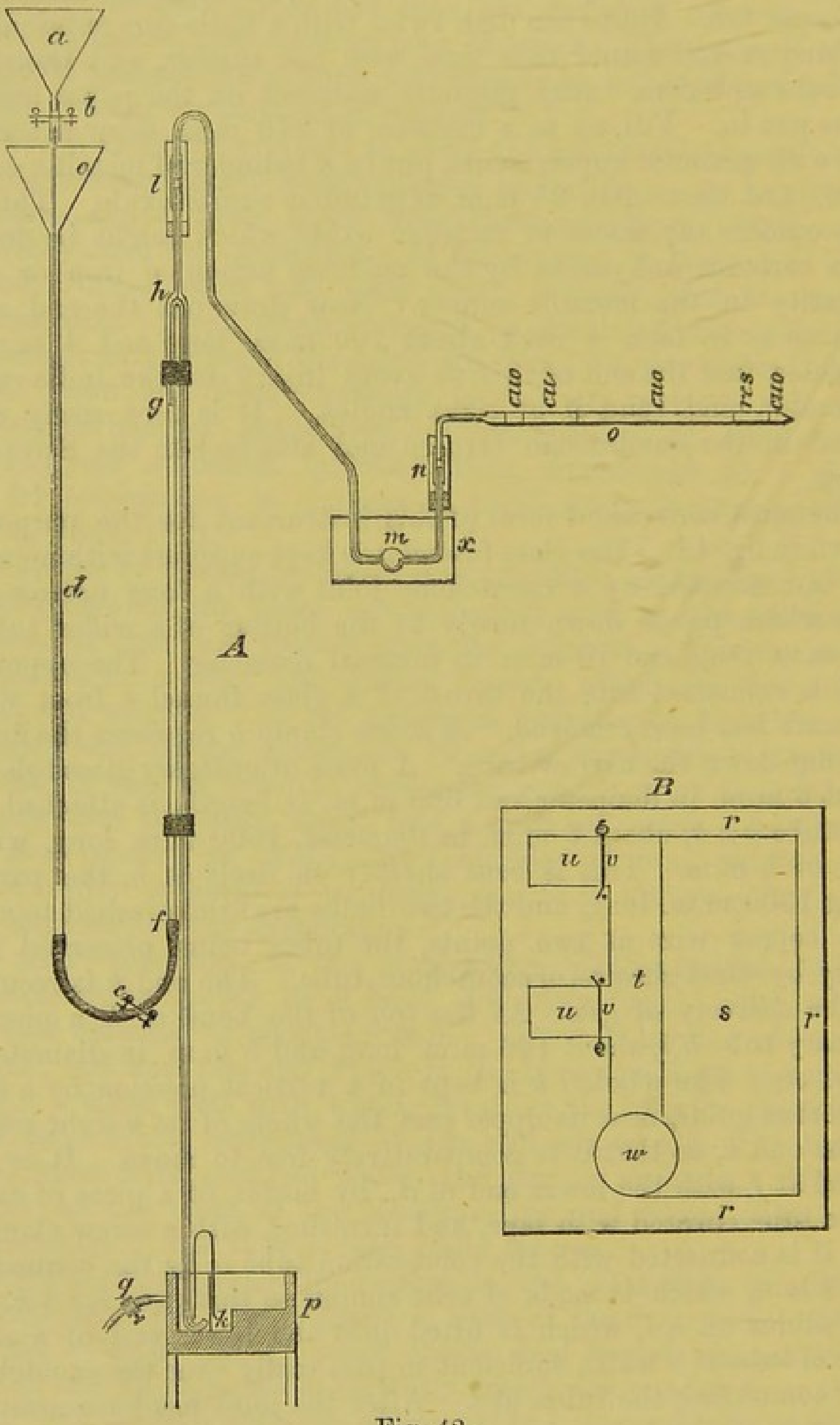

Fig. 42.

for the purpose of receiving water produced in the combustion. This is immersed in a small water trough *x*. The tube *h k* stands in a mercury trough *p*, which is shown in plan on a larger scale at B.

This trough should be cut out of a solid piece of mahogany, as it is extremely difficult to make joints to resist the pressure of such a depth of mercury. It is 200 m.m. long, 155 m.m. wide, and 100 m.m. deep, outside measurement. The edge *r r* is 13 m.m. wide, and the shelf *s* 65 m.m. wide, 174 m.m. long, and 50 m.m. deep from the top of the trough. The channel *t* is 25 m.m. wide, and 75 m.m. deep, having at one end a circular well *w*, 42 m.m. in diameter, and 90 m.m. deep. The recesses *u u* are to receive the ends of two Sprengel pumps. They are each 40 m.m. long, 25 m.m. wide, and of the same depth as the channel *t*. A short iron wire *v*, turning on a small staple, and resting at the other end against an iron pin, stretches across each of these, and serves as a kind of gate to support the test tube, in which the gas delivered by the pump is collected. The trough stands upon four legs, 75 m.m. high, and is provided at the side with a tube and screw clamp *q*, by which the mercury may be drawn off to the level of the shelf *s*.

The combustion tube being placed in the furnace, protected from the direct action of the flame by a sheet-iron trough lined with asbestos, and the water joint at *n* adjusted, the gas is lighted at the front part of furnace so as to heat the whole of the metallic copper and part of the cupric oxide. A small screen of sheet iron is adjusted astride of the combustion tube to protect the part beyond the point up to which the gas is burning from the heat.

At the same time a stream of mercury is allowed to flow from the funnel *a*, which fills the tubes *d* and *f* until it reaches *h*, when it falls in a series of pellets down the narrow tube *h k*, each carrying before it a quantity of air drawn from the combustion tube. The flow of mercury must be controlled by means of the clamps *b* and *e*, so as not to be too rapid to admit of the formation of these separate pistons, and especially, care should be taken not to permit it to go so fast as to mount into the connecting tube *l m n*, as it cannot be removed thence except by disconnecting the tube. During the exhaustion, the trough *x* is filled with hot water to expel from the bulb *m* any water condensed from a previous operation. In about ten minutes the mercury will fall in the tube *h k* with a loud, sharp, clicking sound, showing that the vacuum is complete. As soon as this occurs, the pump may be stopped, a test tube filled with mercury inverted over the delivery end of the tube *k*, cold water substituted for hot in the trough *x*, the iron screen removed, and combustion proceeded with in the usual way. This will take from fifty to sixty minutes. As soon as the whole of the tube is heated to redness, the gas is turned off, and the tube immediately exhausted, the gases produced being transferred to the tube placed to receive them. When the exhaustion is complete, the test tube of gas may be removed in a small beaker, and transferred to the gas analysis apparatus.

This gas collected consists of carbonic anhydride, nitric oxide, nitrogen, and (very rarely) carbonic oxide, which can readily be separated and estimated by the ordinary methods of gas analysis.

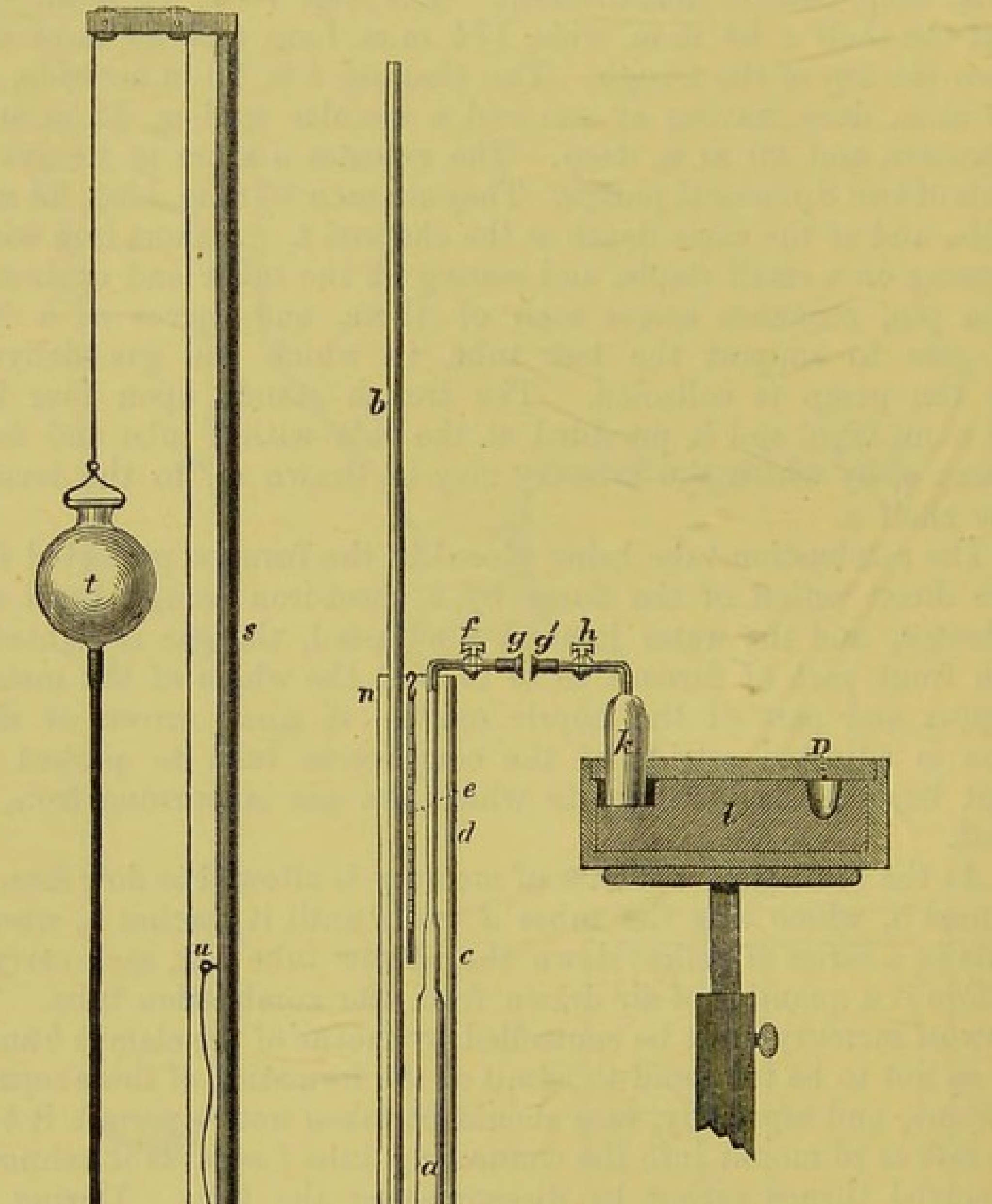

Fig. 43.

This is rapidly accomplished with the apparatus described in Part VII., or the simpler form, shown in the accompanying diagram, which, whilst it does not permit of analysis by explosion, leaves nothing to be desired for this particular operation. It is essentially that described by Frankland (*J. C. S.* [2] vi. 109), but is slightly modified in arrangement. In the diagram, *a c d* is a measuring tube, of which the cylindrical portion *a* is 370 m.m. long, and 18 m.m. in internal diameter, the part *c* 40 m.m. long, and 7 m.m. in diameter, and the part *d* 175 m.m. long, and 2·5 m.m. in diameter. To the upper end of *d* a tube, with a capillary bore and stop-cock *f*, is attached, and bent at right angles. Allowing 20 m.m. for each of the conical portions at the joints between *a* and *c*, and *c* and *d*, and 25 m.m. for the vertical part of the capillary tube, the vertical measurement of the entire tube is 650 m.m. It is graduated carefully from below upward, at intervals of 10 m.m., the zero being about 100 m.m. from the end, as about that length of it is hidden by its support, and therefore unavailable. The topmost 10 m.m. of *d* should be divided into single millimeters. At the free end of the capillary tube a small steel cap, shown in fig. 44, B, is cemented gas-tight. The lower end of *a* is drawn out to a diameter of 5 m.m. The tube *b* is about 1·2 meter long, and 6 m.m. internal diameter, is drawn out like *a* at the lower end, and graduated in millimeters from below upward, the zero being about 100 m.m. from the end.[*] The tubes *a c d* and *b* pass through a caoutchouc stopper *o*, which fits into the lower end of a glass cylinder *n n*, intended to contain water to give a definite temperature to the gas in measuring. The zeros of the graduations should be about 10 m.m. above this stopper. Immediately below this the tubes are firmly clasped by the wooden clamp *p* (shown in end elevation and plan at fig. 43, B, C), the two parts of which are drawn together by screws, the tubes being protected from injury by a piece of caoutchouc tube fitted over each. The clamp is supported on an upright piece of wood, screwed firmly to the base A. If the stopper *o* is carefully fitted, and the tubes tightly clamped, no other support than *p* will be necessary. The tubes below the clamp are connected by joints of caoutchouc covered with tape, and strongly bound with wire, to the vertical legs of the union piece *q*, to the horizontal leg of which is attached a long caoutchouc tube of about 2 m.m. internal diameter, which passes to the glass reservoir *t*. This tube must be covered with strong tape, or (less

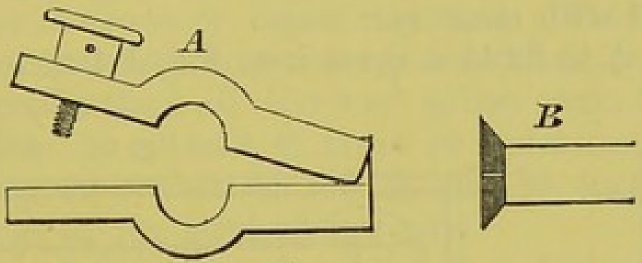

Fig. 44.

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[*] The graduation is not shown in the diagram.

conveniently) have a lining of canvas between two layers of caoutchouc, as it will be exposed to considerable pressure. In its course it passes through the double screw steel pinch-cock *r*, the lower bar of which is fixed to the side of the clamp *p*. It is essential that the screws of the pinch-cock should have smooth collars like that shown in fig. 44 A, and that the upper surface of the upper bar of the pinch-cock should be quite flat, the surfaces between which the tube is passed being cylindrical.

Frankland has introduced a form of joint by which the steel caps and clamp are dispensed with. The capillary tube at the upper end of *a c d* is expanded into a small cup or funnel, and the capillary tube of the laboratory vessel bent *twice* at right angles, the end being drawn out in a conical form to fit into the neck of the above-named cup. The opposed surfaces are fitted by grinding or by covering the conical end of the laboratory vessel with thin sheet caoutchouc. The joint is kept tight by an elastic band attached at one end to the stand, and at the other to a hook on the horizontal tube of the laboratory vessel, and the cup is filled with mercury.

In the base A is fixed a stout iron rod, 1·4 meter long, with a short horizontal arm at its upper end, containing two grooved pulleys. The reservoir *t* is suspended by a cord passing over these pulleys, and attached to an eye *u* in the iron rod, the length of the cord being such that, when at full stretch, the bottom of the reservoir is level with the bottom of the clamp *p*. A loop is made on the cord, which can be secured by a hook *v* on the rod, so that when thus suspended, the bottom of *t* is about 100 m.m. above the stop-cock *f*. A stout elastic band fitted round *t* at its largest diameter acts usefully as a fender to protect it from an accidental blow against the iron rod. A thermometer *e*, suspended by a wire hook from the edge of the cylinder *n n*, gives the temperature of the contained water, the uniformity of which may be insured (though it is scarcely necessary) by passing a slow succession of bubbles of air through it, or by moving up and down in it a wire with its end bent into the form of a ring. The jar *k* is called the laboratory vessel, and is 100 m.m. high, and 38 m.m. in internal diameter, having a capillary tube, glass stop-cock, and steel cap *g′ h* exactly like *f g*. The mercury trough *l* is shown in figs. 45 and 46. It is of solid mahogany, 265 m.m. long, 80 m.m. broad, and

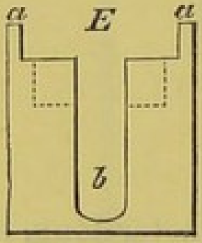

Fig. 45.

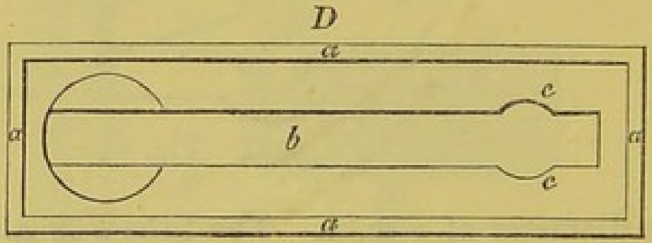

Fig. 46.

90 m.m. deep, outside measurement. The rim *a a a a* is 8 m.m. broad, and 15 m.m. deep. The excavation *b* is 230 m.m. long, 26 m.m. broad, and 65 m.m. deep, with a circular cavity to receive the laboratory vessel sunk at one end, 45 m.m. in diameter, and 20 m.m. in depth below the top of the excavation. Two small lateral indentations *c c* (fig. 46) near the other end accommodate a capsule for transferring to the trough tubes containing gas. This trough rests upon a telescope table, which can be fixed at any height by means of a screw, and is supported on three feet. It must be arranged, so that when the laboratory vessel is in its place in the trough, the two steel caps exactly correspond face to face.

The difference of level of the mercury in the tubes *b* and *a c d*, caused by capillary action, when both are freely open to the air, must be ascertained by taking several careful observations. This will be different for each of the portions *a c* and *d*, and must be added to or deducted from the observed pressure, as the mercury when thus freely exposed in both tubes to the atmospheric pressure stands in *a c* or *d* above or below that in *b*. This correction will include also any that may be necessary for difference of level of the zeros of the graduations of the two tubes, and, if the relative positions of these be altered, it must be redetermined. A small telescope, sliding on a vertical rod, should be used in these and all other readings of the level of mercury.

The capacity of the measuring tube *a c d* at each graduation must now be determined. This is readily done by first filling the whole apparatus with mercury, so that it drips from the cap *g*. The stop-cock *f* is then closed, a piece of caoutchouc tube slipped over the cap, and attached to a funnel supplied with distilled water. The reservoir *t* being lowered, the clamp *r* and the stop-cock *f* are opened, so that the mercury returns to the reservoir, water entering through the capillary tube. As soon as it is below the zero of the graduation, the stop-cock *f* is closed, the funnel and caoutchouc tube removed from the cap, and the face of the last slightly greased in order that water may pass over it without adhering. Now raise the reservoir, open the stop-cock *f*, and allow the water to flow gently out until the top of the convex surface of the mercury in *a* just coincides with the zero of the graduation. The mercury should be controlled by the clamp *r*, so that the water issues under very slight pressure. Note the temperature of the water in the water-jacket, and proceed with the expulsion of the water, collecting it as it drops from the steel cap in a small carefully weighed glass flask. When the mercury has risen through 100 m.m. stop the flow of water, and weigh the flask. The weight of water which was contained between the graduations 0 and 100 on the tube is then known, and if the temperature be 4° C., the weight in grams will express the capacity of that part of the tube in cubic centimeters. If the temperature be other than 4° C., the volume must be calculated by the aid of the co-efficient of expansion of water by heat. In a similar way the capacity of the tube at successive graduations about 100 m.m. apart is ascertained, the last determination in *a* being at the highest, and the first in *c* at the lowest graduation on the cylindrical part of each tube; the tube between these points and similar points on *c* and *d* being so distorted by the glass blower that observations could not well be made. The capacity at a sufficient number of points being ascertained, that at each of the intermediate graduations may be calculated, and a table arranged with the capacity marked against each graduation. As the calculations in the analysis are made by the aid of logarithms, it is convenient to enter on this table the logarithms of the capacities instead of the natural numbers.

In using the apparatus, the stop-cocks on the measuring tube and laboratory vessel should be slightly greased with a mixture of resin cerate and oil, or vaseline, the whole apparatus carefully filled with mercury, and the stop-cock *f* closed; next place the laboratory vessel in position in the mercury trough, and suck out the air. This is readily and rapidly done by the aid of a short piece of caoutchouc tube, placed in the vessel just before it is put into the mercury trough, and drawn away as soon as the air is removed. Suck out any small bubbles of air still left through the capillary tube, and as soon as the vessel is entirely free from air close the stop-cock. Slightly grease the faces of both caps with resin cerate (to which a little oil should be added if very stiff), and clamp them tightly together. On opening both stop-cocks mercury should flow freely through the capillary communication thus formed, and the whole should be quite free from air. To ascertain if the joints are all in good order, close the stop-cock *h*, and lower the reservoir *t* to its lowest position; the joints and stop-cocks will thus be subjected to a pressure of nearly half an atmosphere, and any leakage would speedily be detected. If all be right, restore the reservoir to its upper position.

Transfer the tube containing the gas to be analyzed to an ordinary porcelain mercury trough; exchange the beaker in which it has been standing for a small porcelain capsule, and transfer it to the mercury trough *l*, the capsule finding ample room where the trough is widened by the recess D.

Carefully decant the gas to the laboratory vessel, and add a drop or two of potassic bichromate solution (B. *η*) from a small pipette with a bent capillary delivery tube, to ascertain if the gas contains any sulphurous anhydride. If so, the yellow solution will immediately become green from the formation of a chromic salt, and the gas must be allowed to stand over the chromate for four or five minutes, a little more of the solution being added if necessary. The absorption may be greatly accelerated by gently shaking from time to time the stand on which the mercury trough rests, so as to cause the solution to wet the sides of the vessel. With care this may be done without danger to the apparatus. Mercury should be allowed to pass slowly into the laboratory vessel during the whole time, as the drops falling tend to maintain a circulation both in the gas and in the absorbing liquid. The absence of sulphurous anhydride being ascertained, both stop-cocks are set fully open, the reservoir *t* lowered, and the gas transferred to the measuring tube. The stop-cock *h* should be closed as soon as the liquid from the laboratory vessel is within about 10 m.m. of it. The bore of the capillary tube is so fine, that the quantity of gas contained in it is too small to affect the result. Next bring the top of the meniscus of mercury seen through the telescope exactly to coincide with one of the graduations on the measuring tube, the passage of mercury to or from the reservoir being readily controlled by the pinch-cock *r*. Note the position of the mercury in the measuring tube and in the pressure tube *b*, the temperature of the water-jacket, and the height of the barometer, the level of the mercury in the pressure tube and barometer being read to the tenth of a m.m. and the thermometer to 0·1° C. This done, introduce into the laboratory vessel from a pipette with a bent point, a few drops of potassic hydrate solution (B. $\theta$), and return the gas to the laboratory vessel. The absorption of carbonic anhydride will be complete in about three to five minutes, and if the volume of the gas is large, may be much accelerated by gently shaking the stand from time to time, so as to throw up the liquid on the sides of the vessel. If the small pipettes used to introduce the various solutions are removed from the mercury trough gently, they will always contain a little mercury in the bend, which will suffice to keep the solution from flowing out, and they may be kept in readiness for use standing upright in glass cylinders or other convenient supports. At the end of five minutes the gas, which now consists of nitrogen and nitric oxide, is again transferred to the measuring tube, and the operation of measuring repeated; the barometer, however, need not be observed, under ordinary circumstances, more than once for each analysis, as the atmospheric pressure will not materially vary during the twenty-five to thirty minutes required. Next pass into the laboratory vessel a few drops of saturated solution of pyrogallic acid (B. $\iota$), and return the gas upon it. The object of adding the pyrogallic acid at this stage is to ascertain if oxygen is present, as sometimes happens when the total quantity of gas is very small, and the vacuum during the combustion but slightly impaired. Under such circumstances, traces of oxygen are given off by the cupric oxide, and pass so rapidly over the metallic copper, as to escape absorption. This necessarily involves the loss of any nitric oxide which also escapes the copper, but this is such a very small proportion of an already small quantity that its loss will not appreciably affect the result. If oxygen be present, allow the gas to remain exposed to the action of the pyrogallate until the liquid when thrown up the sides of the laboratory vessel runs off without leaving a dark red stain. If oxygen be not present, a few bubbles of that gas (B. λ) are introduced to oxidize the nitric oxide to pernitric oxide, which is absorbed by the potassic hydrate. The oxygen may be very conveniently added from the gas pipette shown in fig. 47, where *a* *b* are glass bulbs of about 50 m.m. diameter, connected by a glass tube, the bore of which is constricted at *c*, so as to allow mercury to pass but slowly from one bulb to the other, and thus control the passage of gas through the narrow delivery tube *d*. The other end *e* is provided with a short piece of caoutchouc tube, by blowing through which any desired quantity of gas may be readily delivered. Care must be taken after use that the delivery tube is not removed from the trough till the angle *d* is filled with mercury.

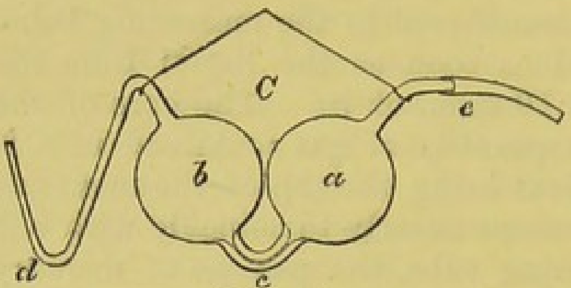

Fig. 47.

To replenish the pipette with oxygen, fill the bulb *b* and the tubes *c* and *d* with mercury; introduce the point of *d* into a tube of oxygen standing in the mercury trough, and draw air from the tube *e*. The gas in *b* is confined between the mercury in *c* and that in *d*.

When the excess of oxygen has been absorbed as above described, the residual gas, which consists of nitrogen, is measured, and the analysis is complete.*

There are thus obtained three sets of observations, from which, by the usual methods, we may calculate A the total volume, B the volume of nitric oxide and nitrogen, and C the volume of nitrogen, all reduced to 0° C. and 760 m.m. pressure; from these may be obtained

$$A - B = \text{vol. of } CO^2,$$

$$\frac{B - C}{2} + C = \frac{B + C}{2} = \text{vol. of N},$$

and hence the weight of carbon and nitrogen can be readily found.

It is much less trouble, however, to assume that the gas in all three stages consists wholly of nitrogen; then, if A be the weight of the total gas, B its weight after treatment with potassic hydrate,

---

* When the quantity of carbon is very large indeed, traces of carbonic oxide are occasionally present in the gas, and will remain with the nitrogen after treatment with alkaline pyrogallate. When such excessive quantities of carbon are found, the stopcock *f* should be closed when the last measurement is made, the laboratory vessel detached, washed, and replaced filled with mercury. Introduce then a little solution of cuprous chloride (**B.** κ), and return the gas upon it. Any carbonic oxide will be absorbed, and after about five minutes the remaining nitrogen may be measured. In more than twenty consecutive analyses of waters of very varying kinds, not a trace of carbonic oxide was found in any of the gases obtained on combustion.

and C after treatment with pyrogallate, the weight of carbon will be $(A-B)\frac{3}{7}$ and the weight of nitrogen $\frac{B+C}{2}$; for the weights of carbon and nitrogen in equal volumes of carbonic anhydride and nitrogen, at the same temperature and pressure, are as 6 : 14; and the weights of nitrogen in equal volumes of nitrogen and nitric oxide are as 2 : 1.

The weight of 1 c.c. of nitrogen at 0° C. and 760 m.m. is 0·0012562 gm., and the formula for the calculation is $w = \frac{0{\cdot}0012562 \times v \times p}{(1+0{\cdot}00367t)\,760}$, in which $w$ = the weight of nitrogen, $v$ the volume, $p$ the pressure corrected for tension of aqueous vapour, and $t$ the temperature in degrees centigrade. To facilitate this calculation, there is given in Table 2 the logarithmic value of the expression $\frac{0{\cdot}0012562}{(1+0{\cdot}00367t)\,760}$ for each tenth of a degree from 0° to 29·9° C., and in Table 1 the tension of aqueous vapour in millimeters of mercury. As the measuring tube is always kept moist with water, the gas when measured is always saturated with aqueous vapour.

The following example will show the precise mode of calculation :—

| | A<br>Total. | B<br>After absorption of $CO^2$. | C<br>Nitrogen. |
|---|---|---|---|
| Volume of gas | 4·4888 c.c. | 0·26227 c.c. | 0·26227 c.c. |
| Temperature | 13·5° | 13·6° | 13·7° |
| | m.m. | | |
| Height of mercury in *a*, *c*, *d* | 310·0 | 480·0 | 480·0 |
| ,, ,, ,, *b* | 193·5 | 343·5 | 328·2 |
| Difference | 116·5 | 136·5 | 151·8 |
| Plus tension of aqueous vapour | 11·5 | 11·6 | 11·7 |
| | 128·0 | | |
| Deduct correction for capillarity | 0·9 | Add for capillarity 2·2 | 2·2 |
| | 127·1 | 150·3 | 165·7 |
| | 769·8 | 769·8 | 769·8 |
| Deduct this from height of bar | 127·1 | 150·3 | 165·7 |
| Tension of dry gas | 642·7 | 619·5 | 604·1 |
| Logarithm of volume of gas | $\overline{0}{\cdot}65213$ | $\overline{1}{\cdot}41875$ | $\overline{1}{\cdot}41875$ |
| ,, ,, $\frac{0{\cdot}0012562}{(1+0{\cdot}00367t)\,760}$ | $\overline{6}{\cdot}19724$ | $\overline{6}{\cdot}19709$ | $\overline{6}{\cdot}19694$ |
| ,, ,, tension of dry gas | 2·80801 | 2·79204 | 2·78111 |
| Logarithm of weight of gas calculated as N. | $\overline{3}{\cdot}65738$ | $\overline{4}{\cdot}40788$ | $\overline{4}{\cdot}39680$ |
| | =0·0045434 | 0·0002558 | 0·0002494 gm. |

From these weights, those of carbon and of nitrogen are obtained by the use of the formulæ above mentioned. Thus—

$$\begin{array}{r} A - B = 0{\cdot}0042876 \\ \times \quad 3 \\ \div 7\,)\,\overline{0{\cdot}0128628} \\ \text{Weight of carbon, } \underline{\overline{0{\cdot}001837}} \end{array} \qquad \begin{array}{r} B + C = 0{\cdot}0005052 \\ \div 2 \\ \text{Weight of nitrogen, } \underline{\overline{0{\cdot}0002526}} \end{array}$$

When carbonic oxide is found, the corresponding weight of nitrogen may be found in a similar manner, and should be added to that corresponding to the carbonic anhydride before multiplying by $\frac{3}{7}$, and must be deducted from the weight corresponding to the volume after absorption of carbonic anhydride.

As it is impossible to attain to absolute perfection of manipulation and materials, each analyst should make several blank experiments by evaporating a liter of pure distilled water (B. *a*) with the usual quantities of sulphurous acid and chloride of iron, and, in addition, 0·1 gm. of freshly ignited sodic chloride (in order to furnish a tangible residue). The residue should be burnt and the resulting gas analyzed in the usual way, and the average amounts of carbon and nitrogen thus obtained deducted from the results of all analyses. This correction, which may be about 0·0001 gm. of C, and 0·00005 gm. of N, includes the errors due to the imperfection of the vacuum produced by the Sprengel pump, nitrogen retained in the cupric oxide, ammonia absorbed from the atmosphere during evaporation, etc.

When the quantity of nitrogen as ammonia exceeds 0·007 part per 100,000, there is a certain amount of loss of nitrogen during the evaporation by dissipation of ammonia. This appears to be very constant, and is given in Table 3, which is calculated from Table 5, which has been kindly furnished by Dr. Frankland. The number in this table corresponding to the quantity of nitrogen as ammonia present in the water analyzed should be added to the amount of nitrogen found by combustion. The number thus obtained includes the nitrogen as ammonia, and this must be deducted to ascertain the *organic* nitrogen. If "ammonia" is determined instead of "nitrogen as ammonia," Table 5 may be used.

When, in operating upon sewage, hydric metaphosphate has been employed, Tables 4 or 6 should be used.

### Rules for Converting Parts per 100,000 into Grains per Gallon, or the reverse.

To convert parts per 100,000 into grains per gallon, multiply by 0·7.

To convert grains per gallon into parts per 100,000, divide by 0·7.

To convert grams per liter into grains per gallon, multiply by 70.

## TABLE 1.

**Elasticity of Aqueous Vapour for each $\frac{1}{10}$th degree centigrade from 0° to 30° C. (Regnault).**

| Temp. C. | Tension in Millimeters of Mercury. | Temp. C. | Tension in Millimeters of Mercury. | Temp. C. | Tension in Millimeters of Mercury. | Temp. C. | Tension in Millimeters of Mercury. | Temp. C. | Tension in Millimeters of Mercury. |
|---|---|---|---|---|---|---|---|---|---|
| 0° | 4·6 | 6·0° | 7·0 | 12·0° | 10·5 | 18·0° | 15·4 | 24·0° | 22·2 |
| ·1 | 4·6 | ·1 | 7·0 | ·1 | 10·5 | ·1 | 15·5 | ·1 | 22·3 |
| ·2 | 4·7 | ·2 | 7·1 | ·2 | 10·6 | ·2 | 15·6 | ·2 | 22·5 |
| ·3 | 4·7 | ·3 | 7·1 | ·3 | 10·7 | ·3 | 15·7 | ·3 | 22·6 |
| ·4 | 4·7 | ·4 | 7·2 | ·4 | 10·7 | ·4 | 15·7 | ·4 | 22·7 |
| ·5 | 4·8 | ·5 | 7·2 | ·5 | 10·8 | ·5 | 15·8 | ·5 | 22·9 |
| ·6 | 4·8 | ·6 | 7·3 | ·6 | 10·9 | ·6 | 15·9 | ·6 | 23·0 |
| ·7 | 4·8 | ·7 | 7·3 | ·7 | 10·9 | ·7 | 16·0 | ·7 | 23·1 |
| ·8 | 4·9 | ·8 | 7·4 | ·8 | 11·0 | ·8 | 16·1 | ·8 | 23·3 |
| ·9 | 4·9 | ·9 | 7·4 | ·9 | 11·1 | ·9 | 16·2 | ·9 | 23·4 |
| 1·0 | 4·9 | 7·0 | 7·5 | 13·0 | 11·2 | 19·0 | 16·3 | 25·0 | 23·5 |
| ·1 | 5·0 | ·1 | 7·5 | ·1 | 11·2 | ·1 | 16·4 | ·1 | 23·7 |
| ·2 | 5·0 | ·2 | 7·6 | ·2 | 11·3 | ·2 | 16·6 | ·2 | 23·8 |
| ·3 | 5·0 | ·3 | 7·6 | ·3 | 11·4 | ·3 | 16·7 | ·3 | 24·0 |
| ·4 | 5·1 | ·4 | 7·7 | ·4 | 11·5 | ·4 | 16·8 | ·4 | 24·1 |
| ·5 | 5·1 | ·5 | 7·8 | ·5 | 11·5 | ·5 | 16·9 | ·5 | 24·3 |
| ·6 | 5·2 | ·6 | 7·8 | ·6 | 11·6 | ·6 | 17·0 | ·6 | 24·4 |
| ·7 | 5·2 | ·7 | 7·9 | ·7 | 11·7 | ·7 | 17·1 | ·7 | 24·6 |
| ·8 | 5·2 | ·8 | 7·9 | ·8 | 11·8 | ·8 | 17·2 | ·8 | 24·7 |
| ·9 | 5·3 | ·9 | 8·0 | ·9 | 11·8 | ·9 | 17·3 | ·9 | 24·8 |
| 2·0 | 5·3 | 8·0 | 8·0 | 14·0 | 11·9 | 20·0 | 17·4 | 26·0 | 25·0 |
| ·1 | 5·3 | ·1 | 8·1 | ·1 | 12·0 | ·1 | 17·5 | ·1 | 25·1 |
| ·2 | 5·4 | ·2 | 8·1 | ·2 | 12·1 | ·2 | 17·6 | ·2 | 25·3 |
| ·3 | 5·4 | ·3 | 8·2 | ·3 | 12·1 | ·3 | 17·7 | ·3 | 25·4 |
| ·4 | 5·5 | ·4 | 8·2 | ·4 | 12·2 | ·4 | 17·8 | ·4 | 25·6 |
| ·5 | 5·5 | ·5 | 8·3 | ·5 | 12·3 | ·5 | 17·9 | ·5 | 25·7 |
| ·6 | 5·5 | ·6 | 8·3 | ·6 | 12·4 | ·6 | 18·0 | ·6 | 25·9 |
| ·7 | 5·6 | ·7 | 8·4 | ·7 | 12·5 | ·7 | 18·2 | ·7 | 26·0 |
| ·8 | 5·6 | ·8 | 8·5 | ·8 | 12·5 | ·8 | 18·3 | ·8 | 26·2 |
| ·9 | 5·6 | ·9 | 8·5 | ·9 | 12·6 | ·9 | 18·4 | ·9 | 26·4 |
| 3·0 | 5·7 | 9·0 | 8·6 | 15·0 | 12·7 | 21·0 | 18·5 | 27·0 | 26·5 |
| ·1 | 5·7 | ·1 | 8·6 | ·1 | 12·8 | ·1 | 18·6 | ·1 | 26·7 |
| ·2 | 5·8 | ·2 | 8·7 | ·2 | 12·9 | ·2 | 18·7 | ·2 | 26·8 |
| ·3 | 5·8 | ·3 | 8·7 | ·3 | 12·9 | ·3 | 18·8 | ·3 | 27·0 |
| ·4 | 5·8 | ·4 | 8·8 | ·4 | 13·0 | ·4 | 19·0 | ·4 | 27·1 |
| ·5 | 5·9 | ·5 | 8·9 | ·5 | 13·1 | ·5 | 19·1 | ·5 | 27·3 |
| ·6 | 5·9 | ·6 | 8·9 | ·6 | 13·2 | ·6 | 19·2 | ·6 | 27·5 |
| ·7 | 6·0 | ·7 | 9·0 | ·7 | 13·3 | ·7 | 19·3 | ·7 | 27·6 |
| ·8 | 6·0 | ·8 | 9·0 | ·8 | 13·4 | ·8 | 19·4 | ·8 | 27·8 |
| ·9 | 6·1 | ·9 | 9·1 | ·9 | 13·5 | ·9 | 19·5 | ·9 | 27·9 |
| 4·0 | 6·1 | 10·0 | 9·2 | 16·0 | 13·5 | 22·0 | 19·7 | 28·0 | 28·1 |
| ·1 | 6·1 | ·1 | 9·2 | ·1 | 13·6 | ·1 | 19·8 | ·1 | 28·3 |
| ·2 | 6·2 | ·2 | 9·3 | ·2 | 13·7 | ·2 | 19·9 | ·2 | 28·4 |
| ·3 | 6·2 | ·3 | 9·3 | ·3 | 13·8 | ·3 | 20·0 | ·3 | 28·6 |
| ·4 | 6·3 | ·4 | 9·4 | ·4 | 13·9 | ·4 | 20·1 | ·4 | 28·8 |
| ·5 | 6·3 | ·5 | 9·5 | ·5 | 14·0 | ·5 | 20·3 | ·5 | 28·9 |
| ·6 | 6·4 | ·6 | 9·5 | ·6 | 14·1 | ·6 | 20·4 | ·6 | 29·1 |
| ·7 | 6·4 | ·7 | 9·6 | ·7 | 14·2 | ·7 | 20·5 | ·7 | 29·3 |
| ·8 | 6·4 | ·8 | 9·7 | ·8 | 14·2 | ·8 | 20·6 | ·8 | 29·4 |
| ·9 | 6·5 | ·9 | 9·7 | ·9 | 14·3 | ·9 | 20·8 | ·9 | 29·6 |
| 5·0 | 6·5 | 11·0 | 9·8 | 17·0 | 14·4 | 23·0 | 20·9 | 29·0 | 29·8 |
| ·1 | 6·6 | ·1 | 9·9 | ·1 | 14·5 | ·1 | 21·0 | ·1 | 30·0 |
| ·2 | 6·6 | ·2 | 9·9 | ·2 | 14·6 | ·2 | 21·1 | ·2 | 30·1 |
| ·3 | 6·7 | ·3 | 10·0 | ·3 | 14·7 | ·3 | 21·3 | ·3 | 30·3 |
| ·4 | 6·7 | ·4 | 10·1 | ·4 | 14·8 | ·4 | 21·4 | ·4 | 30·5 |
| ·5 | 6·8 | ·5 | 10·1 | ·5 | 14·9 | ·5 | 21·5 | ·5 | 30·7 |
| ·6 | 6·8 | ·6 | 10·2 | ·6 | 15·0 | ·6 | 21·7 | ·6 | 30·8 |
| ·7 | 6·9 | ·7 | 10·3 | ·7 | 15·1 | ·7 | 21·8 | ·7 | 31·0 |
| ·8 | 6·9 | ·8 | 10·3 | ·8 | 15·2 | ·8 | 21·9 | ·8 | 31·2 |
| ·9 | 7·0 | ·9 | 10·4 | ·9 | 15·3 | ·9 | 22·1 | ·9 | 31·4 |

## TABLE 2.

**Reduction of Cubic Centimeters of Nitrogen to Grams.**

Log. $\frac{0{\cdot}0012562}{(1 + 0{\cdot}00367t)760}$ for each tenth of a degree from 0° to 30° C.

| t. C. | 0·0 | 0·1 | 0·2 | 0·3 | 0·4 | 0·5 | 0·6 | 0·7 | 0·8 | 0·9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 0° | $\bar{6}$·21824 | 808 | 793 | 777 | 761 | 745 | 729 | 713 | 697 | 681 |
| 1 | 665 | 649 | 633 | 617 | 601 | 586 | 570 | 554 | 538 | 522 |
| 2 | 507 | 491 | 475 | 459 | 443 | 427 | 412 | 396 | 380 | 364 |
| 3 | 349 | 333 | 318 | 302 | 286 | 270 | 255 | 239 | 223 | 208 |
| 4 | 192 | 177 | 161 | 145 | 130 | 114 | 098 | 083 | 067 | 051 |
| 5 | 035 | 020 | 004 | *989 | *973 | *957 | *942 | *926 | *911 | *895 |
| 6 | $\bar{6}$·20879 | 864 | 848 | 833 | 817 | 801 | 786 | 770 | 755 | 739 |
| 7 | 723 | 708 | 692 | 676 | 661 | 645 | 629 | 614 | 598 | 583 |
| 8 | 567 | 552 | 536 | 521 | 505 | 490 | 474 | 459 | 443 | 428 |
| 9 | 413 | 397 | 382 | 366 | 351 | 335 | 320 | 304 | 289 | 274 |
| 10 | 259 | 244 | 228 | 213 | 198 | 182 | 167 | 151 | 136 | 121 |
| 11 | 106 | 090 | 075 | 060 | 045 | 029 | 014 | *999 | *984 | *969 |
| 12 | $\bar{6}$·19953 | 938 | 923 | 907 | 892 | 877 | 862 | 846 | 831 | 816 |
| 13 | 800 | 785 | 770 | 755 | 740 | 724 | 700 | 694 | 679 | 664 |
| 14 | 648 | 633 | 618 | 603 | 588 | 573 | 558 | 543 | 528 | 513 |
| 15 | 497 | 482 | 467 | 452 | 437 | 422 | 407 | 392 | 377 | 362 |
| 16 | 346 | 331 | 316 | 301 | 286 | 271 | 256 | 241 | 226 | 211 |
| 17 | 196 | 181 | 166 | 151 | 136 | 121 | 106 | 091 | 076 | 061 |
| 18 | 046 | 031 | 016 | 001 | *986 | *971 | *956 | *941 | *926 | *911 |
| 19 | $\bar{6}$·18897 | 882 | 867 | 852 | 837 | 822 | 807 | 792 | 777 | 762 |
| 20 | 748 | 733 | 718 | 703 | 688 | 673 | 659 | 644 | 629 | 614 |
| 21 | 600 | 585 | 570 | 555 | 540 | 526 | 511 | 496 | 481 | 466 |
| 22 | 452 | 437 | 422 | 408 | 393 | 378 | 363 | 349 | 334 | 319 |
| 23 | 305 | 290 | 275 | 261 | 246 | 231 | 216 | 202 | 187 | 172 |
| 24 | 158 | 143 | 128 | 114 | 099 | 084 | 070 | 055 | 041 | 026 |
| 25 | 012 | *997 | *982 | *968 | *953 | *938 | *924 | *909 | *895 | *880 |
| 26 | $\bar{6}$·17866 | 851 | 837 | 822 | 808 | 793 | 779 | 764 | 750 | 735 |
| 27 | 721 | 706 | 692 | 677 | 663 | 648 | 634 | 619 | 605 | 590 |
| 28 | 576 | 561 | 547 | 532 | 518 | 503 | 489 | 475 | 460 | 446 |
| 29 | 432 | 417 | 403 | 388 | 374 | 360 | 345 | 331 | 316 | 302 |

## TABLE 3.

### Loss of Nitrogen by Evaporation of $NH^3$.
### With Sulphurous Acid.

**Parts per 100,000.**

| N as $NH^3$. | Loss of N. | N as $NH^3$. | Loss of N. | N as $NH^3$. | Loss of N. | N as $NH^3$. | Loss of N. | N as $NH^3$. | Loss of N. | N as $NH^3$. | Loss of N. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5·0 | 1·741 | 3·9 | 1·425 | 2·8 | ·898 | 1·7 | ·370 | ·6 | ·145 | ·04 | ·009 |
| 4·9 | 1·717 | 3·8 | 1·378 | 2·7 | ·850 | 1·6 | ·338 | ·5 | ·109 | ·03 | ·007 |
| 4·8 | 1·693 | 3·7 | 1·330 | 2·6 | ·802 | 1·5 | ·324 | ·4 | ·075 | ·02 | ·005 |
| 4·7 | 1·669 | 3·6 | 1·282 | 2·5 | ·754 | 1·4 | ·309 | ·3 | ·057 | ·01 | ·003 |
| 4·6 | 1·645 | 3·5 | 1·234 | 2·4 | ·706 | 1·3 | ·295 | ·2 | ·038 | ·008 | ·002 |
| 4·5 | 1·621 | 3·4 | 1·186 | 2·3 | ·658 | 1·2 | ·280 | ·1 | ·020 | ·007 | ·001 |
| 4·4 | 1·598 | 3·3 | 1·138 | 2·2 | ·610 | 1·1 | ·266 | ·09 | ·018 | | |
| 4·3 | 1·574 | 3·2 | 1·090 | 2·1 | ·562 | 1·0 | ·252 | ·08 | ·017 | | |
| 4·2 | 1·550 | 3·1 | 1·042 | 2·0 | ·514 | ·9 | ·237 | ·07 | ·015 | | |
| 4·1 | 1·521 | 3·0 | ·994 | 1·9 | ·466 | ·8 | ·217 | ·06 | ·013 | | |
| 4·0 | 1·473 | 2·9 | ·946 | 1·8 | ·418 | ·7 | ·181 | ·05 | ·011 | | |

## TABLE 4.

### Loss of Nitrogen by Evaporation of $NH^3$.
### With Hydric Metaphosphate.

**Parts per 100,000.**

| Volume evaporated. | N as $NH^3$. | Loss of N. | Volume evaporated. | N as $NH^3$. | Loss of N. | Volume evaporated. | N as $NH^3$. | Loss of N. | Volume evaporated. | N as $NH^3$. | Loss of N. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 100 c.c. | 8·2 | ·482 | 100 c.c. | 5·9 | ·385 | 100 c.c. | 3·6 | ·281 | 100 c.c. | 1·3 | ·142 |
| ... | 8·1 | ·477 | ... | 5·8 | ·381 | ... | 3·5 | ·277 | ... | 1·2 | ·136 |
| ... | 8·0 | ·473 | ... | 5·7 | ·377 | ... | 3·4 | ·272 | ... | 1·1 | ·129 |
| ... | 7·9 | ·469 | ... | 5·6 | ·373 | ... | 3·3 | ·267 | ... | 1·0 | ·123 |
| ... | 7·8 | ·465 | ... | 5·5 | ·368 | ... | 3·2 | ·261 | ... | ·9 | ·117 |
| ... | 7·7 | ·461 | ... | 5·4 | ·364 | ... | 3·1 | ·255 | ... | ·8 | ·111 |
| ... | 7·6 | ·456 | ... | 5·3 | ·360 | ... | 3·0 | ·249 | 250 c.c. | ·7 | ·088 |
| ... | 7·5 | ·452 | ... | 5·2 | ·356 | ... | 2·9 | ·242 | ... | ·6 | ·073 |
| ... | 7·4 | ·448 | ... | 5·1 | ·352 | ... | 2·8 | ·236 | ... | ·5 | ·061 |
| ... | 7·3 | ·444 | ... | 5·0 | ·347 | ... | 2·7 | ·230 | 500 c.c. | ·4 | ·049 |
| ... | 7·2 | ·440 | ... | 4·9 | ·343 | ... | 2·6 | ·223 | ... | ·3 | ·036 |
| ... | 7·1 | ·435 | ... | 4·8 | ·338 | ... | 2·5 | ·217 | 1000 c.c. | ·2 | ·024 |
| ... | 7·0 | ·431 | ... | 4·7 | ·334 | ... | 2·4 | ·211 | ... | ·1 | ·012 |
| ... | 6·9 | ·427 | ... | 4·6 | ·329 | ... | 2·3 | ·205 | ... | ·09 | ·011 |
| ... | 6·8 | ·423 | ... | 4·5 | ·324 | ... | 2·2 | ·198 | ... | ·08 | ·010 |
| ... | 6·7 | ·419 | ... | 4·4 | ·319 | ... | 2·1 | ·192 | ... | ·07 | ·008 |
| ... | 6·6 | ·414 | ... | 4·3 | ·315 | ... | 2·0 | ·186 | ... | ·06 | ·007 |
| ... | 6·5 | ·410 | ... | 4·2 | ·310 | ... | 1·9 | ·180 | ... | ·05 | ·006 |
| ... | 6·4 | ·406 | ... | 4·1 | ·305 | ... | 1·8 | ·173 | ... | ·04 | ·005 |
| ... | 6·3 | ·402 | ... | 4·0 | ·301 | ... | 1·7 | ·167 | ... | ·03 | ·004 |
| ... | 6·2 | ·398 | ... | 3·9 | ·296 | ... | 1·6 | ·161 | ... | ·02 | ·002 |
| ... | 6·1 | ·394 | ... | 3·8 | ·291 | ... | 1·5 | ·154 | ... | ·01 | ·001 |
| ... | 6·0 | ·389 | ... | 3·7 | ·286 | ... | 1·4 | ·148 | | | |

## TABLE 5.

### Loss of Nitrogen by Evaporation of $NH^3$. With Sulphurous Acid.

**Parts per 100,000.**

| $NH^3$. | Loss of N. | $NH^3$. | Loss of N. | $NH^3$. | Loss of N. | $NH^3$. | Loss of N. | $NH^3$. | Loss of N. | $NH^3$. | Loss of N. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 6·0 | 1·727 | 4·8 | 1·451 | 3·6 | ·977 | 2·4 | ·503 | 1·2 | ·250 | ·09 | ·014 |
| 5·9 | 1·707 | 4·7 | 1·411 | 3·5 | ·937 | 2·3 | ·463 | 1·1 | ·238 | ·08 | ·013 |
| 5·8 | 1·688 | 4·6 | 1·372 | 3·4 | ·898 | 2·2 | ·424 | 1·0 | ·226 | ·07 | ·012 |
| 5·7 | 1·668 | 4·5 | 1·332 | 3·3 | ·858 | 2·1 | ·384 | ·9 | ·196 | ·06 | ·010 |
| 5·6 | 1·648 | 4·4 | 1·293 | 3·2 | ·819 | 2·0 | ·345 | ·8 | ·166 | ·05 | ·009 |
| 5·5 | 1·628 | 4·3 | 1·253 | 3·1 | ·779 | 1·9 | ·333 | ·7 | ·136 | ·04 | ·007 |
| 5·4 | 1·609 | 4·2 | 1·214 | 3·0 | ·740 | 1·8 | ·321 | ·6 | ·106 | ·03 | ·006 |
| 5·3 | 1·589 | 4·1 | 1·174 | 2·9 | ·700 | 1·7 | ·309 | ·5 | ·077 | ·02 | ·004 |
| 5·2 | 1·569 | 4·0 | 1·135 | 2·8 | ·661 | 1·6 | ·297 | ·4 | ·062 | ·01 | ·003 |
| 5·1 | 1·549 | 3·9 | 1·095 | 2·7 | ·621 | 1·5 | ·285 | ·3 | ·047 | ·009 | ·001 |
| 5·0 | 1·530 | 3·8 | 1·056 | 2·6 | ·582 | 1·4 | ·274 | ·2 | ·032 | | |
| 4·9 | 1·490 | 3·7 | 1·016 | 2·5 | ·542 | 1·3 | ·262 | ·1 | ·017 | | |

## TABLE 6.

### Loss of Nitrogen by Evaporation of $NH^3$. With Hydric Metaphosphate.

**Parts per 100,000.**

| Volume evaporated. | $NH^3$. | Loss of N. | Volume evaporated. | $NH^3$. | Loss of N. | Volume evaporated. | $NH^3$. | Loss of N. | Volume evaporated. | $NH^3$. | Loss of N. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 100 c.c. | 10·0 | ·483 | 100 c.c. | 7·2 | ·386 | 100 c.c. | 4·4 | ·283 | 100 c.c. | 1·6 | ·143 |
| ... | 9·9 | ·480 | ... | 7·1 | ·382 | ... | 4·3 | ·279 | ... | 1·5 | ·137 |
| ... | 9·8 | ·476 | ... | 7·0 | ·379 | ... | 4·2 | ·275 | ... | 1·4 | ·132 |
| ... | 9·7 | ·473 | ... | 6·9 | ·375 | ... | 4·1 | ·271 | ... | 1·3 | ·127 |
| ... | 9·6 | ·469 | ... | 6·8 | ·372 | ... | 4·0 | ·267 | ... | 1·2 | ·122 |
| ... | 9·5 | ·466 | ... | 6·7 | ·368 | ... | 3·9 | ·262 | ... | 1·1 | ·117 |
| ... | 9·4 | ·462 | ... | 6·6 | ·365 | ... | 3·8 | ·257 | ... | 1·0 | ·112 |
| ... | 9·3 | ·459 | ... | 6·5 | ·361 | ... | 3·7 | ·252 | 250 c.c. | ·9 | ·096 |
| ... | 9·2 | ·455 | ... | 6·4 | ·358 | ... | 3·6 | ·247 | ... | ·8 | ·080 |
| ... | 9.1 | ·452 | ... | 6·3 | ·354 | ... | 3·5 | ·242 | ... | ·7 | ·070 |
| ... | 9·0 | ·448 | ... | 6·2 | ·351 | ... | 3·4 | ·236 | ... | ·6 | ·060 |
| ... | 8·9 | ·445 | ... | 6·1 | ·348 | ... | 3·3 | ·231 | 500 c.c. | ·5 | ·050 |
| ... | 8·8 | ·441 | ... | 6·0 | ·345 | ... | 3·2 | ·226 | ... | ·4 | ·040 |
| ... | 8·7 | ·438 | ... | 5·9 | ·341 | ... | 3·1 | ·221 | ... | ·3 | ·030 |
| ... | 8·6 | ·434 | ... | 5·8 | ·337 | ... | 3·0 | ·216 | 1000 c.c. | ·2 | ·020 |
| ... | 8·5 | ·431 | ... | 5·7 | ·333 | ... | 2·9 | ·211 | ... | ·1 | ·010 |
| ... | 8·4 | ·428 | ... | 5·6 | ·330 | ... | 2·8 | ·205 | ... | ·09 | ·009 |
| ... | 8·3 | ·424 | ... | 5·5 | ·326 | ... | 2·7 | ·200 | ... | ·08 | ·008 |
| ... | 8·2 | ·421 | ... | 5·4 | ·322 | ... | 2·6 | ·195 | ... | ·07 | ·007 |
| ... | 8·1 | ·417 | ... | 5·3 | ·318 | ... | 2·5 | ·190 | ... | ·06 | ·006 |
| ... | 8·0 | ·414 | ... | 5·2 | ·314 | ... | 2·4 | ·184 | ... | ·05 | ·005 |
| ... | 7·9 | ·410 | ... | 5·1 | ·310 | ... | 2·3 | ·179 | ... | ·04 | ·004 |
| ... | 7·8 | ·407 | ... | 5·0 | ·306 | ... | 2·2 | ·174 | ... | ·03 | ·003 |
| ... | 7·7 | ·403 | ... | 4·9 | ·302 | ... | 2·1 | ·169 | ... | ·02 | ·002 |
| ... | 7·6 | ·400 | ... | 4·8 | ·298 | ... | 2·0 | ·164 | ... | ·01 | ·001 |
| ... | 7·5 | ·396 | ... | 4·7 | ·294 | ... | 1·9 | ·158 | | | |
| ... | 7·4 | ·393 | ... | 4·6 | ·291 | ... | 1·8 | ·153 | | | |
| ... | 7·3 | ·389 | ... | 4·5 | ·287 | ... | 1·7 | ·148 | | | |

### 5. Estimation of Total Solid Matter.

Evaporate over a steam or water bath half a liter or a less quantity of the water in a platinum dish which has been heated to redness and carefully weighed. The water should be filtered or unfiltered, according to the decision made in that respect at the commencement of the analysis. The quantity to be taken is regulated chiefly by the amount of nitrate present, as the residue from this operation is, with certain exceptions, employed for the determination of the nitrogen as nitrates and nitrites. As a general rule, for water supplies and river water half a liter should be used; for shallow well waters, a quarter of a liter. Of sewages, 100 c.c., and of waters containing more than 0·08 part of nitrogen as ammonia per 100,000, a quarter of a liter will generally be convenient, as in these cases the residue will not be used for the estimation of nitrogen as nitrates and nitrites; and the only point to be considered is to have a quantity of residue suitable to weigh. It is desirable to support the platinum dish during evaporation in a glass ring with a flange, shaped like the top of a beaker, the cylindrical part being about 20 m.m. deep. This is dropped into the metal ring on the water bath, and thus lines the metal with glass, and keeps the dish clean. A glass disc with a hole in it to receive the dish is not satisfactory, as drops of water conveying solid matter find their way across the under surface from the metal vessel to the dish, and thus soil it. As soon as the evaporation is complete, the dish with the residue is removed, its outer side wiped dry with a cloth, and it is dried in a water or steam oven for about three hours. It is then removed to a desiccator, allowed to cool, weighed as rapidly as possible, returned to the oven, and weighed at intervals of an hour, until between two successive weighings it has lost less than 0·001 gm.

### 6. Estimation of Nitrogen as Nitrates and Nitrites.

The residue obtained in the preceding operation may be used for this estimation. Treat it with about 30 c.c. of hot distilled water, taking care to submit the whole of the residue to its action. To ensure this it is advisable to rub the dish gently with the finger, so as to detach the solid matter as far as possible, and facilitate the solution of the soluble matters. The finger may be covered by a caoutchouc finger-stall. Then filter through a very small filter of Swedish paper, washing the dish several times with small quantities of hot distilled water.

The filtrate must be evaporated in a very small beaker, over a steam bath, until reduced to about 1 c.c., or even to dryness. This concentrated solution is introduced into the glass tube shown

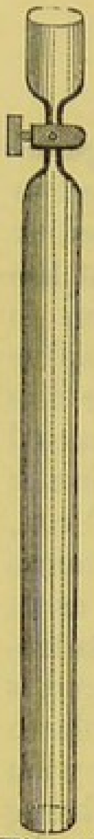

Fig. 48.

in fig. 48, standing in the porcelain mercury trough, filled up to the stop-cock with mercury. (If the nitrometer of Lunge is used in place of Crum's tube, the use of the laboratory tube and gas apparatus is avoided.) The tube is 210 m.m. in total length, and 15 m.m. in internal diameter. By pouring the liquid into the cup at the top, and then cautiously opening the stop-cock, it may be run into the tube without admitting any air. The beaker is rinsed once with a very little hot distilled water, and then two or three times with strong sulphuric acid (c. *a*), the volume of acid being to that of the aqueous solution about as 3 : 2. The total volume of acid and water should be about 6 c.c. Should any air by chance be admitted at this stage, it may readily be removed by suction, the lips being applied to the cup. With care there is but little danger of getting acid into the mouth.

In a few cases carbonic anhydride is given off on addition of sulphuric acid, and must be sucked out before proceeding.

Now grasp the tube firmly in the hand, closing the open end by the thumb, which should be first moistened; withdraw it from the trough, incline it at an angle of about 45°, the cup pointing from you, and shake it briskly with a rapid motion in the direction of its length, so as to throw the mercury up towards the stop-cock. After a very little practice there is no danger of the acid finding its way down to the thumb, the mixture of acid and mercury being confined to a comparatively small portion of the tube. In a few seconds some of the mercury becomes very finely divided; and if nitrates be present, in about a minute or less nitric oxide is evolved, exerting a strong pressure on the thumb. Mercury is allowed to escape as the reaction proceeds, by partially, but not wholly, relaxing the pressure of the thumb. A slight excess of pressure should be maintained within the tube to prevent entrance of air during the agitation, which must be continued until no more gas is evolved.

When the quantity of nitrate is very large, the mercury, on shaking, breaks up into irregular masses, which adhere to one another as if alloyed with lead or tin, and the whole forms a stiff dark-coloured paste, which it is sometimes very difficult to shake; but nitric oxide is not evolved for a considerable time, then comes off slowly, and afterwards with very great rapidity. To have room for the gas evolved, the operator should endeavour to shake the tube so as to employ as little as possible of the contained mercury in the reaction. At the close of the operation the finely-divided mercury will consist for the most part of minute spheres, the alloyed appearance being entirely gone. An experiment with a large quantity of nitrate may often be saved from loss by firmly resisting the escape of mercury, shaking until it is judged by the appearance of the contents of the tube that the reaction is complete, and then on restoring the tube to the mercury trough, allowing the finely-divided mercury also to escape in part. If the gas evolved be not more than the tube will hold, and there be no odour of pernitric oxide from the escaped finely-divided mercury, the operation may be considered successful. If the amount of nitrate be too large, a smaller quantity of the water must be evaporated and the operation repeated. When no nitrate is present, the mercury usually manifests very little tendency to become divided, that which does so remains bright, and the acid liquid does not become so turbid as it does in other cases.

The reaction completed, the tube is taken up closed by the thumb, and the gas is decanted into the laboratory vessel, and measured in the usual way in the gas apparatus. The nitric acid tube is of such a length, that when the cup is in contact with the end of the mercury trough, the open end is just under the centre of the laboratory vessel. If any acid has been expelled from the tube at the close of the shaking operation, the end of the tube and the thumb should be washed with water before introducing into the mercury trough of the gas apparatus, so as to remove any acid which may be adhering, which would destroy the wood of the trough. Before passing the gas into the measuring tube of the gas apparatus, a little mercury should be allowed to run over into the laboratory vessel to remove the acid from the entrance to the capillary tube.

As nitric oxide contains half its volume of nitrogen, if half a liter of water has been employed, the volume of nitric oxide obtained will be equal to the volume of *nitrogen* present as nitrates and nitrites in one liter of the water, and the weight of the nitrogen may be calculated as directed in the paragraph on the estimation of organic carbon and nitrogen.

When more than 0·08 part of nitrogen as ammonia is present in 100,000 parts of liquid, there is danger of loss of nitrogen by decomposition of ammonic nitrite on evaporation; and therefore the residue from the estimation of total solid matter cannot be used. In such cases acidify a fresh quantity of the liquid with dilute hydric sulphate, add solution of potassic permanganate, a little at a time, until the pink colour remains for about a minute, and render the liquid just alkaline to litmus paper with sodic carbonate. The nitrites present will then be converted into nitrates and may be evaporated without fear of loss. Use as little of each re-agent as possible. Sewage may be examined in this way; but it is hardly necessary to attempt the determination, as sewage is almost invariably free from nitrates and nitrites. Out of several hundred specimens, the writer only found two or three which contained any, and even then only in very small quantity.

### 7. Estimation of Nitrogen as Nitrates and Nitrites in Waters containing a very large quantity of Soluble Matter, with but little Ammonia or Organic Nitrogen.

When the quantity of soluble matter is excessive, as, for example, in sea-water, the preceding method is inapplicable, as the solution to be employed cannot be reduced to a sufficiently small bulk to go into the shaking tube. If the quantity of organic nitrogen be less than 0·1 part in 100,000, the nitrogen as nitrates and nitrites may generally be determined by the following modification of Schulze's method devised by E. T. Chapman. To 200 c.c. of the water add 10 c.c. of sodic hydrate solution (C. ε), and boil briskly in an open porcelain dish until it is reduced to about 70 c.c. When cold pour the residue into a tall glass cylinder of about 120 c.c. capacity, and rinse the dish with water free from ammonia. Add a piece of aluminium foil of about 15 sq. centim. area, loading it with a piece of clean glass rod to keep it from floating. Close the mouth of the cylinder with a cork, bearing a small tube filled with pumice (C. ζ) moistened with hydric chloride free from ammonia (C. η).

Hydrogen will speedily be given off from the surface of the aluminium, and in five or six hours the whole of the nitrogen as nitrates and nitrites will be converted into ammonia. Transfer to a small retort the contents of the cylinder, together with the pumice, washing the whole apparatus with a little water free from ammonia. Distil, and estimate ammonia in the usual way with Nessler solution. It appears impossible wholly to exclude ammonia from the re-agents and apparatus, and therefore some blank experiments should be made to ascertain the correction to be applied for this. This correction is very small, and appears to be nearly constant.

### 8. Estimation of Nitrogen as Nitrates and Nitrites by the Indigo Process.

This method has been fully described in § 67.6.

### 9. Estimation of Nitrates as Ammonia by the Copper-zinc Couple.

It is well known that when zinc is immersed in copper sulphate solution it becomes covered with a spongy deposit of precipitated copper. If the solution of copper sulphate be sufficiently dilute, this deposit of copper is black in colour and firmly adherent to the zinc. It is, however, not so generally known that the zinc upon which copper has thus been deposited possesses the power of decomposing pure distilled water at the ordinary temperature, and that it is capable of effecting many other decompositions which zinc alone cannot. Among these is the decomposition of nitrates, and the transformation of the nitric acid into ammonia. Gladstone and Tribe have shown that the action of the "copper-zinc couple" (as they call the conjoined metals) upon a nitre solution consists in the electrolysis of the nitre, resulting in the liberation of hydrogen and the formation of zinc oxide. This hydrogen is liberated upon and occluded by the spongy copper, and when thus occluded, it is capable of reducing the nitre solution in its vicinity. The nitrate is first reduced to nitrite, and the nitrous acid is subsequently transformed into ammonia by the further action of the hydrogen. M. W. Williams has shown (*J. C. S.* 1881, 100) that even in very dilute solutions of nitre the nitric acid can be completely converted into ammonia in this manner with considerable rapidity; and further, that the reaction may be greatly hastened by taking advantage of the influence of temperature, acids, and certain neutral salts, which increase the electrolytic action of the couple. His experiments prove that carbonic acid—feeble acid as it is—suffices to treble the speed of the reaction, and that traces of sodic chloride (0·1 per cent.) accelerated it nearly as much as carbonic acid. A rise of a few degrees in temperature was also found to hasten the reaction in a very marked degree. The presence of alkalies, alkaline earths, and salts having an alkaline reaction, was found to retard the speed of the reduction.

Williams has, upon those experiments, founded a simple and expeditious process for estimating the nitric and nitrous acid in water analysis, which, when used with skill, may be applied to by far the greater number of waters with which the analyst is usually called upon to deal (*Analyst*, 1881, 36). The requisite copper-zinc couple is prepared in the following manner:—The zinc employed should be clean, and for the sake of convenience should be in the form of foil or very thin sheet. It should be introduced into a flask or bottle, and covered with a solution of copper sulphate, containing about 3 per cent. of the crystallized salt, which should be allowed to remain upon it until a copious, firmly adherent coating of black copper has been deposited. This deposition should not be pushed too far, or the copper will be so easily detached that the couple cannot be washed without impairing its activity. When sufficient copper has been deposited the solution should be poured off, and the conjoined metals washed with distilled water. The wet couple is then ready for use.

To use it for the estimation of nitrates it should be made in a wide-mouthed stoppered bottle. After washing, it is soaked with distilled water; to displace this, it is first washed with some of the water to be analyzed, and the bottle filled up with a further quantity of the water. The stopper is then inserted, and the bottle allowed to digest in a warm place for a few hours. If the bottle be well filled and stoppered, the temperature may be raised to 30° C., or even higher, without any fear of losing ammonia. The reaction will then proceed very rapidly; but if it be desired to hasten the reaction still more, a little salt should be added (about 0·1 gm. to every 100 c.c.), or if there be any objection to this, the water may have carbonic acid passed through it for a few minutes before it is poured upon the couple. In the case of calcareous waters, the same hastening effect may be obtained, and the lime may at the same time be removed by adding a very little pure oxalic acid to the water before digesting it upon the couple. Williams has shown that nitrous acid always remained in the solution until the reaction was finished. By testing for nitrous acid the completeness of the reaction may be ascertained with certainty, and perhaps the most delicate test that can be applied for this purpose is that of Griess, in which metaphenylene-diamine is the re-agent employed. When a solution of this substance is added to a portion of the fluid, and acidified with sulphuric acid, a yellow colouration is produced in about half an hour if the least trace of a nitrite be present. The reaction easily detects one part of nitrous acid in ten millions of water. When no nitrous acid is found, the water is poured off the couple into a stoppered bottle, and, if turbid, allowed to subside. A portion of the clear fluid, more or less according to the concentration of the nitrates in the water, is put into a Nessler glass, diluted if necessary, and titrated with Nessler's re-agent in the ordinary way.

This process may be used for the majority of ordinary waters—for those that are coloured, and those that contain magnesium or other substances sufficient to interfere with the Nessler re-agent, a portion of the fluid poured off the couple should be put into a small retort, and distilled with a little pure lime or sodic carbonate, and the titration of the ammonia performed upon the distillates.

About one square decimeter of zinc should be used for every 200 c.c. of a water containing five parts or less of nitric acid in 100,000. A large proportion should be used with waters richer in nitrates. The couple, after washing, may be used for two or three waters more. When either carbonic or oxalic or any other acid has been added to the water, a larger proportion of Nessler re-agent should be employed in titrating it than it is usual to add. 3 c.c. to 100 of the water are sufficient in almost all cases.

Blunt (*Analyst*, vi. 202) points out that the above process may be used without distillation, and with accuracy, in the case of any water, by adding oxalic acid to a double quantity of the sample, dividing, and using one portion (clarified completely by subsidence in a closely stoppered bottle) as a comparison liquid for testing against the other, which has been treated with the copper-zinc couple. Where dilution is used it must be done in both portions equally. This plan possesses the advantages that an equal turbidity is produced by Nessler in both portions, and any traces of ammonia contained in the oxalic acid will have the error due to it corrected.

In calculating the amount of nitric acid contained in a water from the amount of ammonia obtained in this process, deductions must of course be made for any ammonia pre-existing in the water, as well as for that derived from any nitrous acid present.

### 10. Estimation of Nitrites by Griess's Method.

100 c.c. of the water are placed in a Nessler glass, and 1 c.c. each of metaphenylene-diamine and dilute acid (p. 335) added. If

colour is rapidly produced the water must be diluted with distilled water free from $N^2O^3$, and other trials made. The dilution is sufficient when colour is plainly seen at the end of one minute. The weak point of the process is that the colour is progressively developed; however, this is of little consequence if the comparison with standard nitrite is made under the same conditions of temperature, dilution, and duration of experiment. Twenty minutes is a sufficient time for allowing the colours to develop before final comparison.

M. W. Williams obviates the uncertainty of the comparison tests by using colourless Nessler tubes, 30 m.m. wide and 200 m.m. long, graduated into millimeters. They are used as follows:—The comparison of the water to be examined with the standard nitrite is roughly ascertained; the glasses are then filled to the same height, and the test added, and allowed to stand a few minutes. Usually one will be somewhat deeper than the other. The height of the deeper coloured liquid is read off on the scale, and a portion removed with a pipette until the colours correspond. The amount of $N^2O^3$ in the shortened column is taken as equal to the other, when a simple calculation will show the amount sought.

### 11. Estimation of Nitrites by Napthylamine.

Warington (*J. C. S.* 1881, 231) has drawn attention to this test, originally devised by Griess, and which is of such extreme delicacy, that by its means it is possible to detect one part of $N^2O^3$ in a thousand millions of water.

The experiments conducted by Warington were made on columns of liquid three inches deep, contained in test tubes. To 10 c.c. of the liquid to be tested were added successively one drop of dilute HCl (1 : 4), one drop of nearly saturated solution of sulphanilic acid, and one drop of saturated solution of hydrochloride of napthylamine. The colour produced varies from a faint pink to a deep ruby red. In strong solutions a dark precipitate is speedily produced.

This test is almost too delicate to be used quantitatively, but is evidently very serviceable as a qualitative test for very minute quantities of nitrous acid. By its means Warington has detected nitrous acid in the atmosphere of various places by exposing water containing a few drops of the requisite solutions to the air in a basin for a few hours; the like mixture kept in a closed flask or cylinder at the same time undergoing no change of colour.

### 12. Estimation of Nitrites by Potassic Iodide and Starch.

Ekin has pointed out (*Pharm. Trans.* 1881, 286) that this well-known test will give the blue colour with nitrous acid in a few minutes, when the proportion is one part in ten millions; in twelve hours when one part in a hundred millions; and in forty-eight hours when one in a thousand millions. (See page 228.)

Ekin used acetic acid for acidifying the water to be tested, and blank experiments with pure water were simultaneously carried on. Sulphuric or hydrochloric acid will, no doubt, give a sharper reaction, but both these acids are more liable to contain impurities affecting the reaction than is the case with pure acetic acid. Owing to the instability of alkaline iodides, this method of testing can hardly be considered so satisfactory as the methods of Griess.

### 13. Estimation of Suspended Matter.

Filters of Swedish paper, about 110 m.m. in diameter, are packed one inside another, about 15 or 20 together, so that water will pass through the whole group, moistened with dilute hydrochloric acid, washed with hot distilled water until the washings cease to contain chlorine, and dried. The ash of the paper is thus reduced by about 60 per cent., and must be determined for each parcel of filter paper by incinerating 10 filters, and weighing the ash. For use in estimating suspended matter, these washed filters must be dried for several hours at 120—130° C., and each one then weighed at intervals of an hour until the weight ceases to diminish, or at least until the loss of weight between two consecutive weighings does not exceed 0·0003 gm. It is most convenient to enclose the filter during weighing in two short tubes fitting closely one into the other. The closed ends of test tubes, 50 m.m. long, cut off by leading a crack round with the aid of a pastille or very small gas jet, the sharp edges being afterwards fused at the blow-pipe, answer perfectly. Each pair of tubes should have a distinctive number, which is marked with a diamond on both tubes. In the air-bath they should rest in grooves formed by a folded sheet of paper, the tubes being drawn apart, and the filter almost, but not quite, out of the smaller tube. They can then be shut up whilst hot by gently pushing the tubes together, being guided by the grooved paper. They require to remain about twenty minutes in a desiccator to cool before weighing. Filtration will be much accelerated if the filters be ribbed before drying. As a general rule, it will be sufficient to filter a quarter of a liter of a sewage, half a liter of a highly polluted river, and a liter of a less polluted water; but this must be frequently varied to suit individual cases. Filtration is hastened, and trouble diminished, by putting the liquid to be filtered into a narrow-necked flask, which is inverted into the filter, being supported by a funnel-stand, the ring of which has a slot cut through it to allow the neck of the flask to pass. With practice the inversion may be accomplished without loss, and without previously closing the mouth of the flask. When all has passed through, the flask should be rinsed out with distilled water, and the rinsings added to the filter. Thus any particles of solid matter left in the flask are secured, and the liquid adhering to the suspended matter and filter is displaced. The filtrate from the washings should not be added to the previous filtrate, which may be employed for determination of total solid matter, chlorine, hardness, etc.

Thus washed, the filter with the matter upon it is dried at 100° C., then transferred from the funnel to the same pair of tubes in which it was previously weighed, and the operation of drying at 120°–130° C. and weighed until constant repeated. The weight thus obtained, minus the weight of the empty filter and tubes, gives the weight of the total suspended matter dried at 120°–130° C.

To ascertain the quantity of mineral matter in this, the filter with its contents is incinerated in a platinum crucible, and the total ash thus determined, minus the ash of the filter alone, gives the weight of the mineral suspended matter.

### 14. Estimation of Chlorine present as Chloride.

To 50 c.c. of the water add two or three drops of solution of potassic chromate (**D.** $\beta$), so as to give it a faint tinge of yellow, and add gradually from a burette standard solution of argentic nitrate (**D.** $a$), until the red argentic chromate which forms after each addition of the nitrate ceases to disappear on shaking. The number of c.c. of silver solution employed will express the chlorine present as chloride in parts in 100,000. If this amount be much more than 10, it is advisable to take a smaller quantity of water.

If extreme accuracy be necessary, after completing a determination, destroy the slight red tint by an excess of a soluble chloride, and repeat the estimation on a fresh quantity of the water in a similar flask placed by the side of the former. By comparing the contents of the flasks, the first tinge of red in the second flask may be detected with great accuracy. It is absolutely necessary that the liquor examined should not be acid, unless with carbonic acid, nor more than very slightly alkaline. It must also be colourless, or nearly so. These conditions are generally found in waters, but, if not, they may be brought about in most cases by rendering the liquid just alkaline with lime water (free from chlorine), passing carbonic anhydride to saturation, boiling, and filtering. The calcic carbonate has a powerful clarifying action, and the excess of alkali is exactly neutralized by the carbonic anhydride. If this is not successful, the water must be rendered alkaline, evaporated to dryness, and the residue gently heated to destroy organic matter. The chlorine may then be extracted with water, and estimated in the ordinary way, either gravimetrically or volumetrically.

### 15. Estimation of Hardness.

The following method, devised by the late Dr. Thomas Clark, of Aberdeen, is in general use; and from its ease, rapidity, and accuracy, is of great value. (For estimating the hardness of waters without soap solution see page 58.)

Uniformity in conducting it is of great importance; especially the titration of the soap solution, and the estimation of the hardness of waters, should be performed in precisely similar ways.

Measure 50 c.c. of the water into a well-stoppered bottle of about 250 c.c. capacity, shake briskly for a few seconds, and suck the air from the bottle by means of a glass tube, in order to remove any carbonic anhydride which may have been liberated from the water. Add standard soap solution (E. $\beta$) from a burette, one c.c. at a time at first, and smaller quantities towards the end of the operation, shaking well after each addition, until a soft lather is obtained, which, if the bottle is placed at rest on its side, remains continuous over the whole surface for five minutes. The soap should not be added in larger quantities at a time, even when the volume required is approximately known. This is very important.

When more than 16 c.c. of soap solution are required by 50 c.c. of the water, a less quantity (as 25 or 10 c.c.) of the latter should be taken, and made up to 50 c.c. with recently boiled distilled water, so that less than 16 c.c. of soap solution will suffice, and the number expressing the hardness of the diluted water multiplied by 2 or 5, as the case may be.

When the water contains much magnesium, which may be known by the lather having a peculiar curdy appearance, it should be diluted, if necessary, with distilled water, until less than 7 c.c. are required by 50 c.c.

The volume of standard soap solution required for 50 c.c. of the water being known, the weight of calcic carbonate ($CaCO^3$) corresponding to this may be ascertained from the following table 7*:—

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* The table is calculated from that originally constructed by Dr. **Clark**, which is as follows:—

| Degree of Hardness. | Measures of Soap Solution. | Differences for the next 1° of hardness. |
|---|---|---|
| 0° (Distilled water)... | 1·4 | 1·8 |
| 1 | 3·2 | 2·2 |
| 2 | 5·4 | 2·2 |
| 3 | 7·6 | 2·0 |
| 4 | 9.6 | 2·0 |
| 5 | 11·6 | 2·0 |
| 6 | 13·6 | 2·0 |
| 7 | 15·6 | 1·9 |
| 8 | 17·5 | 1·9 |
| 9 | 19·4 | 1·9 |
| 10 | 21·3 | 1·8 |
| 11 | 23·1 | 1·8 |
| 12 | 24·9 | 1·8 |
| 13 | 26·7 | 1·8 |
| 14 | 28·5 | 1·8 |
| 15 | 30·3 | 1·7 |
| 16 | 32·0 | — |

Each "measure" being 10 grains, the volume of water employed 1000 grains, and each "degree" 1 grain of calcic carbonate in a gallon.

If the old weights and measures, grains and gallons, be preferred, this table may be used, the process being exactly as above described, but 1000 grains of water taken instead of 50 c.c., and the soap solution measured in 10-grain measures instead of cubic centimeters. If the volume of soap solution used be found exactly in the second column of the table, the hardness will, of course, be that shown on the same line in the first column. But if it be not, deduct from it the next lower number in the second column, when the corresponding degree of hardness in the first column will give the integral part of the result; divide the remainder by the difference on the same line in the third column, and the quotient will give the fractional part. For example, if 1000 grains of water require 16 "measures" of soap, the calculation will be as follows:—

## TABLE 7.

**Table of Hardness, Parts in 100,000.**

| Volume of Soap Solution. | $CaCO^3$ ⅌ 100,000. | Volume of Soap Solution. | $CaCO^3$ ⅌ 100,000. | Volume of Soap Solution. | $CaCO^3$ ⅌ 100,000. | Volume of Soap Solution. | $CaCO^3$ ⅌ 100,000. |
|---|---|---|---|---|---|---|---|
| c.c. | | c.c. | | c.c. | | c.c. | |
| | | 4·0 | 4·57 | 8·0 | 10·30 | 12·0 | 16·43 |
| | | 1 | ·71 | 1 | ·45 | 1 | ·59 |
| | | 2 | ·86 | 2 | ·60 | 2 | ·75 |
| | | 3 | 5·00 | 3 | ·75 | 3 | ·90 |
| | | 4 | ·14 | 4 | ·90 | 4 | 17·06 |
| | | 5 | ·29 | 5 | 11·05 | 5 | ·22 |
| | | 6 | ·43 | 6 | ·20 | 6 | ·38 |
| 0·7 | ·00 | 7 | ·57 | 7 | ·35 | 7 | ·54 |
| 0·8 | ·16 | 8 | ·71 | 8 | ·50 | 8 | ·70 |
| 0·9 | ·32 | 9 | ·86 | 9 | ·65 | 9 | ·86 |
| 1·0 | ·48 | 5·0 | 6·00 | 9·0 | ·80 | 13·0 | 18·02 |
| 1 | ·63 | 1 | ·14 | 1 | ·95 | 1 | ·17 |
| 2 | ·79 | 2 | ·29 | 2 | 12·11 | 2 | ·33 |
| 3 | ·95 | 3 | ·43 | 3 | ·26 | 3 | ·49 |
| 4 | 1·11 | 4 | ·57 | 4 | ·41 | 4 | ·65 |
| 5 | ·27 | 5 | ·71 | 5 | ·56 | 5 | ·81 |
| 6 | ·43 | 6 | ·86 | 6 | ·71 | 6 | ·97 |
| 7 | ·56 | 7 | 7·00 | 7 | ·86 | 7 | 19·13 |
| 8 | ·69 | 8 | ·14 | 8 | 13·01 | 8 | ·29 |
| 9 | ·82 | 9 | ·29 | 9 | ·16 | 9 | ·44 |
| 2·0 | ·95 | 6·0 | ·43 | 10·0 | ·31 | 14·0 | ·60 |
| 1 | 2·08 | 1 | ·57 | 1 | ·46 | 1 | ·76 |
| 2 | ·21 | 2 | ·71 | 2 | ·61 | 2 | ·92 |
| 3 | ·34 | 3 | ·86 | 3 | ·76 | 3 | 20·08 |
| 4 | ·47 | 4 | 8·00 | 4 | ·91 | 4 | ·24 |
| 5 | ·60 | 5 | ·14 | 5 | 14·06 | 5 | ·40 |
| 6 | ·73 | 6 | ·29 | 6 | ·21 | 6 | ·56 |
| 7 | ·86 | 7 | ·43 | 7 | ·37 | 7 | ·71 |
| 8 | ·99 | 8 | ·57 | 8 | ·52 | 8 | ·87 |
| 9 | 3·12 | 9 | ·71 | 9 | ·68 | 9 | 21·03 |
| 3·0 | ·25 | 7·0 | ·86 | 11·0 | ·84 | 15·0 | ·19 |
| 1 | ·38 | 1 | 9·00 | 1 | 15·00 | 1 | ·35 |
| 2 | ·51 | 2 | ·14 | 2 | ·16 | 2 | ·51 |
| 3 | ·64 | 3 | ·29 | 3 | ·32 | 3 | ·68 |
| 4 | ·77 | 4 | ·43 | 4 | ·48 | 4 | ·85 |
| 5 | ·90 | 5 | ·57 | 5 | ·63 | 5 | 22·02 |
| 6 | 4·03 | 6 | ·71 | 6 | ·79 | 6 | ·18 |
| 7 | ·16 | 7 | ·86 | 7 | ·95 | 7 | ·35 |
| 8 | ·29 | 8 | 10·00 | 8 | 16·11 | 8 | ·52 |
| 3·9 | ·43 | 7·9 | ·15 | 11·9 | ·27 | 9 | ·69 |
| | | | | | | 16·0 | ·86 |

16·0
—15·6 (=7° hardness).

(Difference=) 1·9) ·4

·21

therefore the hardness is 7·21 grains of $CaCO^3$ per gallon. The water must be diluted with distilled water if necessary, so that the quantity of soap required does not exceed 32 measures in ordinary waters, and 14 measures in water containing much magnesia.

When water containing calcic and magnesic carbonates, held in solution by carbonic acid, is boiled, carbonic anhydride is expelled, and the carbonates precipitated. The hardness due to these is said to be *temporary*, whilst that due to sulphates, chlorides, etc., and to the amount of carbonates soluble in pure water (the last-named being about three parts per 100,000) is called *permanent*.

To estimate permanent hardness, a known quantity of the water is boiled gently for half an hour in a flask, the mouth of which is freely open. At the end of the boiling, the water should be allowed to cool, and the original weight made up by adding recently boiled distilled water.

Much trouble may be avoided by using flasks of about the same weight, and taking so much water in each as will make up the same uniform weight. Thus if all the flasks employed weigh less than 50 gm. each, let each flask with its contents be made to weigh 200 gm.

After boiling and making up to the original weight, filter the water, and determine the hardness in the usual way. The hardness thus found, deducted from that of the unboiled water, will give the *temporary* hardness.

### 16. Mineral Constituents and Metals.

The quantities of the following substances which may be present in a sample of water are subject to such great variations, that no definite directions can be given as to the volume of water to be used. The analyst must judge in each case from a preliminary experiment what will be a convenient quantity to take.

*Sulphuric Acid.*—Acidify a liter or less of the water with hydrochloric acid, concentrated on the water bath to about 100 c.c., and while still hot add a slight excess of baric chloride. Filter, wash, ignite, and weigh as baric sulphate, or estimate volumetrically, as in § 73.

*Sulphuretted Hydrogen.*—Titrate with a standard solution of iodine, as in § 74.3.

*Phosphoric Acid.*—This substance is best determined in the solid residue obtained by evaporation, by moistening it with nitric acid, and again drying to render silica insoluble; the residue is again treated with dilute nitric acid, filtered, molybdic solution (p. 240) added, and set aside for twelve hours in a warm place; filter, dissolve the precipitate in ammonia, precipitate with magnesia mixture, and weigh as magnesic pyrophosphate, or estimate volumetrically as in § 69.5.

*Silicic Acid.*—Acidify a liter or more of the water with hydrochloric acid, evaporate, and dry the residue thoroughly.

Then moisten with hydrochloric acid, dilute with hot water, and filter off, wash, ignite, and weigh the separated silica.

*Iron.*—To filtrate from the estimation of silicic acid add a few drops of nitric acid, dilute to about 100 c.c., and estimate by colour titration, as in § 60.4; or where the amount is large, add excess of ammonia, and heat gently for a short time. Filter off the precipitate, and estimate the iron in the washed precipitate volumetrically, as in § 59 or 60.

*Calcium.*—To the filtrate from the iron estimation add excess of ammonic oxalate, filter off the calcic oxalate, ignite and weigh as calcic carbonate, or estimate volumetrically with permanganate, as in § 48.

*Magnesium.*—To the concentrated filtrate from the calcium estimation add sodic phosphate (or, if alkalies are to be determined in the filtrate, ammonic phosphate), and allow to stand for twelve hours in a warm place. Filter, ignite the precipitate, and weigh as magnesic pyrophosphate, or, before ignition, titrate with uranium.

*Barium.*—Is best detected in a water by acidifying with hydrochloric acid, filtering perfectly clear if necessary, then add a clear solution of calcic sulphate, and set aside in a warm place. Any white precipitate which forms is due to barium.

*Potassium and Sodium.*—These are generally determined jointly, and for this purpose the filtrate from the magnesium estimation may be used. Evaporate to dryness, and heat gently to expel ammonium salts, remove phosphoric acid with plumbic acetate, and the excess of lead in the hot solution by ammonia and ammonic carbonate. Filter, evaporate to dryness, heat to expel ammonium salts, and weigh the alkalies as chlorides.

It is, however, generally less trouble to employ a separate portion of water. Add to a liter or less of the water enough pure baric chloride to precipitate the sulphuric acid, boil with pure milk of lime, filter, concentrate, and remove the excess of lime with ammonic carbonate and a little oxalate. Filter, evaporate, and weigh the alkaline chlorides in the filtrate. If the water contains but little sulphate, the baric chloride may be omitted, and a little ammonic chloride added to the solution of alkaline chlorides.

If potassium and sodium must each be estimated, separate them by means of platinic chloride; or, after weighing the mixed chlorides, determine the *chlorine* present in them, and calculate the amounts of potassium and sodium by the following formula:—Calculate all the chlorine present as potassic chloride; deduct this from the weight of the mixed chlorides, and call the difference $d$. Then as 16·1 : 58·37 : : $d$ : NaCl present. (See also § 38.)

*Lead.*—May be estimated by the method proposed by Miller. Acidulate the water with two or three drops of acetic acid, and add $\frac{1}{20}$ of its bulk of saturated aqueous solution of sulphuretted hydrogen. Compare the colour thus produced in the colorimeter or a convenient cylinder, with that obtained with a known quantity of a standard solution of a lead salt, in a manner similar to that described for the estimation of iron (§ 60.4). The lead solution should contain 0·1831 gm. of normal crystallized plumbic acetate in a liter of distilled water, and therefore each c.c. contains 0·0001 gm. of metallic lead.

It is obvious that in the presence of copper or other heavy metals the colour produced by the above method will all be ascribed to lead; it is preferable, therefore, to adopt the method of Harvey (*Analyst*, vi. 146), in which the lead is precipitated as chromate. The results, however, are not absolute as to quantity, except so far as the eye may be able to measure the amount of precipitate.

The standard lead solution is the same as in the previous method. The precipitating agent is pure potassic bichromate, in fine crystals or powder.

250 c.c. or so of the water is placed in a Phillips' jar with a drop or two of acetic acid, and a few grains of the re-agent added, and agitated by shaking. One part of lead in a million parts of water will show a distinct turbidity in five minutes or less. In six or eight hours the precipitate will have completely settled, and the yellow clear liquid may be poured off without disturbing the sediment, which may then be shaken up with a little distilled water, and its quantity judged by comparison with a similar experiment made with the standard lead solution.

*Copper.*—Estimate by colour titration, as in § 54.9.

*Arsenic.*—Add to half a liter or more of the water enough sodic hydrate, free from arsenic, to render it slightly alkaline, evaporate to dryness, and extract with a little concentrated hydrochloric acid. Introduce this solution into the generating flask of a small Marsh's apparatus, and pass the evolved hydrogen, first through a U-tube filled with pumice, moistened with plumbic acetate, and then through a piece of hard glass tube about 150 m.m. in length, and 3 m.m. in diameter (made by drawing out combustion tube). At about its middle, this tube is heated to redness for a length of about 20 m.m. by the flame of a small Bunsen burner, and here the arsenetted hydrogen is decomposed, arsenic being deposited as a mirror on the cold part of the tube. The mirror obtained after the gas has passed slowly for an hour is compared with a series of standard mirrors obtained in a similar way from known quantities of arsenic. Care must be taken to ascertain in each experiment that the hydrochloric acid, zinc, and whole apparatus are free from arsenic, by passing the hydrogen slowly through the heated tube before introducing the solution to be tested.

*Zinc.*—This metal exists in waters as bicarbonate, and on exposure of such waters in open vessels a film of zinc carbonate forms on the surface; this is collected on a platinum knife or foil and ignited. The residue is of a yellow colour when hot, and turns white on cooling. The reaction is exceedingly delicate.

## THE INTERPRETATION OF THE RESULTS OF ANALYSIS.

§ 89. The primary form of natural water is rain, the chief impurities in which are traces of organic matter, ammonia, and ammonic nitrate derived from the atmosphere. On reaching the ground it becomes more or less charged with the soluble constituents of the soil, such as calcic and magnesic carbonates, potassic and sodic chlorides, and other salts, which are dissolved, some by a simple solvent action, others by the agency of carbonic acid in solution. Draining off from the land, it will speedily find its way to a stream which, in the earlier part of its course, will probably be free from pollution by animal matter, except that derived from any manure which may have been applied to the land on which the rain fell. Thus comparatively pure, it will furnish to the inhabitants on its banks a supply of water which, after use, will be returned to the stream in the form of sewage charged with impurity derived from animal excreta, soap, household refuse, etc., the pollution being perhaps lessened by submitting the sewage to some purifying process, such as irrigation of land, filtration, or clarification. The stream in its subsequent course to the sea will be in some measure purified by slow oxidation of the organic matter, and by the absorbent action of vegetation, but not to any great extent. Some of the rain will not, however, go directly to a stream, but sink through the soil to a well. If this be shallow, it may be considered as merely a pit for the accumulation of drainage from the immediately surrounding soil, which, as the well is in most cases close to a dwelling, will be almost inevitably charged with excretal and other refuse; so that the water when it reaches the well will be contaminated with soluble impurities thence derived, and with nitrites and nitrates resulting from their oxidation. After use the water from the well will, like the river water, form sewage, and find its way to a river, or again to the soil, according to circumstances.

In the case of a deep well, from which the surface water is excluded, the conditions are different. The shaft will usually pass through an impervious stratum, so that the water entering it will not be derived from the rain which falls on the area immediately surrounding its mouth, but from that which falls on the outcrop of the pervious stratum below the impervious one just mentioned; and if this outcrop be in a district which is uninhabited and uncultivated, the water of the well will probably be entirely free from organic impurity or products of decomposition. But even if the water be polluted at its source, still it must pass through a very extensive filter before it reaches the well, and its organic matter will probably be in great measure converted by oxidation into bodies in themselves innocuous.

This is very briefly the general history of natural waters, and the problem presented to the analyst is to ascertain, as far as possible, from the nature and quantity of the impurities present, the previous history of the water, and its present condition and fitness for the purpose for which it is to be used.

It is impossible to give any fixed rule by which the results obtained by the foregoing method of analysis should be interpreted. The analyst must form an independent opinion for each sample from a consideration of all the results he has obtained. Nevertheless, the following remarks, illustrated by reference to the examples given in the accompanying table, which may be considered as fairly typical, will probably be of service. (See pages 376 and 377.)

**TABLE 8.**

**Results of Analysis expressed**

| Number of Sample. | DESCRIPTION. | REMARKS. |
|---|---|---|
| | **Upland Surface Waters.** | |
| I. | The Dee above Balmoral, March 9th, 1872 ... ... | Clear ... ... |
| II. | Glasgow Water supply from Loch Katrine—average of monthly analyses during five years, 1876—81 | Clear; very pale br |
| III. | Liverpool Water supply from Rivington Pike, June 4th, 1869 | Clear ... ... |
| IV. | Manchester Water supply, May 9th, 1874 ... ... | Turbid ... ... |
| V. | Cardiff Water supply, Oct. 18th, 1872 ... ... | Clear ... ... |
| | **Surface Water from Cultivated Land.** | |
| VI. | Dundee Water supply, March 12th, 1872 ... ... | Turbid; brownish yel |
| VII. | Norwich Water supply, June 18th, 1872 ... ... | Slightly turbid ... |
| | **Shallow Wells.** | |
| VIII. | Cirencester, Market Place, Nov. 4th, 1870 ... ... | Slightly turbid ... |
| IX. | Marlborough, College Yard, Aug. 22nd, 1873 ... ... | Clear ... ... |
| X. | Birmingham, Hurst Street, Sept. 18th, 1873 ... ... | Clear; strong saline t |
| XI. | Sheffield, Well near, Sept. 27th, 1870 ... ... | Very turbid & offen sive. Swarmin with bacteria, &c |
| XII. | London, Aldgate Pump, June 5th, 1872 ... ... | Clear ... ... |
| XIII. | London, Wellclose Square, June 5th, 1872 ... ... | Slightly turbid; salinet |
| XIV. | Leigh, Essex, Churchyard Well, Nov. 28th, 1871 ... | Slightly turbid ... |
| | **Deep Wells.** | |
| XV. | Birmingham, Short Heath Well, May 16th, 1873 ... | Clear ... ... |
| XVI. | Caterham, Water Works Well, Feb. 14th, 1873 ... | Clear ... ... |
| | Ditto, Softened (Water supply) ... ... ... | ... ... ... |
| XVII. | London, Albert Hall, May, 1872 ... ... ... | Slightly turbid ... |
| XVIII. | Gravesend, Railway Station, Jan. 17th, 1873 ... ... | Clear ... ... |
| | **Springs.** | |
| XIX. | Dartmouth Water supply, Jan. 8th, 1873 ... ... | Turbid ... ... |
| XX. | Grantham Water supply, July 11th, 1873 ... ... | Clear ... ... |
| | **London Water supply—average monthly analyses during 12 years, 1869–** | |
| XXI. | From the Thames ... ... ... ... ... | ... ... ... |
| XXII. | From the Lea ... ... ... ... ... | ... ... ... |
| XXIII. | From Deep Chalk Wells (Kent Company) ... ... | ... ... ... |
| XXIV. | Ditto (Colne Valley Co.) softened—four years, 1877—80 | ... ... ... |
| XXV. | Ditto (Tottenham)—four years, 1877—80 ... ... | ... ... ... |
| XXVI. | **Birmingham Water supply—average monthly analyses, 1875–1880.** | |
| | **Average Composition of Unpolluted Water.** | |
| XXVII. | Rain Water ... ... ... 39 samples | ... ... ... |
| XXVIII. | Upland Surface Water ... ... 195 " | ... ... ... |
| XXIX. | Deep Well Water ... ... ... 157 " | ... ... ... |
| XXX. | Spring Water ... ... ... 198 " | ... ... ... |
| XXXI. | Sea Water ... ... ... 23 " | ... ... ... |
| | **Sewage.** | |
| XXXII. | Average from 15 "Midden" Towns, 37 analyses ... | ... ... ... |
| XXXIII. | Average from 16 "Water Closet" Towns, 50 analyses ... | ... ... ... |
| XXXIV. | Salford, Wooden Street Sewer, March 15th, 1869 ... | ... ... ... |
| XXXV. | Merthyr Tydfil, average 10 a.m. to 5 p.m., Oct. 20th, 1871 (after treatment with lime) | ... ... ... |
| XXXVI. | Ditto, Effluent Water ... ... ... ... | ... ... ... |

in parts per 100,000.

TABLE 8.

| Total solid Matter. | Organic Carbon. | Organic Nitrogen. | Organic. C/N | Nitrogen as Ammonia. | Nitrogen as Nitrates and Nitrites. | Total Inorganic Nitrogen. | Total Combined Nitrogen. | Chlorine. | Hardness. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Temporary. | Permanent. | Total. |
| 1·52 | ·132 | ·014 | 9·4 | 0 | 0 | 0 | ·014 | ·50 | 0 | 1·5 | 1·5 |
| 2·94 | ·148 | ·016 | 9·2 | 0 | ·005 | ·005 | ·022 | ·64 | — | — | ·9 |
| 9·66 | ·210 | ·029 | 7·2 | ·002 | 0 | ·002 | ·031 | 1·53 | ·3 | 3·7 | 4·0 |
| 7·00 | ·132 | ·031 | 4·1 | ·002 | 0 | ·002 | ·038 | ·90 | 0 | 2·7 | 2·7 |
| 23·50 | ·212 | ·031 | 6·8 | 0 | ·034 | ·034 | ·065 | 1·40 | 7·1 | 12·9 | 20·0 |
| 11·16 | ·418 | ·059 | 7·1 | ·001 | ·081 | ·082 | ·141 | 1·75 | 0 | 6·0 | 6·0 |
| 30·92 | ·432 | ·080 | 5·4 | ·012 | ·036 | ·048 | ·128 | 3·10 | 21·3 | 5·3 | 26·6 |
| 31·00 | ·041 | ·008 | 5·1 | 0 | ·362 | ·362 | ·370 | 1·60 | 18·4 | 4·6 | 23·0 |
| 32·48 | ·049 | ·015 | 3·3 | 0 | ·613 | ·613 | ·628 | 1·90 | 15·6 | 10·1 | 25·7 |
| 240·20 | ·340 | ·105 | 3·2 | ·511 | 14·717 | 15·228 | 15·333 | 36·50 | 27·5 | 99·6 | 127·1 |
| 18·50 | 1·200 | ·126 | 9·5 | ·091 | 0 | ·091 | ·217 | 2·20 | 2·0 | 1·4 | 3·4 |
| 123·10 | ·144 | ·141 | 1·0 | ·181 | 6·851 | 7·032 | 7·173 | 12·85 | 37·1 | 40·0 | 77·1 |
| 396·50 | ·278 | ·087 | 3·2 | 0 | 25·840 | 25·840 | 25·927 | 34·60 | 26·7 | 164·3 | 191·0 |
| 112·12 | ·210 | ·065 | 3·2 | 0 | 5·047 | 5·047 | 5·112 | 13·75 | 14·3 | 45·7 | 60·0 |
| 15·08 | ·009 | ·004 | 2·2 | 0 | ·447 | ·447 | ·451 | 1·30 | 4·6 | 5·1 | 9·7 |
| 27·68 | ·028 | ·009 | 3·1 | 0 | ·021 | ·021 | ·030 | 1·55 | 15·2 | 6·0 | 21·2 |
| 8·80 | ·015 | ·003 | 5·0 | — | — | — | — | — | — | — | 4·4 |
| 61·68 | ·168 | ·042 | 4·0 | ·007 | ·066 | ·073 | ·115 | 15·10 | 3·4 | 2·2 | 5·6 |
| 68·00 | ·127 | ·029 | 4·4 | ·063 | 2·937 | 3·000 | 3·029 | 5·40 | 27·9 | 14·5 | 42·4 |
| 17·36 | ·060 | ·016 | 3·7 | 0 | ·330 | ·330 | ·346 | 2·45 | 1·6 | 10·0 | 11·6 |
| 30·20 | ·048 | ·018 | 2·7 | 0 | ·833 | ·833 | ·851 | 2·05 | 17·1 | 6·5 | 23·6 |
| 27·96 | ·210 | ·034 | 6·1 | 0 | ·207 | ·207 | ·241 | 1·68 | — | — | 20·4 |
| 28·44 | ·148 | ·026 | 5·8 | 0 | ·209 | ·209 | ·235 | 1·74 | — | — | 21·0 |
| 41·38 | ·054 | ·012 | 4·4 | 0 | ·434 | ·434 | ·446 | 2·45 | — | — | 28·2 |
| 13·75 | ·068 | ·015 | 4·4 | ·001 | ·333 | ·334 | ·349 | 1·44 | — | — | 6·2 |
| 44·12 | ·063 | ·014 | 4·5 | ·026 | ·266 | ·292 | ·306 | 3·12 | — | — | 25·4 |
| 26·01 | ·245 | ·054 | 4·6 | ·002 | ·231 | ·233 | ·287 | 1·73 | 7·7 | 8·8 | 16·5 |
| 2·95 | ·070 | ·015 | 4·7 | ·024 | ·003 | ·027 | ·042 | ·22 | — | — | ·3 |
| 9·67 | ·322 | ·032 | 10·1 | ·002 | ·009 | ·011 | ·043 | 1·13 | 1·5 | 4·3 | 5·4 |
| 43·78 | ·061 | ·018 | 3·4 | ·010 | ·495 | ·505 | ·523 | 5·11 | 15·8 | 9·2 | 25·0 |
| 28·20 | ·056 | ·013 | 4·3 | ·001 | ·383 | ·384 | ·397 | 2·49 | 11·0 | 7·5 | 18·5 |
| 3898·7 | ·278 | ·165 | 1·7 | ·005 | ·033 | ·038 | ·203 | 1975·6 | 48·9 | 748·0 | 796·9 |
| | | | | | | | | | Suspended Matter. | | |
| | | | | | | | | | Mineral. | Organic. | Total. |
| 82·4 | 4·181 | 1·975 | 2·1 | 4·476 | 0 | 4·476 | 6·451 | 11·54 | 17·81 | 21·30 | 39·11 |
| 72·2 | 4·696 | 2·205 | 2·1 | 5·520 | ·003 | 5·523 | 7·728 | 10·66 | 24·18 | 20·51 | 44·69 |
| 419·6 | 11·012 | 7·634 | 1·4 | 5·468 | 0 | 5·468 | 13·102 | 20·50 | 18·88 | 26·44 | 45·32 |
| 49·20 | 1·282 | ·952 | 1·3 | 1·054 | ·052 | 1·106 | 2·058 | 5·25 | 7·88 | 6·56 | 14·44 |
| 33·48 | ·123 | ·031 | 4·0 | ·018 | ·300 | ·348 | ·379 | 2·60 | | Trace. | |

### Total Solid Matter.

Waters which leave a large residue on evaporation are, as a rule, less suited for general domestic purposes than those which contain less matter in solution, and are unfit for many manufacturing purposes. The amount of residue is also of primary importance as regards the use of the water for steam boilers, as the quantity of incrustation produced will chiefly depend upon it. It may vary considerably, apart from any unnatural pollution of the water, as it depends principally on the nature of the soil through or over which the water passes. River water, when but slightly polluted, contains generally from 10 to 40 parts. Shallow well water varies greatly, containing from 30 to 150 parts, or even more, as in examples X. and XIII., the proportion here depending less on the nature of the soil than on the original pollution of the water. Deep well water also varies considerably; it usually contains from 20 to 70 parts, but this range is frequently overstepped, the quantity depending largely upon the nature of the strata from which the water is obtained. Example XV., being in the New Red Sandstone, has a small proportion, but XVII. and XVIII. in the Chalk have a much larger quantity. Spring waters closely resemble those from deep wells. Sewage contains generally from 50 to 100 parts, but occasionally less, and frequently much more, as in example XXXIV. The total solid matter, as a rule, exceeds the sum of the constituents determined; the nitrogen, as nitrates and nitrites, being calculated as potassic nitrate, and the chlorine as sodic chloride; but occasionally this is not the case, owing, it is likely, to the presence of some of the calcium as calcic nitrate or chloride.

### Organic Carbon or Nitrogen.

The existing condition of the sample, as far as organic contamination is concerned, must be inferred from the amount of these two constituents. In a good water, suitable for domestic supply, the former should not, under ordinary circumstances, exceed 0·2 and the latter 0·02 part.

Waters from districts containing much peat are often coloured more or less brown, and contain an unusual quantity of organic carbon, but this peaty matter is probably innocuous unless the quantity be extreme. The large proportion of organic carbon and nitrogen given in the average for unpolluted upland surface water in Table 8 (XXVIII.), is chiefly due to the fact that upland gathering grounds are very frequently peaty. The examples given (I. to V.) may be taken as fairly representative of the character of upland surface waters free from any large amount of peaty matter. In surface waters from cultivated areas the quantity of organic carbon and nitrogen is greater, owing to increased density of population, the use of organic manures, etc., the proportion being about 0·25 to 0·3 part of organic carbon, and 0·04 to 0·05 part of organic nitrogen. The water from shallow wells varies so widely in its character that it is impossible to give any useful average. In many cases, as for example in XIII. and XIV., the amount is comparatively small, although the original pollution, as shown by the total inorganic nitrogen and the chloride, was very large; the organic matter in these cases having been almost entirely destroyed by powerful oxidation. In VIII. and IX. the original pollution was slight; and oxidation being active, the organic carbon and nitrogen have been reduced to extremely small quantities. On the other hand, in XI. the proportion of organic matter is enormous, the oxidizing action of the surrounding soil being utterly insufficient to deal with the pollution. The danger attending the use of shallow well waters, which contain when analyzed very small quantities of organic matter, arises chiefly from the liability of the conditions to variation.

Change of weather and many other circumstances may at any time prevent the purification of the water, which at the time of the analysis appeared to be efficient. Moreover, it is by no means certain, that an oxidizing action which would be sufficient to reduce the organic matter in a water to a very small proportion, would be equally competent to remove the specific poison of disease. Hence the greater the impurity of the source of a water the greater the risk attending its use.

In deep well waters the quantity of organic carbon and nitrogen also extends through a wide range, but is generally low, the average being about 0·06 part carbon and 0·02 part nitrogen (XXIX.). Here the conditions are usually very constant, and if surface drainage be excluded, the source of the water is of less importance. Springs in this, as in most other respects, resemble deep wells; the water from them being generally, however, somewhat purer. In sewage great variations are met with. On the average it contains about four parts of organic carbon and two parts of organic nitrogen (XXXII. and XXXIII.), but the range is very great. In the table, XXXIV. is a very strong sample, and XXXV. a weak one. The effluent water from land irrigated with sewage is usually analogous to waters from shallow wells, and its quality varies greatly according to the character of the sewage and the conditions of the irrigation.

## Ratio of Organic Carbon to Organic Nitrogen.

The ratio of the organic carbon to the organic nitrogen given in the seventh column of the table (which shows the fourth term of the proportion —organic nitrogen : organic carbon : : 1 : $x$), is of great importance as furnishing a valuable indication of the nature of the organic matter present. When this is of vegetable origin, the ratio is very high, and when of animal origin very low. This statement must, however, be qualified, on account of the different effect of oxidation on animal and vegetable substances. It is found that when organic matter of vegetable origin, with a high ratio of carbon to nitrogen, is oxidized, it loses carbon more rapidly than nitrogen, so that the ratio is reduced. Thus unoxidized peaty waters exhibit a ratio varying from about 8 to 20 or even more, the average being about 12; whereas, the ratio in spring water originally containing peaty matter, varies from about 2 to 5, the average being about 3·2. When the organic matter is of animal origin the action is reversed, the ratio being increased by oxidation. In unpolluted upland surface waters the ratio varies from about 6 to 12, but in peaty waters it may amount to 20 or more. In surface water from cultivated land it ranges from about 4 to 10, averaging about 6. In water from shallow wells it varies from about 2 to 8, with an average of about 4, but instances beyond this range in both directions are very frequent. In water from deep wells and springs, the ratio varies from about 2 to 6, with an average of 4, being low on account, probably, of the prolonged oxidation to which it has been subjected, which, as has been stated above, removes carbon more rapidly than nitrogen. In sea water this action reaches a maximum, the time being indefinitely prolonged, and the ratio is on the average about 1·7. This is probably complicated by the presence, in some cases, of multitudes of minute living organisms. In sewage the ratio ranges from about 1 to 3, with an average of about 2.

When, in the case of a water containing much nitrogen as nitrates and nitrites, this ratio is unusually low, incomplete destruction of nitrates during the evaporation may be suspected, and the estimation should be repeated. To provide for this contingency, if a water contain any considerable quantity of ammonia, it is well, when commencing the evaporation in the first instance, to set aside a quantity sufficient for this repetition, adding to it the usual proportion of sulphurous acid.

### Nitrogen as Ammonia.

The ammonia in natural waters is derived almost exclusively from anima contamination, and its quantity varies between very wide limits. In upland surface waters it seldom exceeds 0·008 part, the average being about 0·002 part. In water from cultivated land the average is about 0·005, and the range is greater, being from *nil* to 0·025 part or even more. In water from shallow wells the variation is so great that it would be useless to attempt to state an average, all proportions from *nil* to as much as 2·5 parts having been observed. In waters from deep wells a very considerable proportion is often found, amounting to 0·1 part or even more, the average being 0·01 part, and the variations considerable. In spring water it is seldom that more than 0·01 part of nitrogen as ammonia occurs, the average being only 0·001 part. Sewage usually contains from 2 to 6 parts, but occasionally as much as 9 or 10 parts, the average being about five. Ammonia is readily oxidized to nitrates and nitrites, and hence its presence, in considerable quantity, usually indicates the absence of oxidation, and is generally coincident with the presence of organic matter. That sometimes found in waters from very deep wells is, however, probably due to subsequent decomposition of nitrates.

### Nitrogen as Nitrates and Nitrites.

Nitrates and nitrites are produced by the oxidation of nitrogenous organic matter, and almost always from animal matter. In upland surface waters the proportion varies from *nil* to 0·05 part or very rarely more, but the majority of samples contain none or mere traces (I. to V.), the average being about 0·009 part. In surface waters from cultivated land the quantity is much greater, varying from *nil*, which seldom occurs, to 1 part, the average being about 0·25 part. The proportion in shallow wells is usually much greater still, ranging from *nil*, which very rarely occurs, to as much as 25 parts. It would be probably useless to attempt to state an average, but quantities of from 2 to 5 parts occur most frequently. In water from deep wells the range is from *nil* to about 3 parts, and occasionally more, the average being about 0·5 part. In spring water the range is about the same as in deep well water, but the average is somewhat lower.

It sometimes happens that, when the supply of atmospheric oxygen is deficient, the organic matter in water is oxidized at the expense of the nitrates present; and occasionally, if the quantities happen to be suitably proportioned, they are mutually destroyed, leaving no evidence of pollution. This reduction of nitrates often occurs in deep well water, as for example, in that from wells in the Chalk beneath London Clay, where the nitrates are often totally destroyed. In sewages, putrefaction speedily sets in, and during this condition the nitrates are rapidly destroyed, and so completely and uniformly that it is probably needless to attempt their estimation, except in sewages which are very weak, or for other special reasons abnormal. Out of a large number of samples, only a very few have been found which contained any nitrates, and those only very small quantities.

Nitrites occurring in deep springs or wells no doubt arise from the deoxidation of nitrates by ferrous oxide, or contain forms of organic matter of a harmless nature; but whenever they occur in shallow wells or river water, they may be of much greater significance. Their presence in such cases is most probably due to recent sewage contamination, and such waters must be looked upon with great suspicion.

### Total Inorganic Nitrogen.

When organic matter is oxidized it is ultimately resolved into inorganic substances. Its carbon appears as carbonic acid, its hydrogen as water, and its nitrogen as ammonia, nitrous acid, or nitric acid; the last two combining with the bases always present in water to form nitrites and nitrates. The carbon and hydrogen are thus clearly beyond the reach of the analyst; but the nitrogen compounds, as has been shown, can be accurately determined, and furnish us with a means of estimating the amount of organic matter which was formerly present in the water, but which has already undergone decomposition.

The sum of the amounts of nitrogen found in these three forms constitutes then a distinct and valuable term in the analysis, the *organic* nitrogen relating to the *present*, and the total *inorganic* nitrogen to the *past* condition of the water. Since ammonia, nitrites, and nitrates are quite innocuous, the total inorganic nitrogen does not indicate *actual* evil like the organic nitrogen, but *potential* evil, as it is evident that the innocuous character of a water which contains much nitrogen in these forms depends wholly on the permanence of the conditions of temperature, aëration, filtration through soil, etc., which have broken up the original organic matter; if these should at any time fail, the *past* contamination would become *present*, the nitrogen appearing in the organic form, the water being loaded in all likelihood with putrescent and contagious matter.

In upland surface waters which have not been contaminated to any extent by animal pollution the total inorganic nitrogen rarely exceeds 0·03 part. In water from cultivated districts the amount is greater, ranging as high as 1 part, the average of a large number of samples being about 0·22 part. It is useless to attempt any generalization for shallow wells, as the proportion depends upon local circumstances. The amount is usually large and may reach, as seen in Example XIII., the enormous quantity of twenty-five parts per 100,000. Waters containing from one to five parts are very commonly met with. In water from deep wells and springs, quantities ranging up to 3·5 parts have been observed, the average on a large series of analyses being 0·5 part for deep wells and about 0·4 part for springs. It must be remembered that the conditions attending deep wells and springs are remarkably permanent, and the amount of filtration which the water undergoes before reaching the well itself, or issuing from the spring is enormous. Meteorological changes here have either no effect, or one so small and slow as not to interfere with any purifying actions which may be taking place. All other sources of water, and especially shallow wells, are on the other hand subject to considerable changes. A sudden storm after drought will wash large quantities of polluting matter into the water-course; or dissolve the filth which has been concentrating in the pores of the soil during the dry season, and carry it into the well. Small indications therefore of a polluted origin are very serious in surface waters and shallow well waters, but are of less moment in water from deep wells and springs; the *present* character of these being of chief importance, since whatever degree of purification may be observed may usually be trusted as permanent. The term "total inorganic nitrogen" has been chosen, chiefly because it is based on actual results of analysis without the introduction of any theory whatever. It will be seen that it corresponds very nearly with the term "previous sewage or animal contamination," which was introduced by Dr. Frankland, and which was employed in the second edition of this work. Perhaps few terms have been more wonderfully misunderstood and misrepresented than that phrase, and it is hoped that the new term will be less liable to misconception. It will be remembered that the "previous sewage contamination" of a water was calculated by multiplying the sum of the quantities of nitrogen present as ammonia, nitrates, and nitrites, by 10,000, and deducting 320 from the product, the number thus obtained representing the previous animal contamination of the water in terms of average filtered London sewage. It was purely conventional, for the proportion of organic nitrogen present in such sewage was assumed to be 10 parts per 100,000, whereas in the year 1857 it was actually 8·4 parts, and in 1869 only 7 parts. The deduction of 320 was made to correct for the average amount of inorganic nitrogen in rain water, and this is omitted in calculating "total inorganic nitrogen" for the following reasons:—The quantity is small, and the variations in composition of rain water at different times and under different circumstances very considerable, and it appears to obscure the significance of the results of analysis of very pure waters to deduct from all the same fixed amount. As, too, the average amount of total inorganic nitrogen in unpolluted surface waters is only 0·011 part (XXVIII.), it cannot be desirable to apply a correction amounting to nearly three times that average, and so place a water which contains 0·032 part of total inorganic nitrogen on the same level as one which contains no trace of any previous pollution.

### Chlorine.

This is usually present as sodic chloride, but occasionally, as has been mentioned before, it is most likely as a calcic salt. It is derived, in some cases, from the soil, but more usually from animal excreta (human urine contains about 500 parts per 100,000), and is therefore of considerable importance in forming a judgment as to the character of a water. Unpolluted river and spring waters usually contain less than one part; average town sewage about eleven parts. Shallow well water may contain any quantity from a mere trace up to fifty parts or even more. Its amount is scarcely affected by any degree of filtration through soil; thus, the effluent water from land irrigated with sewage contains the same proportion of chlorine as the sewage, unless it has been diluted by subsoil water or concentrated by evaporation. Of course, attention should be given to the geological nature of the district from which the water comes, the distance from the sea or other source of chlorine, etc., in order to decide on the origin of the chlorine. Under ordinary circumstances, a water containing more than three or four parts of chlorine should be regarded with suspicion.

### Hardness.

This is chiefly of importance as regards the use of the water for cleansing and manufacturing purposes, and for steam boilers. It is still a moot point as to whether hard or soft water is better as an article of food. The temporary hardness is often said to be that due to carbonates held in solution by carbonic acid, but this is not quite correct; for even after prolonged boiling, water will still retain about three parts of carbonate in solution, and therefore when the total hardness exceeds three parts, that amount should be deducted from the permanent hardness and added to the temporary, in order to get the quantity of carbonate in solution. But the term "temporary" hardness properly applies to the amount of hardness which may be removed by boiling, and hence, if the total hardness be less than three parts, there is usually no *temporary*. As the hardness depends chiefly on the nature of the soil through and over which the water passes, the variations in it are very great; that from igneous strata has least hardness, followed in approximate order by that from Metamorphic, Cambrian, Silurian and Devonian rocks, Millstone Grit, London Clay, Bagshot Beds, New Red Sandstone, Coal Measures, Mountain Limestone, Oolite, Chalk, Lias, and Dolomite, the average in the case of the first being 2·4 parts, and of the last 41 parts. As animal excreta contains a considerable quantity of lime, highly polluted waters are usually extremely hard. Water from shallow wells contains varying proportions up to nearly 200 parts of total hardness (XIII.). No generalization can be made as to the proportion of permanent to temporary hardness.

### Suspended Matter.

This is of a less degree of importance than the matters hitherto considered. From a sanitary point of view it is of minor interest, because it may be in most cases readily and completely removed by filtration. Mineral suspended matter is, however, of considerable mechanical importance as regards the formation of impediments in the river bed by its gradual deposition, and as regards the choking of the sand filters in water-works: and organic suspended matter is at times positively injurious, and always favours the growth of minute organisms.

From the determinations which have been described, it is believed that a sound judgment as to the character of a water may be made, and the analyst should hardly be content with a less complete examination. If, however, from lack of time or other cause, so much cannot be done, a tolerably safe opinion may be formed, omitting the determination of total solid matter, and organic carbon and nitrogen. But it must not be forgotten that by so doing the enquiry is limited as regards organic impurity, to the determination of that which was formerly present, but has already been converted into inorganic substances. If still less must suffice, the estimation of nitrogen as nitrates and nitrites may be omitted, its place being to a certain extent supplied by that of chlorine, but especial care must then be taken to ascertain the source of the latter by examination of the district. If it be in any degree of mineral origin, no opinion can be formed from it as to the likelihood of organic pollution. At best, so slight an examination must be of but little value, and considering the rapidity with which the nitrogen as nitrates can be determined by the indigo process, the saving of time would be very small.

### General Considerations.

In judging of the character of a sample of water, due attention must of course be paid to the purpose for which it is proposed to be used. The analyst frequently has only to decide broadly whether the water is good or bad; as, for example, in cases of the domestic supply to isolated houses or of existing town supplies. Water which would be fairly well suited for the former might be very objectionable for the latter, where it would be required to a certain extent for manufacturing purposes. Water which would be dangerous for drinking or cooking may be used for certain kinds of cleansing operations; but it must not be forgotten, that unless great care and watchfulness are exercised there is considerable danger of this restriction being neglected, and especially if the objectionable water is nearer at hand than the purer supply. There would for this reason, probably, be some danger attending a double supply on a large scale in a town, even if the cost of a double service of mains, etc., were not prohibitive.

It is often required to decide between several proposed sources of supply, and here great care is necessary, especially if the differences between the samples are not great. If possible, samples should be examined at various seasons of the year; and care should be taken that the samples of the several waters are collected as nearly as possible sumultaneously and in a normal condition. The general character of a water is most satisfactorily shown by the average of a systematic series of analyses; and for this reason the average analysis of the water supplies of London, taken from the Reports of Dr. Frankland to the Registrar General, of Glasgow by Dr. Mills, and of Birmingham by Dr. Hill, are included in the table. River waters should, as a rule, not be examined immediately after a heavy rain when they are in flood. A sudden rainfall after a dry season will often foul a river more than a much heavier and more prolonged downfall after average weather. Similarly the sewage discharged from a town at the beginning of a heavy rainstorm is usually extremely foul, the solid matter which has been accumulating on the sides of the sewers and in corners and recesses, being rapidly washed out by the increased stream.

The possibility of *improvement* in quality must also be considered. A turbid water may generally be rendered clear by filtration, and this will often also effect some slight reduction in the quantity of organic matter; but while somewhat rapid filtration through sand or similar material will usually remove all solid suspended matter, it is generally necessary to pass the water very slowly through a more efficient material to destroy any large proportion of the organic matter in solution. Very fine sand, animal charcoal, and spongy iron are all in use for this purpose. The quantity of available oxygen must not be neglected in considering the question of filtration. If the water contains only a small quantity of organic matter and is well aërated, the quantity of oxygen in solution may be sufficient, and the filtration may then be continuous; but in many instances this is not the case, and it is then necessary that the filtration should be intermittent, the water being allowed at intervals to drain off from the filtering material in order that the latter may be well aërated, after which it is again fit for work.

Softening water by Clark's process generally removes a large quantity of organic matter (see Table 8, XVI.) from solution, it being carried down with the calcic carbonate precipitate.

It is evident that no very definite distinction can be drawn between deep and shallow wells. In the foregoing pages, deep wells generally mean such as are more than 100 feet deep, but there are many considerations which qualify this definition. A deep well may be considered essentially as one the water in which has filtered through a considerable thickness of porous material, and whether the shaft of such a well is deep or shallow will depend on circumstances. If the shaft passes through a bed of clay or other impervious stratum, and the surface water above that is rigidly excluded, the well should be classed as "deep," even if the shaft is only a very few feet in depth, because the water in it must have passed for a considerable distance below the clay. On the other hand, however deep the shaft of a well, it must be considered as "shallow" if water can enter the shaft near the surface, or if large cracks or fissures give free passage for surface water through the rock in which the well is sunk. With these principles in view, the water from wells may often be improved. Every care should be taken to exclude surface water from deep wells; that is to say, all water from strata within about 100 feet from the surface or above the first impervious bed. In very deep wells which pass through several such beds, it is desirable to examine the water from each group of pervious strata, as this often varies in quality, and if the supply is sufficient, exclude all but the best.

In shallow wells much may occasionally be accomplished in a similar manner by making the upper part of the shaft water-tight. It is also desirable that the surface for some distance round the well should be puddled with clay, concreted, or otherwise rendered impervious, so as to increase the thickness of the soil through which the water has to pass. Drains passing near the well should be, if possible, diverted; and of course cesspools should be either abolished, or, if that is impracticable, removed to as great a distance from the well as is possible, and in addition made perfectly water-tight. Changes such as these tend to diminish the uncertainty of the conditions attending a shallow well, but in most cares such a source of supply should, if possible, be abandoned as dangerous at best.

### Clark's Process for Softening Hard Water.

The patent right of this process having expired, the public are free to use it.

This method of softening consists in adding lime to the hard water. It is only applicable to water which owes its hardness entirely, or chiefly, to the calcic and magnesic carbonates held in solution by carbonic acid (*temporary hardness*). Water which owes its hardness to calcic or magnesic sulphate (*permanent hardness*) cannot be thus softened; but any water which softens on boiling for half an hour will be softened to an equal extent by Clark's process. The hard water derived from chalk, limestone, or oolite districts, is generally well adapted for this operation.

To soften 700 gallons of water, about one ounce of quicklime is required for each part of temporary hardness in 100,000 parts of water. The quantity of quicklime required is thoroughly slaked in a pailful of water. Stir up the milk of lime thus obtained, and pour it immediately into the cistern containing at least 50 gallons of the water to be softened, taking care to leave in the pail any heavy sediment that may have settled to the bottom in the few seconds that intervened between the stirring and pouring. Fill the pail again with water, and stir and pour as before. The remainder of the 700 gallons of water must then be added, or allowed to run into the cistern from the supply pipe. If the rush of the water does not thoroughly mix the contents of the cistern, this must be accomplished by stirring with a suitable wooden paddle. The water willl now appear very milky, owing to the precipitation of the chalk which it previously contained in solution, together with an equal quantity of chalk which is formed from the quicklime added.

After standing for three hours the water will be sufficiently clear to use for washing; but to render it clear enough for drinking, at least twelve hours' settlement is required. This process not only softens water, but it removes to a great extent objectionable organic matter present.

The proportion of lime to water may be more accurately adjusted during the running in of the hard water, by taking a little water from the cistern at intervals in a small white cup, and adding to it a drop or two of solution of nitrate of silver, which will produce a yellow or brownish colouration as long as there is lime present in excess. As soon as this becomes very faint, and just about to disappear, the flow of water must be stopped. The carbonate may be removed by filtration in a very short time after the addition of lime, and on the large scale this may be done with great rapidity by means of a filter press, as in Porter's process. This latter method of rapidly softening and purifying water is the invention of J. Henderson Porter, C.E., Queen Victoria Street, London, whose apparatus is largely coming into use for public water supplies, and for softening waters used in manufacturing processes, and the prevention of boiler incrustations, etc. The chief objections to the original Clark process are, the large space required for mixing and settling tanks, and the time required for subsidence of the precipitate. On the contrary, in Porter's process, the space occupied is small, and the clarification immediate. The results are admirable, and are achieved at a very moderate cost.

## METHODS OF ESTIMATING THE ORGANIC IMPURITIES IN WATER WITHOUT GAS APPARATUS.

§ 90. The foregoing methods of estimating the organic impurities in potable waters, though very comprehensive and trustworthy, yet possess the disadvantage of occupying a good deal of time, and necessitate the use of a complicated and expensive set of apparatus, which may not always be within the reach of the operator.

Nothing of a strictly reliable character as to the nature of the organic matter or its quantity can be gained from the use of standard permanganate solution as originally devised by Forschammer, and the same remark applies to the loss on ignition of the residue, both of which have been in past time largely used.

The Forschammer or oxygen process, however, as improved by Letheby, and further elaborated by Tidy, may be considered as worthy of considerable confidence in determining the amount of organic substances contained in a water.

### The Oxygen Process.

*Principle.*—This process depends upon the estimation of the amount of oxygen required to oxidize the organic and other oxidizable matters in a known volume of water, slightly acidified with pure sulphuric acid. For this purpose, a standard solution of potassic permanganate is employed in excess. The amount of unchanged permanganate, after a given time, is ascertained by means of a solution of sodic hyposulphite, by the help of the iodine and starch reaction.

Tidy and Frankland in all cases make a blank experiment with pure distilled water, side by side with the sample.

*Duration of experiment and temperature.*—As regards the time during which the sample of water should be exposed to the action of the permanganate, authorities somewhat differ. It is manifest that, if the water contains certain reducing agents such as nitrites, ferrous salts, or sulphuretted hydrogen, an immediate reduction of the re-agent will occur, and Tidy is disposed to register the reduction which occurs in three minutes, in the known absence of iron and sulphuretted hydrogen, as due to nitrites. The same authority adopts the plan of making two observations, one at the end of one hour and another at the end of three hours, at the ordinary temperature of the laboratory (say 60° Fahr. or 16° C.).

Frankland admits this process to be the best volumetric method in existence for the estimation of organic matters, but is content with one experiment lasting three hours (also at ordinary temperature).

The Water Committee of the Society of Public Analysts of Great Britain and Ireland have adopted the periods of fifteen minutes and four hours for the duration of the experiment, at the fixed temperature of 80° Fahr. or 27° C.*

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* Dupré in further comment on the temperature at which it is advisable to carry out this method (*Analyst*, x. 118), and also as to the reactions involved, points out one feature which has in all probability impressed itself upon other operators, that is to say, the effect of chlorides when present in any quantity. It is evident that if in this case the permanganate is used at a high temperature and in open vessels, chlorine will be liberated; part escaping into the air, and the rest nullifying the reducing effect of any organic matter present on the permanganate. If, however, the experiment be conducted at high temperature in a closed vessel, the probable error is eliminated, because the chlorine is retained, and subsequently, when cool and the potassic iodide added, the free Cl liberates exactly the same amount of iodine as would have been set free by the permanganate from which it was produced. It thus becomes possible to estimate the amount of oxidizable organic matter, even in sea water. In order, however, to reduce the probable error from the presence of chlorides, Dupré prefers to carry on the experiment at a very low temperature, in fact, as near 0° C. or 32° F. as possible, and uses phosphoric acid in place of sulphuric (250 gm. glacial acid to the liter; 10 c.c. of which is used for each quarter or half liter of water). The sample is cooled, the reagent added in a stoppered bottle, and kept in an ordinary refrigerator for twenty-four hours. The same operator very rightly condemns the practice adopted by some chemists, especially those of Germany, in boiling a water with permanganate and sulphuric acid. The presence of chlorides in varying proportions must in such case totally vitiate the results.

Dupré has carried out experiments (*Analyst*, vii. 1), the results of which are in favour of the modifications adopted by the Committee. The chief conclusions arrived at are—

(1) That, practically, no decomposition of permanganate takes place during four hours when digested in a closed vessel at 80° with perfectly pure water and the usual proportion of pure sulphuric acid.

By adopting the closed vessel, all dust or reducing atmospheric influence is avoided.

(2) The standardizing of the hyposulphite and permanganate, originally and from time to time, must be made in a closed vessel in the same manner as the analysis of a water, since it has been found that when the titration is made slowly in an open beaker less hyposulphite is required than in a stoppered bottle. This is probably due to a trifling loss of iodine by evaporation.

(3) That with very pure waters no practical difference is produced by a rise or fall of temperature, the same results being obtained at 32° F. as at 80° F. On the other hand, with polluted waters, the greater the organic pollution, the greater the difference in the amount of oxygen absorbed according to temperature.

(4) As to time, it appears that very little difference occurs in good waters between three and four hours' digestion; but with bad waters there is often a very considerable increase in the extra hour; and thus Dupré doubts whether even four hours' digestion suffices for very impure waters.

The necessary standard solutions for working the process will be described further on.

**Comparison of the Results of this Process with the Combustion Method.**—I cannot do better than quote Dr. Frankland's remarks on this subject, as contained in his treatise on *Water Analysis*:—

"The objections to the oxygen process are, first, that its indications are only comparative, and not absolute; and, second, that its comparisons are only true when the organic matter compared is substantially identical in composition.

"For many years, indeed, after this process was first introduced, the action of the permanganate of potash was tacitly assumed to extend to the complete oxidation of the organic matter in the water, and, therefore, the result of the experiment was generally stated as 'the amount of oxygen required to oxidize the organic matter;' whilst some chemists even employed the number so obtained to calculate the actual weight of organic matter in the water on the assumption that equal weights of all kinds of organic matter required the same weight of oxygen for their complete oxidation.

"Both these assumptions have been conclusively proved to be entirely fallacious, for it has been experimentally demonstrated by operating upon known quantities of organic substances dissolved in water, that there is no relation either between the absolute or relative weight of different organic matters and the oxygen which such matters abstract from permanganate of potash.

"Nevertheless, in the periodical examination of waters from the same source, I have noticed a remarkable parallelism between the proportions of organic carbon and of oxygen abstracted from permanganate of potash. Thus, for many years past, I have seen in the monthly examination of the waters of the Thames and Lea supplied to London such a parallelism between the numbers given by Dr. Tidy, expressing 'oxygen consumed,' and those obtained by myself in the determination of 'organic carbon.'

"This remarkable agreement of the two processes, extending as it did to 1,418 out of 1,686 samples, encouraged me to hope that a constant multiplier might be found, by which the 'oxygen consumed' of the Forschammer process could be translated into the 'organic carbon' of the combustion method of analysis. To test the possibility of such a conversion, my pupil, Mr. Woodland Toms made, at my suggestion, the comparative experiments recorded in the following tables:—

### I.—River Water.

| Source of Sample. | Oxygen consumed. | × | $\frac{C}{O}$ | = | Organic carbon by combustion. |
|---|---|---|---|---|---|
| Chelsea Company's supply ... ... | 0·098 | × | 2·6 | = | 0·256 |
| West Middlesex Co.'s ,, ... ... | 0·116 | × | 2·5 | = | 0·291 |
| Lambeth Co.'s ,, ... ... | 0·119 | × | 2·43 | = | 0·282 |
| Southwark Co.'s ,, ... ... | 0·121 | × | 2·22 | = | 0·269 |
| New River Co.'s ,, ... ... | 0·076 | × | 2·4 | = | 0·183 |
| Chelsea Co.'s second sample ... ... | 0·070 | × | 2·69 | = | 0·188 |
| Lambeth Co.'s ,, ... ... | 0·119 | × | 1·99 | = | 0·234 |
| New River Co.'s ,, ... ... | 0·107 | × | 2·25 | = | 0·221 |

"As the result of these experiments, the average multiplier is 2·38, and the maximum errors incurred by its use would be —0·021 part of organic carbon in the case of the second sample of the Chelsea Company's water, and +0·049 part in that of the second sample of the Lambeth Company's water. These errors would practically have little or no influence upon the analyst's opinion of the quality of the water. It is desirable that this comparison should be extended to the water of other moderately polluted rivers.

### II.—Deep Well Water.

| Source of Sample. | Oxygen consumed. | × | $\frac{C}{O}$ | = | Organic carbon by combustion. |
|---|---|---|---|---|---|
| Kent Company's supply ... ... | 0·015 | × | 5·1 | = | 0·077 |
| Colne Valley Co.'s ,, ... ... | 0·0135 | × | 6·9 | = | 0·094 |
| Hodgson's Brewery well ... ... | 0·03 | × | 5·3 | = | 0·158 |

"The relation between 'oxygen consumed' and 'organic carbon' in the case of deep well waters is thus very different from that which obtains in the case of river waters, and the average multiplier deduced from the foregoing examples is 5·8, with maximum errors of + 0·01 of organic carbon in the case of the Kent Company's water, and — 0·015 in that of the Colne Valley water. Such slight errors are quite unimportant.

"Similar comparative experiments made with shallow well and upland surface waters showed amongst themselves a wider divergence, but pointed to an average multiplier of 2·28 for shallow well water, approximately the same as that found for moderately polluted river water, and 1·8 for upland surface water.

"In the interpretation of the results obtained, either by the Forschammer or combustion process, the adoption of a scale of organic purity is often useful to the analyst, although a classification according to such a scale may require to be modified by considerations derived from the other analytical data. It is indeed necessary to have a separate and more liberal scale for upland surface water, the organic matter of which is usually of a very innocent nature, and derived from sources precluding its infection by zymotic poisons.

"Subject to modification by the other analytical data, the following scale of classification has been suggested by Dr. Tidy and myself:—

### Section I.—Upland Surface Water.

"**Class I.** *Water of great organic purity*, absorbing from permanganate of potash not more than 0·1 part of oxygen per 100,000 parts of water, or 0·07 grain per gallon.

"**Class II.** *Water of medium purity*, absorbing from 0·1 to 0·3 part of oxygen per 100,000 parts of water, or 0·07 to 0·21 grain per gallon.

"**Class III.** *Water of doubtful purity*, absorbing from 0·3 to 0·4 part per 100,000, or 0·21 to 0·28 grain per gallon.

"**Class IV.** *Impure water*, absorbing more than 0·4 part per 100,000, or 0·28 grain per gallon.

### Section II.—Water other than Upland Surface.

"**Class I.** *Water of great organic purity*, absorbing from permanganate of potash not more than 0·05 part of oxygen per 100,000 parts of water, or 0·035 grain per gallon.

"**Class II.** *Water of medium purity*, absorbing from 0·05 to 0·15 part of oxygen per 100,000, or 0·035 to 0·1 grain per gallon.

"**Class III.** *Water of doubtful purity*, absorbing from 0·15 to 0·2 part of oxygen per 100,000, or 0·1 to 0·15 grain per gallon.

"**Class IV.** *Impure water*, absorbing more than 0·2 part of oxygen per 100,000, or 0·15 grain per gallon."

### The Albuminoid Ammonia Process.

*Principle.*—Wanklyn, Chapman, and Smith are the authors of this well-known method of estimating the quantity of nitrogenous organic matter in water, which depends upon the conversion of the nitrogen in such organic matter into ammonia, when distilled with an alkaline solution of potassic permanganate (*J. C. S.* 1867, 591).

The authors have given the term "Albuminoid ammonia" to the $NH^3$ produced from nitrogenous matter by the action of the permanganate, doubtless because the first experiments made in the process were made with albuminous substances; but the authors also proved that ammonia may be obtained in a similar way from a great variety of nitrogenous organic substances, such as hippuric acid, narcotine, strychnine, morphine, creatine, gelatine, casein, etc.

Unfortunately, however, although the proportion of nitrogen yielded by any one substance when treated with boiling alkaline permanganate appears to be definite, yet different substances give different proportions of their nitrogen. Thus hippuric acid and narcotine yield the whole, but strychnine and morphine only one-half of their known proportion of nitrogen. Hence the value of the numerical results thus obtained depends entirely on the assumption that the nitrogenous organic matter in water is *uniform in its nature*, and the authors say that in a river polluted mainly by sewage "the disintegrating animal refuse would be pretty fairly measured by ten times the albuminoid ammonia which it yields."

It is stated by the authors that the albuminoid ammonia from a really good drinking water should not exceed 0·008 part in 100,000. The average of fifteen samples of Thames water supplied to London by the various Water Companies in 1867 was 0·0089, and in five samples supplied by the New River Company 0·0068 part per 100,000.

The necessary standard solutions and directions for working the process will be described further on (page 397).

*Other methods of estimating the organic constituents in Drinking Waters.*—The best of these are the processes of Dittmar and Robinson, and of Dupré and Hake; but as the results are mainly obtained by the balance, and not by volumetric means, the reader is referred to the original papers contributed to the *Journal of the Chemical Society*.

## PREPARATION OF THE RE-AGENTS FOR THE SANITARY ANALYSIS OF WATERS WITHOUT GAS APPARATUS.

§ 91. The Water Committee of the Society of Public Analysts of Great Britain and Ireland have drawn up some very concise directions for the practice of water analysis for sanitary purposes, based upon well-known processes, the essential parts of which are given below. There are some slight modifications, such as the use of the decem or 10-grain measure instead of the grain, etc. The insertion here of these directions in full, or nearly so, necessarily repeats some processes which have been already described in §§ 87 and 88, but it avoids cross-references and at the same time gives some slight practical modifications which, to some operators, may seem desirable. The Committee recommend the results to be recorded in grains per imperial gallon; but whatever system of weights and measures the individual analyst may use, a slight calculation will enable him to state the results in any required way.

### Re-agents for the Estimation of Chlorine.

*Standard Solution of Silver Nitrate.*—Dissolve 4·7887 parts of pure recrystallized silver nitrate in distilled water, and make the solution up to 1000 parts. The solution is to be standardized against the standard solution of sodic chloride, and adjusted if necessary. 1 c.c. = 0·001 gm. of chlorine, or 1 dm. = 0·01 grn. of chlorine.

*Standard Solution of Sodic Chloride.*—Dissolve 1·648 part of pure dry sodic chloride in distilled water, and make the solution up to 1000 parts. 1 c.c. contains 0·001 gm. chlorine, or 1 dm. = 0·01 grn. of chlorine.

*Potassic Monochromate.*—50 parts of potassic monochromate are dissolved in 1000 parts of distilled water. A solution of silver nitrate is added, until a permanent red precipitate is produced, which is allowed to settle. This removes any accidental chlorine in the salt.

### Re-agent for the Estimation of Phosphoric Acid.

*Molybdic Solution.*—One part pure molybdic acid is dissolved in 4 parts of ammonia, sp. gr. 0·960. This solution, after filtration, is poured with constant stirring into 15 parts of nitric acid of 1·20 sp. gr. It should be kept in the dark, and carefully decanted from any precipitate which may form.

### Re-agents for the Estimation of Nitrogen in Nitrates.

*Concentrated Sulphuric Acid.*—In order to ensure freedom from oxides of nitrogen, this should be kept in a bottle containing mercury, and agitated from time to time, which will ensure their absence.

*Metallic Aluminium.*—As thin foil.

*Solution of Sodic Hydrate.*—Dissolve 100 parts of solid sodic hydrate in 1000 parts of distilled water. When cold, introduce a strip of about 100 square c.m., say fifteen square inches, of aluminium foil, previously heated just short of redness, wrapped round a glass rod. When the aluminium is dissolved, boil the solution briskly in a porcelain basin until about one-third of its volume has been evaporated, allow it to cool, and make it up to its original volume with water free from ammonia. The solution must be tested by a blank experiment to prove the absence of nitrates.

*Broken Pumice.*—Clean pumice, broken into pieces of the size of small peas, sifted free from dust, heated to redness, and kept in a closely stoppered bottle.

*Hydrochloric Acid free from Ammonia.*—If the ordinary pure acid is not free from ammonia, it should be distilled. As only two or three drops are used in each experiment, it will be sufficient if that quantity does not contain an appreciable proportion of ammonia.

*Copper Sulphate Solution.*—Dissolve 30 parts of pure copper sulphate in 1000 parts of distilled water.

*Metallic Zinc.*—As thin foil. This should be kept in a dry atmosphere, so as to be preserved as far as possible from oxidation.

*Standard Solution of Ammonic Chloride* (see below).

*Nessler's Solution* (see below).

### Re-agents for the Estimation of Nitrogen as Ammonia and Albuminoid Ammonia.

*Concentrated Standard Solution of Ammonic Chloride.*—Dissolve 3·15 parts of pure ammonic chloride in 1000 parts of distilled water free from ammonia.

*Standard Solution of Ammonic Chloride.*—Dilute the above with pure distilled water to 100 times its bulk. This solution is used for comparison in nesslerizing, and contains one part of ammonia ($NH^3$) in 100,000, or $\frac{1}{100}$ m.gm. in each c.c.

*Nessler Solution.*—Dissolve 35 parts of potassic iodide in 100 parts of water. Dissolve 17 parts of mercuric chloride in 300 parts of water. The liquids may be heated to aid solution, but if so must be cooled. Add the latter solution to the former until a permanent precipitate is produced. Then dilute with a 20 per cent. solution of sodic or potassic hydrate to 1000 parts; add mercuric chloride solution until a permanent precipitate again forms; allow to stand till settled, and decant off the clear solution. The bulk should be kept in an accurately stoppered bottle, and a quantity transferred from time to time to a small bottle for use. The solution improves by keeping. It will be noticed that this solution is only about half the strength of the one given on page 330; of course a larger volume has to be used in testing.

*Sodic Carbonate.*—A 20 per cent. solution of recently ignited pure sodic carbonate.

*Alkaline Permanganate Solution.*—Dissolve 200 parts of potassic hydrate and eight parts of pure potassic permanganate in 1100 parts of distilled water, and boil the solution rapidly till concentrated to 1000 parts.

*Distilled Water free from Ammonia* (see page 330).

### Re-agents for the Estimation of Oxygen absorbed.

*Standard Solution of Potassic Permanganate.*—Dissolve 0·395 part of pure potassic permanganate in 1000 of water. Each c.c. contains 0·0001 gm. of available oxygen, and each dm. contains 0·001 grn.

*Potassic Iodide Solution.*—One part of the pure salt recrystallized from alcohol, dissolved in ten parts of distilled water.

*Dilute Sulphuric Acid.*—One part by volume of pure sulphuric acid is mixed with three parts by volume of distilled water, and solution of potassic permanganate dropped in until the whole retains a *very faint* pink tint, after warming to 80° F. for four hours.

*Sodic Thiosulphate.*—One part of the pure crystallized salt dissolved in 1000 parts of water.

*Starch Water.*—One part of starch to be intimately mixed with 500 parts of cold water, and the whole briskly boiled for five minutes, and filtered, or allowed to settle.

### Re-agents for the Estimation of Hardness.

*Concentrated Standard Solution of Calcic Chloride.*—Dissolve 1·144 gm. of pure crystallized calc-spar in dilute hydrochloric acid (with the precautions given on page 336), then dissolve in water, and make up to a liter. On the grain system, a solution of the same strength is made by dissolving 11·44 grn. of calc-spar in 1000 dm.

*Standard Water of 8° Hardness.*—This is made by diluting the foregoing concentrated solution to ten times its volume with freshly boiled and cooled distilled water.

*Standard Soap Solution* (is made precisely as directed on p. 336).—It should be of such strength as just to form a permanent lather, when 18 c.c. or dm. measures are shaken with 100 c.c. or dm. of water of 8° hardness. The following table will then give the degrees of hardness corresponding to the number of c.c. or dm. measures employed.

| Hardness. | c.c. or dm. Measures. | Hardness. | c.c. or dm. Measures. |
|---|---|---|---|
| 0° | 0·9 | 5° | 12·0 |
| 1° | 2·9 | 6° | 14·0 |
| 2° | 5·4 | 7° | 16·0 |
| 3° | 7·7 | 8° | 18·0 |
| 4° | 9·9 | | |

After which one degree = 2 c.c. or dm. measures. This is the last solution recommended by Dr. Clark, and differs slightly from the scale given on page 370; the variation, however, is very insignificant, except in the two first stages of the table.

### The Analytical Processes.

**Collection of Samples.**—The same as directed on p. 337.

**Appearance in Two-foot Tube.**—The colour or tint of the water must be ascertained, by examination, in a tube two feet long and two inches in diameter. This tube should be made of glass as nearly colourless as may be, and should be covered at each end with a disc of perfectly colourless glass, cemented on, an opening being left for filling and emptying the tube. This opening may be made, either by cutting a half-segment off the glass disc at one end, or by cutting a small segmental section out of the tube itself, before the disc is cemented on. These tubes are most conveniently kept on hooks in a horizontal position to prevent the entrance of dust.

The tube must be about half-filled with the water to be examined, brought into a horizontal position level with the eye, and directed towards a well-illuminated white surface. The comparison of tint has to be made between the lower half of the tube containing the water under examination, and the upper half containing atmospheric air only.

**Smell.**—Put not less than three or four ounces of the water into a clean eight-ounce wide-mouthed stoppered glass bottle, which has been previously rinsed with the same water. Insert the stopper, and warm the water in a water-bath to 100°F. (38° C.). Remove the bottle from the water-bath, rinse it outside with good water perfectly free from odour, and shake it rapidly for a few seconds; remove the stopper, and immediately observe if the water has any smell. Insert the stopper again, and repeat this test.

When the water has a *distinct* odour of any known or recognised polluting matter, such as peat or sewage, it should be so described; when this is not the case, the smell must be reported simply as none, very slight, slight, or marked, as the case may be.

**Chlorine.**—Titrate at least 100 c.c. or dm. of the water with the standard silver nitrate solution, either in a white porcelain basin or in a glass vessel standing on a porcelain slab, using potassic chromate as an indicator. The titration is conducted as follows:—The sample of water is measured into the basin or beaker, and 1 c.c. or 1 dm. of potassic chromate solution added. The standard silver nitrate solution is then run in cautiously from a burette, until the red colour of the precipitated silver chromate, which is always observed at the point where the silver solution drops in, is no longer entirely discharged on stirring. The burette is then read off. It is best to repeat the experiment, as follows:—Add a few drops of dilute sodic chloride solution to the water last titrated, which will discharge the red colour. Measure out a fresh portion of the water to be titrated into another basin, and repeat the titration, keeping the first sample, the colour of which has been discharged, side by side with the second, so as to observe the first permanent indication of *difference* of colour. If the quantity of chlorine be so small that still greater accuracy is necessary, the titration may be conducted in the same way as last described, but instead of the operator looking directly at the water containing the chromate solution, he may place between the basin containing the water and his eye, a flat glass cell containing some water tinted with the chromate solution to the same tint as the water which is being tested, or may look through a glass coated with a gelatine film coloured with the same salt (see § 41). Care must always be taken that the water is as nearly neutral as possible before titration. If originally acid, it should be neutralized with precipitated carbonate of lime. If the proportion of chlorine be less than 0·5 grain per gallon, it is desirable to take a larger quantity of the water, say 250 c.c. or 350 dm., for the estimation, and to concentrate this quantity on the water-bath before titrating it, so as to bring it to about 100 c.c. or 150 dm. This titration may be performed by gas-light.

**Phosphoric Acid.**—The ignited total residue, obtained as hereafter directed, is to be treated with a few drops of nitric acid, and the silica rendered insoluble by evaporation to dryness. The residue is then taken up with a few drops of dilute nitric acid, some water is added, and the solution is filtered through a filter previously washed with dilute nitric acid. The filtrate, which should measure 3 c.c. (or 5 dm.), is mixed with 3 c.c. of molybdic solution, gently warmed, and set aside for fifteen minutes, at a temperature of 80° F. The result is reported as "traces," "heavy traces," or "very heavy traces," when a colour, turbidity, or definite precipitate, are respectively produced, after standing for fifteen minutes.

**Nitrogen in Nitrates.**—This may be determined by one of the following processes: viz., *Crum*, *Copper-zinc*, *Aluminium*, or *Indigo*. Analysts should report which process is employed.

*Crum Process.*—This is described on p. 361, or it may be carried out in a Lunge's nitrometer as follows:—250 c.c. or dm. of the water must be concentrated in a basin to 2 c.c. or 3 dm. measure. A Lunge's nitrometer is charged with mercury, and the three-way stop-cock closed, both to measuring tube and waste pipe. The concentrated filtrate is poured into the cup at the top of the measuring tube, and the vessel which contained it rinsed with 1 c.c. of water, and the contents added. The stop-cock is opened to the measuring tube, and, by lowering the pressure tube, the liquid is sucked out of the cup into the tube. The basin is again rinsed with 5 c.c. of pure strong sulphuric acid, and this is also transferred to the cup and sucked into the measuring tube. The stop-cock is once more closed, and 12 c.c. more sulphuric acid put into the cup, and the stop-cock opened to the measuring tube until 10 c.c. of acid have passed in. The excess of acid is discharged, and the cup and waste pipe rinsed with water. Any gas which has collected in the measuring tube is expelled by opening the stop-cock and raising the pressure tube, taking care no liquid escapes. The stop-cock is closed, the measuring tube taken from its clamp and shaken by bringing it slowly to a nearly horizontal position, and then suddenly raising it to a vertical one. This shaking is continued until no more gas is given off, the operation being, as a rule, complete in fifteen minutes. Now prepare a mixture of one part of water with five parts of sulphuric acid, and let it stand to cool. After an hour, pour enough of this mixture into the pressure tube to equal the length of the column of acidulated water in the working tube, bring the two tubes side by side, raise or lower the pressure tube until the mercury is of the same level in both tubes, and read off the volume of nitric oxide (for calculation of nitrogen see p. 227). This volume, expressed in c.c.'s and corrected to normal temperature and pressure, gives, when multiplied by 0·175, the nitrogen in nitrates, in *grains per gallon*, if 250 c.c. of the water have been used.

*Copper-zinc Process* (already described on p. 364).

*Aluminium Process.*—This is carried out as follows:—50 c.c. or 100 dm. of the water are introduced into a retort, and 50 c.c. or 100 dm. of a 10 per cent. solution of caustic soda, free from nitrates, added. If necessary, the contents of the retort should be distilled until the sample is free from ammonia. The retort is then cooled, and a piece of aluminium foil introduced into it. The neck of the retort is inclined upwards, and its mouth closed with a perforated cork, through which passes the narrow end of a small chloride of calcium tube filled with powdered pumice or glass beads wetted with very dilute hydrochloric acid free from ammonia. This tube is connected with a second tube containing pumice stone moistened with strong sulphuric acid, which serves to prevent any ammonia from the air entering the apparatus, which is allowed to stand in this way for a few hours or overnight. The contents of the first absorption tube—that next the retort—are washed into the retort with a little distilled water free from ammonia, and the retort adapted to a condenser. The contents of the retort are distilled to about half their original volume. The distillate is collected, and an aliquot part nesslerized; and, if necessary, the rest of the distillate is diluted, and an aliquot part again nesslerized as hereafter directed.

*Indigo Process* (already described on page 218).

**Ammonia, Free and Saline.**—The estimation of ammonia present in the water in a free or saline form, and of that yielded by the nitrogenous matter present in the water (commonly called albuminoid ammonia), is to be made on the same portion of the sample to be analyzed.

Take not less than 500 c.c. or 700 dm. (one deci-gallon) of the water for these determinations, and distil in a 40-oz. stoppered retort, which is large enough to prevent the probability of portions of the water being spirted over into the condenser. The neck of the retort should be small enough to pass three or four inches into the internal glass tube of a Liebig's condenser. If the fit between the retort and the inside tube of the condenser is good, the joint may be made by wrapping a small piece of washed tinfoil round the retort tube so as to pass just inside the mouth of the condenser tube. Many analysts prefer, however, to work with a retort fitting loosely into the condenser; and, in such cases, the joint between the two may be made in one of the two following ways:—(1) Either by an ordinary india-rubber ring—such as those used for the top of umbrellas—which has been previously soaked in a dilute solution of soda or potash—being stretched over the retort tube in such a position, that when the retort tube is inserted in the condenser it shall fit fairly tightly within the mouth of the tube, about half-an-inch from the end; (2) Preferably, when the shape of the large end of the condenser admits of it, by a short length, say not more than two inches, of large size india-rubber tubing, which has been previously soaked in a dilute solution of soda or potash, being stretched outside both retort tube and condenser tube, so as to couple them together, so that the tube of the retort still projects some inches into that of the condenser. It is very desirable to have a constant stream of water round the condenser, whenever it can be obtained. Before distillation, a portion of the water must be tested with cochineal, in order to ascertain if it shows an alkaline reaction. The portion so tested must, of course, be rejected, and not put into the retort. If the water does not show an alkaline reaction, a sufficient quantity of ignited sodic carbonate, to render the water distinctly alkaline, must be added. The distillation should then be commenced, and not less than 100 c.c. or 150 dm. distilled over. The receiver should fit closely, but not air-tight, on the condenser. The distillation should be conducted as rapidly as is compatible with a certainty that no spirting takes place. After 100 c.c. or 150 dm. have been distilled over, the receiver should be changed, that containing the distillate being stoppered to preserve it from access of ammoniacal fumes. 100 c.c. measuring flasks make convenient receivers. The distillation must be continued until 50 c.c., or, say 75 dm. more, are distilled over; and this second portion of the distillate must be tested with Nessler's re-agent, to ascertain if it contains any ammonia. If it does not, the distillation for free ammonia may be discontinued, and this last distillate rejected; but, if it does contain any, the distillation must be continued still longer, until a portion of 50 c.c., or 75 dm., when collected, shows no colouration with the Nessler test. The whole of the distillates must be nesslerized as follows:—The standard solution of ammonia for comparison is that given on p. 392. The distillate is transferred to a clean Nessler glass, and one-twentieth of its volume of Nessler solution added. No turbidity must ensue on the addition of the Nessler solution to the water, as such turbidity would be a proof that the distillate was contaminated, and must, therefore, be rejected, and the determination repeated.

After thoroughly mixing the water and Nessler solution in the glass, an approximate estimate can be formed of the amount of ammonia present, by the amount of colouration produced in the solution. It will now be necessary to mix one or more standard solutions with which to compare the tint thus obtained. These solutions must be made by mixing the standard solution of ammonic chloride with distilled water absolutely free from ammonia, and subsequently adding some of the same Nessler solution as was previously added to the distillate. This precaution is essential, because the tint given by different samples of Nessler solution varies. The colorimeter may be used, if preferred, instead of Nessler glasses.

**Albuminoid Ammonia.**—As soon as the distillation of the free ammonia has been started, the alkaline solution of permanganate should be measured out into a flask, ready for addition to the water under examination, for the distillation of the albuminoid ammonia. The volume of the alkaline permanganate solution to be taken must be at least one-tenth of that of the water which is being distilled; and should not exceed that proportion unless the water is of very bad quality, and the solution must be made in accordance with the directions contained in these instructions. This solution must be diluted with four times its own volume of water, and must be placed in a flask and boiled during the whole time that the distillation of the sample for free ammonia is being carried on, care being taken that the concentration does not proceed to too great an extent. There must be enough of this boiled and diluted alkaline permanganate solution to make up the residue in the retort to about 500 c.c. or 700 dm. When the distillation of the sample of water for free and saline ammonia is completed, the alkaline permanganate solution, which has been thus diluted and boiled, will be ready for use, and the distillation for albuminoid ammonia may be proceeded with, as follows:—

To the residue left in the retort from which the free ammonia has been distilled, add the alkaline permanganate solution to make it up again to a volume of at least 500 c.c., or say 700 dm., and the lamp being replaced, the distillation must be continued, and successive portions of the distillate again collected in precisely the same way as during the process of distillation for free ammonia.

After 200 c.c. or 300 dm., say two-fifths of the volume contained in the retort, have been distilled over, the receiver should be changed and further portions of 50 c.c. or 75 dm. collected separately, until the distillate is practically free from ammonia. The distillate must then be mixed, and nesslerized in the same way as previously directed for free ammonia. The result so obtained must be calculated to ammonia in grams per liter or grains per gallon, and returned as *albuminoid* ammonia.

Special care must be taken that the atmosphere of the room in which these distillations are performed is kept free from ammoniacal vapours, and that the receivers fit close, but not air-tight, to the end of the Liebig's condenser. It is also specially necessary to observe that the colour of the distillate deepens gradually after the addition of the Nessler re-agent, and that it is not possible to read off the amount of colour correctly until the nesslerized liquor has stood for at least three minutes, and been intimately mixed with the Nessler solution.

Special care must be taken that the retort, condensers, receivers, funnels, Nessler glasses, etc., used are all rendered perfectly free from ammonia before use. Where the water in use in the laboratory is good, this may be used to thoroughly rinse the apparatus two or three times, draining out the adhering water; otherwise pure distilled water must be used. These ammonia and albuminoid ammonia determinations should be made as soon as possible after the water has been received for analysis.

**Oxygen Absorbed.**—Two separate determinations have to be made, viz., the amount of oxygen absorbed during fifteen minutes, and that absorbed during four hours. Both are to be made at a temperature of 80° F. (27° C.). It is most convenient to make these determinations in 12-oz. stoppered flasks, which have been rinsed with sulphuric acid and then with water. Put 250 c.c. or dm. into each flask, which must be stoppered and immersed in a water bath or suitable air-bath until the temperature rises to 80° F. Now add to each flask 10 c.c. or 10 dm. of the dilute sulphuric acid, and then 10 c.c. or 10 dm. of the standard permanganate solution. Fifteen minutes after the addition of the permanganate, one of the flasks must be removed from the bath and two or three drops of the solution of potassic iodide added to remove the pink colour. After thorough admixture, run from a burette the standard solution of thiosulphate, until the yellow colour is nearly destroyed, then add a few drops of starch water, and continue the addition of the thiosulphate until the blue colour is just discharged. If the titration has been properly conducted, the addition of one drop of permanganate will restore the blue colour. At the end of four hours remove the other flask, add potassic iodide, and titrate with thiosulphate, as just described. Should the pink colour of the water in the flask diminish rapidly during the four hours, further measured quantities of the standard solution of permanganate must be added from time to time so as to keep it markedly pink.

The thiosulphate solution must be standardized, not only at first, but (since it is liable to change) from time to time in the following way:—To 250 c.c. or dm. of pure redistilled water add two or three drops of the solution of potassic iodide, and then 10 c.c. or dm. of the standardized solution of permanganate. Titrate with the thiosulphate solution as above described. The quantity used will be the amount of thiosulphate solution corresponding to 10 c.c. or 10 dm., as may be, of the standardized permanganate, and the factor so found must be used in calculating the results of the thiosulphate titrations to show the amount of the standard permanganate solution used, and thence the amount of oxygen absorbed.

Great care should be taken that absolutely pure and fresh distilled water is used in standardizing the solution, which should also be kept in the dark and cool. It suffices to compare the solution, if kept in this way, once in three or four days.

The amount of thiosulphate solution thus found to be required to combine with the iodine liberated by the permanganate left undecomposed in the water is noted down, and the calculation made as follows:—Let A=amount of thiosulphate used in distilled water, and B=that used for water under examination. Then A expresses the amount of permanganate added to the water under examination, and B the amount of permanganate in excess of that which the organic matter in the water has destroyed. Therefore A—B is the amount actually consumed. If the amount of available oxygen in the quantity of permanganate originally added be $a$, the oxygen required to oxidize the organic matter in the water operated on would be $\frac{(A-B)a}{A}$. But $a$ (available oxygen in the 10 c.c. of standard permanganate used)=0·001 gm. Therefore $\frac{A-B \times 0{\cdot}001}{A}$=oxygen for 250 c.c.; or, $\frac{A-B \times 0{\cdot}4}{A}$=parts of oxygen required for 100,000 parts of water. Or, in other words, the difference between the quantity of thiosulphate used in the blank experiment and that used in the titration of the samples of water multiplied by the amount of available oxygen contained in the permanganate added, and the product divided by the volume of thiosulphate corresponding to the latter, is equal to the amount of oxygen absorbed by the water.

**Hardness before and after Boiling.**—Place 100 c.c. or 100 dm. of the water in an accurately stoppered 8-oz. flask. Run in the soap solution from a burette in small quantities at a time. If the water be soft, not more than ½ c.c. or dm. at a time; if hard, in quantities of 1 c.c. at first. After each addition, shake the flask vigorously for about a quarter of a minute. As soon as a lather is produced, lay the flask on its side after each addition, and observe if the lather remains permanent for five minutes. To ascertain this, at the end of five minutes roll the flask half-way round; if the lather breaks instead of covering the whole surface of the water, it is not permanent; if it still covers the whole surface it is permanent: now read the burette.

Repeat the experiment, adding gradually the quantity of soap solution employed in the first experiment, less about 2 c.c. or 2 dm.; shake as before, add soap solution very gradually till the permanent lather is formed: read the burette, and take out the corresponding hardness from the table. If magnesian salts are present in the water the character of the lather will be very much modified, and a kind of scum (simulating a lather) will be seen in the water before the reaction is completed. The character of this scum must be carefully watched, and the soap test added more carefully, with an increased amount of shaking between each addition. With this precaution it will be comparatively easy to distinguish the point when the false lather due to the magnesian salts ceases, and the true persistent lather is produced.

If the water is of more than 16° of hardness, mix 50 c.c. or dm. of the sample with an equal volume of recently boiled distilled water which has been cooled in a closed vessel, and make the determination on this mixture of the sample and distilled water. In this case it will, of course, be necessary to multiply the figures obtained from the table by 2.

To determine the hardness after boiling, boil a measured quantity of the water in a flask briskly for half an hour, adding distilled water from time to time to make up for loss by evaporation. It is not desirable to boil the water under a vertical condenser, as the dissolved carbonic acid is not so freely liberated. At the end of half an hour, allow the water to cool, the mouth of the flask being closed; make the water up to its original volume with recently boiled distilled water, and, if possible, decant the quantity necessary for testing. If this cannot be done quite clear, it must be filtered. Conduct the test in the same manner as described above.

The hardness is be returned in each case to the nearest half-degree.

**Total Solid Matters.**—Evaporate 250 c.c. or $\frac{1}{20}$th of a gallon, in a weighed platinum dish on a water bath; dry the residue at 220° F. (104° C.), and cool under a desiccator. Weigh the dish containing the residue accurately, and note its colour and appearance, and especially whether it rapidly increases in weight. Return to the water bath for half an hour and re-weigh until it ceases to lose weight, then gradually heat it to redness, and note the changes which take place during this ignition. Especially among these changes should be observed the smell, scintillation, change of colour, separation of more or less carbon, and partial fusion, if any. The ignited residue is to be used for the estimation of phosphoric acid, as before directed.

**Microscopical Examination of Deposit.**—The most convenient plan of collecting the deposit is to place a circular microscopical covering glass at the bottom of a large conical glass holding about 20 oz. The glass should have no spout, and should be ground smooth on the top. After shaking up the sample, this vessel is filled with the water, covered with a plate of ground glass, and set aside to settle. After settling, the supernatant water is drawn off by a fine syphon, and the glass bearing the deposit lifted out, either by means of a platinum wire (which should have been previously passed under it), or in some other convenient way, and inverted on to an ordinary microscopical slide for examination. It is desirable to examine the deposit first by a $\frac{1}{6}$th and then by a $\frac{1}{8}$th objective. The examination should be made as soon as the water has stood overnight. If the water be allowed to stand longer, organisms peculiar to stagnant water may be developed and mislead the observer. Particular notice should be taken of bacteria, infusoria, ciliata or flagellata, disintegrated fibres of cotton, or linen, or epithelial *débris*.

It is particularly desirable to report clearly on this microscopical examination; not merely giving the general fact that organisms were present, but stating as specifically as possible the names or classes of the organisms, so that more data may be obtained for the application of the examination of this deposit to the characters of potable waters.

It is also desirable to examine the residue left on a glass slide by the evaporation of a single drop of the water. This residue is generally most conveniently examined without a covering glass. The special appearances to be noticed are the presence or absence of particles of organic matter, or organized structure, contained in the crystallized forms which may be seen; and also whether any part of the residue left, especially at the edges, is tinted more or less with green, brown, or yellow.

In connection with the microscopical examination it may be desirable to adopt Heisch's sugar process as follows:—

**Sugar Test.**—The name of this process relates simply to the re-agent which is used; namely, pure crystallized sugar. It is believed to be a test for the presence of the germs or spores of the sewage fungus. This special form of fungus grows very rapidly in water containing even a small admixture of sewage water, especially if sugar be present. It grows as well in a closed bottle of the liquid being tested, as in water exposed to the air, and even better in an atmosphere of carbonic acid.

To apply the test:—Take a 5-oz. stoppered flask which has been thoroughly cleaned and rinsed with the water to be tested. Fill with the water to be examined, add about 10 grn., or say, 0·5 gm. of crystals of pure sugar, insert the stopper, and put the flask in a good light; keep it at a temperature of as nearly as possible 80° F. (27° C.). The water should be free from suspended matters before the experiment is made.

The flask must be carefully examined after two or three hours, and again if necessary at intervals. The fungus appears first in the form of minute floating white specks, which are generally easily visible to the naked eye in a good side-light when the flask is looked at against a black background. A pocket lens may sometimes be used with advantage.

If any suspected speck is seen it must be caught by a fine pipette and transferred to a glass slide, covered, and examined with a ¼th objective.

When first seen, these specks are found to consist of small isolated cells with a bright nucleus. In the second stage the form resembles a bunch of grapes. The bright nucleus is still seen. This second stage generally takes not more than four to six hours for full development. A few hours after the second stage has become clear, the cells assume the form of moniliform threads. After this they assume the form of ordinary mycelium, with sparsely diffused cells. Finally the cells disappear and leave only ordinary mycelium.

When the proportion of sewage is large, it is often accompanied by a distinct smell of butyric acid.

A few experiments on mixtures of small proportions of sewage matter with water will give sufficient data to enable this peculiar fungus to be readily recognized.

## OXYGEN DISSOLVED IN WATERS.

§ 92. THE necessary apparatus and standard solutions for carrying out this estimation are described in § 68 (page 230), together with the methods of manipulation.*

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* The statement on page 230 that Schützenberger's process had been little used in England I now find to be incorrect. It has been long in use by Dr. Tidy in his examination of potable waters.

The interpretation of the results as regards polluted waters, as given by Dupré, may be summarized as follows:—

The method depends on the fact that, if a perfectly pure water is once fully aërated, and then kept in a bottle so that it could neither lose nor gain oxygen, it would remain fully aërated for any length of time; but, on the other hand, if the water contained living organic matters capable of absorbing oxygen, such water would after a period of time contain less oxygen, the loss so found being taken as the measure of impurity. The method is really another form of ascertaining the presence of germs and their amount in contrast to the method of cultivation by gelatine and microscopic analysis.

The practical results from various experiments made by Dupré, and reported by him to the Medical Department of the Local Government Board, 1884, are as follows:—

(1) A water which does not diminish in its degree of aëration during a given period of time, may or may not contain organic matter, but presumably does not contain growing organisms. Such organic matter therefore as it may be found to contain by chemical analysis (permanganate or otherwise) need not be considered as dangerous impurity.

(2) A water which by itself, or after the addition of gelatine or other appropriate cultivating matter, consumes oxygen from the dissolved air at lower temperatures, but does not consume any after heating for say three hours at 60° C., may be regarded as having contained living organisms, but none of a kind able to survive exposure to that temperature.

(3) A water which by itself, or after addition of gelatine or the like, continues to absorb oxygen from its contained air after heating to 60° C, may be taken as containing spores or germs able to survive that temperature.

The exact nature of organisms differing in this way is of course not revealed by the method. Dupré's conclusion is, that in the vast majority of cases the consumption of oxygen from the dissolved air of a natural water is due to growing organisms, and that in the complete absence of such organisms little or no oxygen would be then consumed.

The paper is accompanied by tables of results of analysis by this and other methods, which are too voluminous to insert here.

*Principle of the method.*—A water, fully aërated, contains at 20° C. and 760 m.m. pressure 0·594 grain of oxygen per gallon, or 0·04158 gm. per liter. The proportion varies with the temperature and pressure. The formula given by Bunsen is adopted in this method—

$$\alpha = 2{\cdot}0225\,\beta\text{; and }\beta = 0{\cdot}020346 - 0{\cdot}00052887t + 0{\cdot}000011156t^2\text{;}$$

where $\alpha$ is the co-efficient of absorption of oxygen in cubic centimeters, $\beta$ the co-efficient for absorption of nitrogen, and $t$ the temperature.

The variation due to atmospheric pressure is so slight that it may practically be disregarded. The composition of air is taken as 21 volumes oxygen and 79 nitrogen. Dupré adopts the temperature of 20° C. for all waters under experiment; and as a rule the samples were all placed in an appropriate bottle, and kept at a constant temperature of 20° C. for ten days previous to the estimation of the oxygen.

The maximum degree of oxygen which a pure water should contain at this temperature is called 100, and any less degree found on analysis is recorded as a percentage of this maximum.

*The Analysis.*—The sample of water is placed in an ordinary bottle, and vigorously shaken to ensure full aëration; after standing the requisite time it is poured into the experimental bottle, and the estimation of oxygen carried out as described in § 68.

### Calculation of the Results of Water Analysis.

| Substance estimated. | Measure of water taken. | Volume or weight obtained or used. | Factor for grains per gallon. |
|---|---|---|---|
| Cl . . . | 100 c.c. or dm. . | c.c. or dm. standard $AgNO^3$ | × 0·7 = Cl |
| ,, . . . | 140 dm. ($\frac{1}{50}$-gal.) | dm. ,, ,, ,, | × 0·5 = Cl |
| N as $HNO^3$ (Crum) | 250 c.c. . . | c.c. of NO | × 0·175 = N |
| | 250 dm. . . | ,, ,, | × 0·27 = N |
| | 350 dm. ($\frac{1}{20}$-gal.) | ,, ,, | × 0·193 = N |
| $NH^3$ copper-zinc or aluminium | 100 c.c. . . | grams of $NH^3$ | × 576·45 = N |
| | 50 c.c. . . | ,, ,, | × 1152·9 = N |
| | 150 dm. . . | grains of $NH^3$ | × 38·43 = N |
| | 100 dm. . . | ,, ,, | × 57·64 = N |
| Free or Alb. $NH^3$ | 500 c.c. . . | c.c. standard $NH^4Cl$ | × 0·0014 = $NH^3$ |
| ,, ,, ,, | 700 dm. . . | dm. ,, ,, ,, | × 0·01 = $NH^3$ |
| O absorbed . . | 250 c.c. . . | 10, 15, or 20 c.c. permanganate | × 0·28 (1 or 1·5 or $2-\frac{B}{A}$*) = O |
| ,, ,, ,, | 350 dm. . . | 10, 15, or 20 dm. permanganate | × 0·02 (1 or 1·5 or $2-\frac{B}{A}$*) = O |
| Total solids . . | 250 c.c. . . | grams | × 280·0 |
| ,, ,, | 350 dm. . . | grains | × 20·0 |

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* A = c.c. or dm. of thiosulphate solution corresponding to 10 c.c. or dm. of permanganate. B = c.c. or dm. of thiosulphate solution used after the time of reaction is complete.

# PART VII.

# VOLUMETRIC ANALYSIS OF GASES.

## Description of the necessary Apparatus, with Instructions for Preparing, Etching, Graduating, etc.

§ 93. This branch of chemical analysis, on account of its extreme accuracy, and in consequence of the possibility of its application to the analysis of carbonates, and of many other bodies from which gases may be obtained, deserves more attention than it has generally received, in this country at least. It will, therefore, be advisable to devote some considerable space to the consideration of the subject.

For an historical sketch of the progress of gas analysis, the reader is referred to Dr. Frankland's article in the *Handwörterbuch der Chemie*, and more complete details of the process than it will be necessary to give here will be found in that article; also in Bunsen's *Gasometry*, and in Dr. Russell's contributions to Watt's *Chemical Dictionary*.

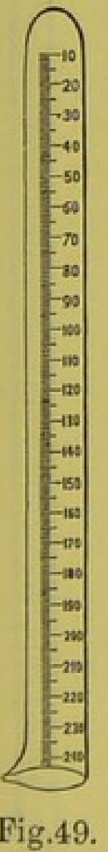


Fig.49.

The apparatus employed by Bunsen, who was the first successfully to work out the processes of gas analysis, is very simple. Two tubes, the absorption tube and the eudiometer, are used, in which the measurement and analysis of the gases are performed. The first of these tubes is about 250 m.m. long and 20 m.m. in diameter, closed at one end, and with a lip at one side of the open extremity, to facilitate the transference of the gas from the absorption tube (fig. 49) to the eudiometer (fig. 50). The eudiometer has a length of from 500 to 800 m.m., and a diameter of 20 m.m. Into the closed end two platinum wires are sealed, so as to enable the operator to pass an electric spark through any gas which the tube may contain. The mode of sealing in the platinum wires is as follows:—When the end of the tube is closed, and while still hot, a finely pointed blowpipe flame is directed against the side of the tube at the base of the hemispherical end. When the glass is soft, a piece of white-hot platinum wire is pressed against it and rapidly drawn away. By this means a small conical tube is produced. This operation is then repeated on the opposite side (fig. 51). One of the conical tubes is next cut off near to the eudiometer, so as to leave a small orifice (fig. 52), through which a piece of the moderately thin platinum wire, reaching about two-thirds across the tube, is passed. The fine blow-pipe flame is now brought to play on the wire at the point where it enters the tube; the glass rapidly fuses round the wire, making a perfectly gas-tight joint. If it should be observed that the tube has any tendency to collapse during the heating, it will be necessary to blow gently into the open end of the tube. This may be conveniently done by means of a long piece of caoutchouc connector, attached to the eudiometer, which enables the operator to watch the effect of the blowing more easily than if the mouth were applied directly to the tube. When a perfect fusion of the glass round the wire has been effected, the point on the opposite side is cut off, and a second wire sealed in in the same manner (fig. 53). The end of the tube must be allowed to cool very slowly; if proper attention is not paid to this, fracture is very liable to ensue. When perfectly cold, a piece of wood with a rounded end is passed up the eudiometer, and the two wires carefully pressed against the end of the tube, so as to lie in contact with the glass, with a space of 1 or 2 m.m. between their points (fig. 54). It is for this purpose that the wires, when sealed in, are made to reach so far across the tube. The ends of the wires projecting outside the tube are then bent into loops. These loops must be carefully treated, for if frequently bent they are very apt to break off close to the glass; besides this, the bending of the wire sometimes causes a minute crack in the glass, which may spread and endanger the safety of the tube. These difficulties may be overcome by cutting off the wire close to the glass, and carefully smoothing the ends by rubbing them with a piece of ground glass until they are level with the surface of the tube (fig. 55). In order to make contact with the induction coil, a wooden American paper-clip, lined with platinum foil, is made to grasp the tube; the foil is connected with two strong loops of platinum wire, and to these the wires from the coil are attached (fig. 56). In this way no strain is put on the eudiometer wires by the weight of the wires from the coil, and perfect contact is ensured between the foil and platinum wires. It is also easy to clean the outside of the eudiometer without fear of injuring the instrument.

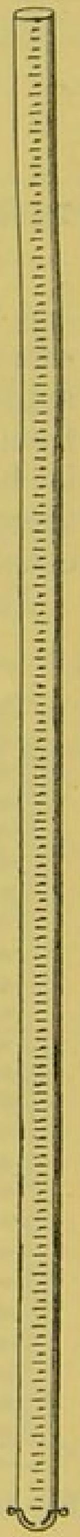


Fig. 50.

It will now be necessary to examine if the glass is perfectly fused to the wires. For this purpose the eudiometer is filled with mercury, and inverted in the trough. If the tube has 800 m.m. divisions, a vacuous space will be formed in the upper end. Note the height of the mercury, and if this remains constant for a while the wires are properly sealed. Should the eudiometer be short, hold it in the hands, and bring it down with a quick movement upon the edge of the india-rubber cushion at the bottom of the trough, taking care that the force of impact is slight, else the mercury may fracture the sealed end of the tube. By jerking the eudiometer thus, a momentary vacuum is formed, and if there is any leakage, small bubbles of air will arise from the junction of the wires with the glass.

Fig. 51.

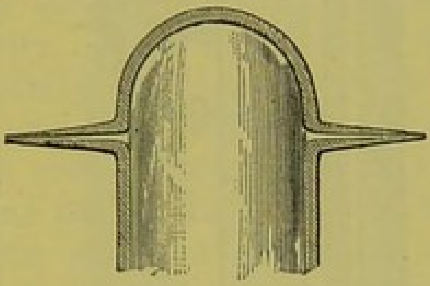
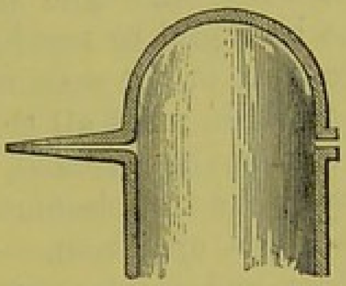


Fig. 52.



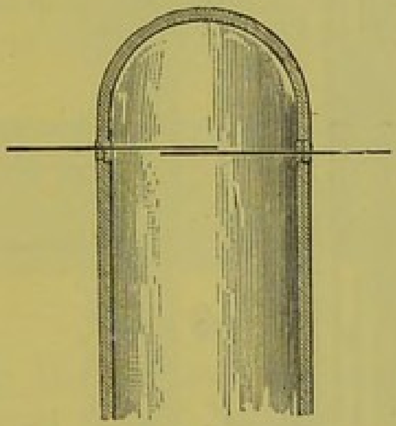


Fig. 53.

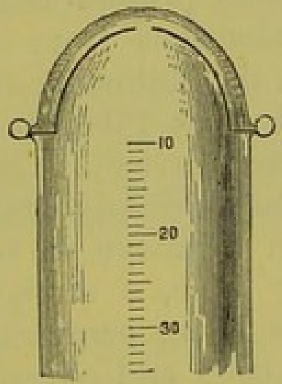


Fig. 54.

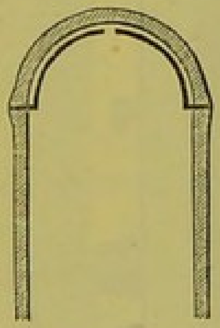


Fig. 55.

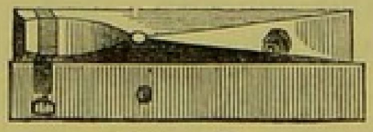


Fig. 56.

The tubes are graduated by the following processes:—A cork is fitted into the end of the tube, and a piece of stick, a file, or anything that will make a convenient handle, is thrust into the cork. The tube is heated over a charcoal fire or combustion furnace, and coated with melted wax by means of a camel's-hair brush. Sometimes a few drops of turpentine are mixed with the wax to render it less brittle, but this is not always necessary. If, on cooling it should be found that the layer of wax is not uniform, the tube may be placed in a perpendicular position before a fire and slowly rotated so as to heat it evenly. The wax will then be evenly distributed on the surface of the glass, the excess flowing off. The tube must not be raised to too high a temperature, or the wax may become too thin; but all thick masses should be avoided, as they may prove troublesome in the subsequent operation.

The best and most accurate mode of marking the millimeter divisions on the wax is by a graduating machine; but the more usual process is to copy the graduations from another tube in the following manner. A hard glass tube, on which millimeter divisions have already been deeply etched, is fixed in a groove in the graduating table, a straight-edge of brass being screwed down on the tube and covering the ends of the lines. The standard tube is shown in the figure at the right-hand end of the apparatus (fig. 57). The waxed tube is secured at the other end of the same groove, and above it are fixed two brass plates, one with a straight-edge, and the other with notches at intervals of 5 m.m., the alternate notches being longer than the intermediate ones (fig. 58). A stout rod of wood provided with a sharp steel point near one end, and a penknife blade at the other (fig. 59), is held so that the steel point rests in one of the

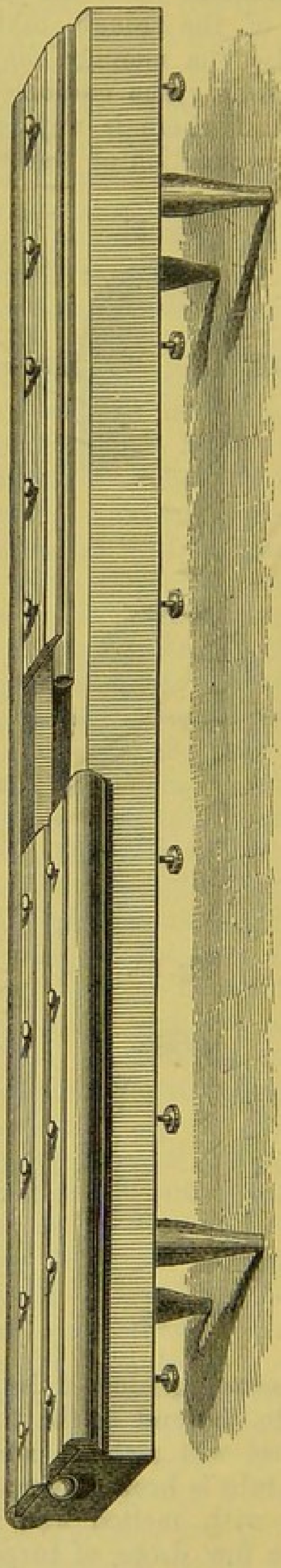


Fig. 57.

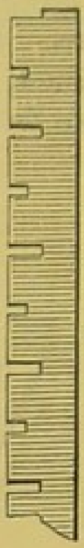


Fig. 58.

Fig. 59.

divisions of the graduated tube, being gently pressed at the same time against the edge of the brass plate; the point of the knife-blade is then moved by the operator's right hand across the portion of the waxed tube which lies exposed between the two brass plates. When the line has been scratched on the wax, the point is moved along the tube until it falls into the next division; another line is now scratched on the wax, and so on. At every fifth division the knife-blade will enter the notches in the brass plate, making a longer line on the tube. After a little practice it will be found easy to do fifty or sixty divisions in a minute, and with perfect regularity. Before the tube is removed from the apparatus, it must be carefully examined to see if any mistake has been made. It may have happened that during the graduation the steel point slipped out of one of the divisions in the standard tube; if this has taken place, it will be found that the distance between the line made at that time and those on each side of it will not be equal, or a crooked or double line may have been produced. This is easily obliterated by touching the wax with a piece of heated platinum wire, after which another line is marked. The tube is now taken out of the table, and once more examined. If any portions of wax have been scraped off by the edges of the apparatus, or by the screws, the coating must be repaired with the hot platinum wire. Numbers have next to be marked opposite each tenth division, beginning from the closed end of the tube, the first division, which should be about 10 m.m. from the end, being marked 10 (see fig. 54). The figures may be well made with a steel pen. This has the advantage of producing a double line when the nib is pressed against the tube in making a down-stroke. The date, the name of the maker of the tube, or its number, may now be written on the tube.

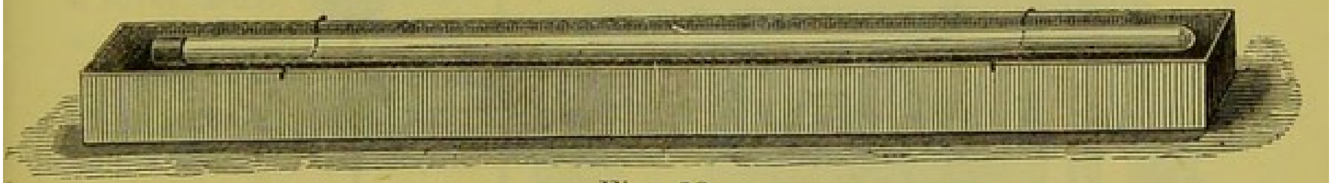


Fig. 60.

The etching by gaseous hydrofluoric acid is performed by supporting the tube by two pieces of wire over a long narrow leaden trough containing sulphuric acid and powdered fluor-spar (fig. 60), and the whole covered with a cloth or sheet of paper. Of course it is necessary to leave the cork in the end of the tube to prevent the access of hydrofluoric acid to the interior, which might cause the tube to lose its transparency to a considerable extent. The time required for the action of the gas varies with the kind of glass employed. With ordinary flint glass from ten minutes to half an hour is quite sufficient; if the leaden trough is heated, the action may take place even still more rapidly. The tube is removed from time to time, and a small portion of the wax scraped off from a part of one of the lines; and if the division can be felt with the finger-nail or the point of a knife, the operation is finished; if not, the wax must be replaced, and the tube restored to the trough. When sufficiently etched, the tube is washed with water, heated before a fire, and the wax wiped off with a warm cloth.

The etching may also be effected with liquid hydrofluoric acid, by applying it to the divisions on the waxed tube with a brush, or by placing the eudiometer in a gutta-percha tube closed at one end, and containing some of the liquid.

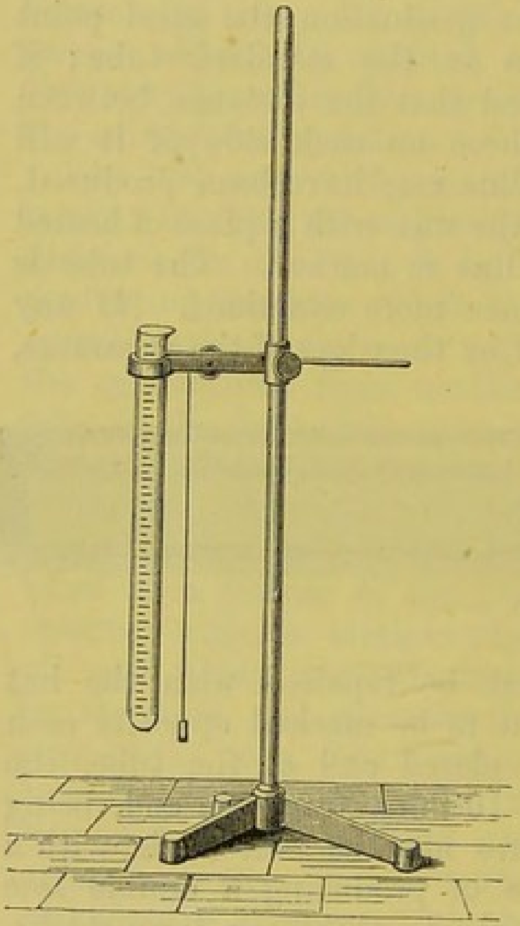


Fig. 61.

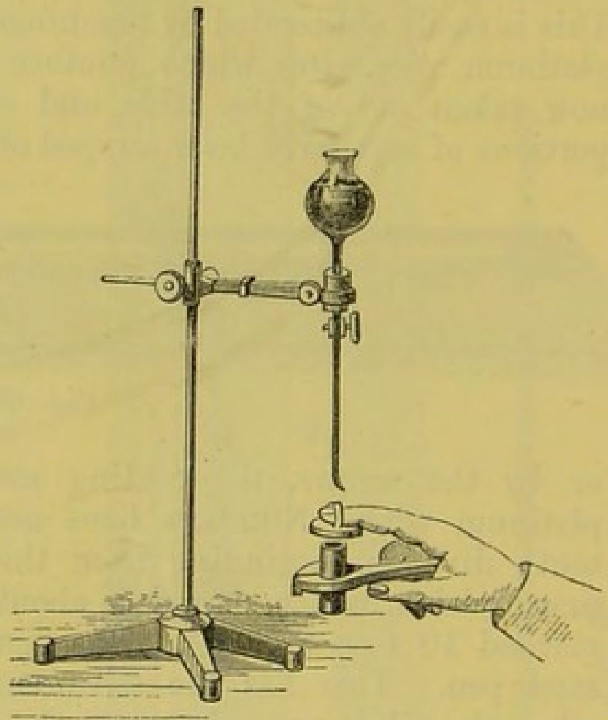


Fig. 62.

As all glass tubes are liable to certain irregularities of diameter, it follows that equal lengths of a graduated glass tube will not contain exactly equal volumes; hence it is, of course, impossible to obtain by measurement of length the capacity of the closed end of the tube.

In order to provide for this, the tube must be carefully calibrated. For this purpose it is supported vertically (fig. 61), and successive quantities of mercury poured in from a measure. This measure should contain about as much mercury as ten or twenty divisions of the eudiometer, and is made of a piece of thick glass tube, closed at one end, and with the edges of the open end ground perfectly flat. The tube is fixed into a piece of wood in order to avoid heating its contents during the manipulation. The measure may be filled with mercury from a vessel closed with a stop-cock terminating in a narrow vertical tube, which is passed to the bottom of the measure (fig. 62). On carefully opening the stop-cock the mercury flows into the measure without leaving any air-bubbles adhering to the sides. A glass plate is now pressed on the ground edges of the tube, which expels the excess of mercury and leaves the measure entirely filled. The mercury may be introduced into the measure in a manner which is simpler and as effectual, though perhaps not quite so convenient, by first closing it with a glass plate, and depressing it in the mercurial trough, removing the plate from the tube, and again replacing it before raising the measure above the surface of the mercury. After pouring each measured quantity of mercury into the eudiometer, the air-bubbles are carefully detached from the sides by means of a thin wooden rod or piece of whalebone, and the level of the mercury at the highest part of the curved surface carefully observed.

In all measurements in gas analysis it is, of course, essential that the eye should be exactly on a level with the surface of the mercury, for the parallax ensuing if this were not the case would produce grave errors in the readings. The placing of the eye in the proper position may be ensured in two ways. A small piece of looking-glass (the back of which is painted, or covered with paper to prevent the accidental soiling of the mercury in the trough) is placed behind, and in contact with the eudiometer. The head is now placed in such a position that the reflection of the pupil of the eye is precisely on a level with the surface of the mercury in the tube, and the measurement made. As this process necessitates the hand of the operator being placed near the eudiometer, which might cause the warming of the tube, it is preferable to read off with a telescope placed at a distance of from two to six feet from the eudiometer. The telescope is fixed on a stand in a horizontal position, and the support is made to slide on a vertical rod. The image of the surface of the mercury is brought to the centre of the field of the telescope, indicated by the cross wires in the eye-piece, and the reading taken. The telescope has the advantage of

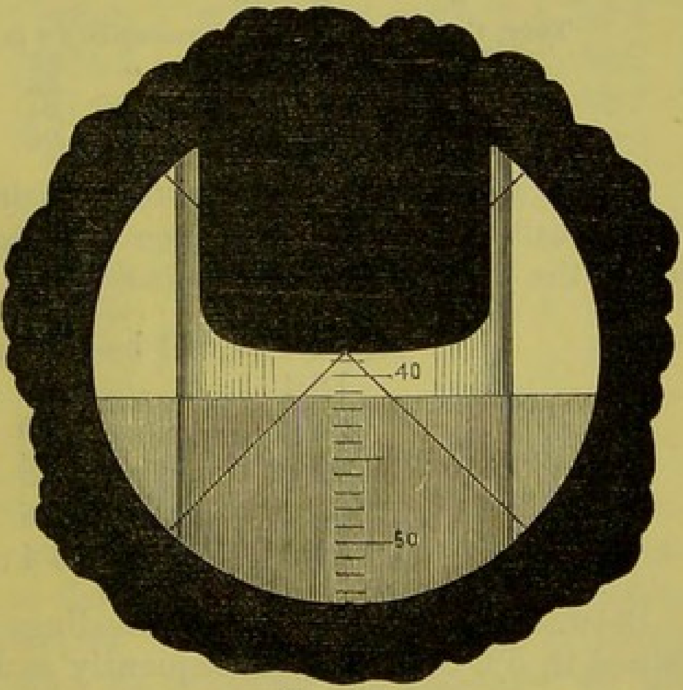


Fig. 63.

magnifying the graduations, and thus facilitating the estimation by the eye of tenths of the divisions. Fig. 63 represents the appearance of the tube and mercury as seen by an inverting telescope.

By this method the capacity of the tube at different parts of its length is determined. If the tube were of uniform bore, each measure of mercury would occupy the same length in the tube ; but as this is never the case, the value of the divisions at all parts of the tube will not be found to be the same.

From the data obtained by measuring the space in the tube which is occupied by equal volumes of mercury, a table is constructed by which the comparative values of each millimeter of the tube can be found. The following results were obtained in the calibration of a short absorption eudiometer :—

On the introduction of the 3rd volume of mercury, the reading was 12·8 m.m.
,, ,, ,, 4th ,, ,, 18·4
,, ,, ,, 5th ,, ,, 24·0
,, ,, ,, 6th ,, ,, 29·8
,, ,, ,, 7th ,, ,, 35·2
,, ,, ,, 8th ,, ,, 41·0

Thus, the standard volumes occupied 5·6 m.m., between 12·8 and 18·4
,, ,, ,, 5·6 ,, 18·4 ,, 24·0
,, ,, ,, 5·8 ,, 24·0 ,, 29·8
,, ,, ,, 5·4 ,, 29·8 ,, 35·2
,, ,, ,, 5·8 ,, 35·2 ,, 41·0

If we assume the measure of mercury to contain 5·8 volumes (the greatest difference between two consecutive readings on the tube), the volume at the six points above given will be as follows :—

At 12·8 it will be 17·4 or 5·8 × 3
18·4 ,, 23·2 ,, 5·8 × 4
24·0 ,, 29·0 ,, 5·8 × 5
29·8 ,, 34·8 ,, 5·8 × 6
35·2 ,, 40·6 ,, 5·8 × 7
41·0 ,, 46·4 ,, 5·8 × 8

Between the first and second readings these 5·8 volumes are contained in 5·6 divisions, consequently each millimeter corresponds to $\frac{5·8}{5·6}=1·0357$ vol. This is also the value of the divisions between the second and third readings. Between the third and fourth 1 m.m. contains 1 vol. ; between the fourth and fifth, 1 m.m. contains $\frac{5·8}{5·4}=1·0741$ vol. ; and between the fifth and sixth m.m. = 1 vol.

From these data the value of each millimeter on the tube can readily be calculated. Thus 13 will contain the value of 12·8 + the value of 0·2 of a division at this part of the tube, or 17·4 + (1·0357 × 0·2) = 17·60714. There is, however, no need to go beyond the second place of decimals, and, for all practical purposes, the first place is sufficient. Thus, by adding or subtracting the necessary volumes from the experimental numbers, we find the values of the divisions nearest to the six points at which the readings were taken, to be—

13=17·61 or 17·6
18=22·79 ,, 22·8
24=29·00 ,, 29·0
30=35·00 ,, 35·0
35=40·38 ,, 40·4
41=46·40 ,, 46·4

In a precisely similar manner the values of the intermediate divisions are calculated, and we thus obtain the following table :—

| Readings. | Values. | | Readings. | Values. | | Readings. | Values. | |
|---|---|---|---|---|---|---|---|---|
| 10 | 14·50 | 14·5 | 21 | 25·89 | 25·9 | 32 | 37·15 | 37·1 |
| 11 | 15·54 | 15·5 | 22 | 26·93 | 26·9 | 33 | 38·22 | 38·2 |
| 12 | 16·57 | 16·6 | 23 | 27·96 | 28·0 | 34 | 39·30 | 39·3 |
| 13 | 17·61 | 17·6 | 24 | 29·00 | 29·0 | 35 | 40·38 | 40·4 |
| 14 | 18·65 | 18·6 | 25 | 30·00 | 30·0 | 36 | 41·40 | 41·4 |
| 15 | 19·68 | 19·7 | 26 | 31·00 | 31·0 | 37 | 42·40 | 42·4 |
| 16 | 20·71 | 20·7 | 27 | 32·00 | 32·0 | 38 | 43·40 | 43·4 |
| 17 | 21·75 | 21·8 | 28 | 33·00 | 33·0 | 39 | 44·40 | 44·4 |
| 18 | 22·79 | 22·8 | 29 | 34·00 | 34·0 | 40 | 45·40 | 45·4 |
| 19 | 23·82 | 23·8 | 30 | 35·00 | 35·0 | 41 | 46·40 | 46·4 |
| 20 | 24·86 | 24·9 | 31 | 36·07 | 36·1 | &c. | &c. | &c. |

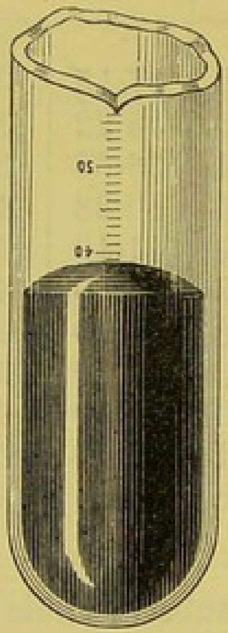
If it be desired to obtain the capacity of the tube in cubic centimeters, it is only necessary to determine the weight of the quantity of mercury the measure delivers, and the temperature at which the calibration was made, and to calculate the contents by the following formula :—

$$C = \frac{g \times (1 + 0{\cdot}0001815t)}{13{\cdot}596V}$$

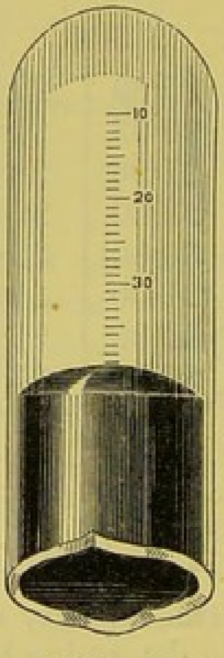
in which $g$ represents the weight of the mercury contained in the measure, $t$ the temperature at which the calibration is made, 0·0001815 being the coefficient of expansion of mercury for each degree centigrade, V the volume read off in the eudiometer, and C the number of cubic centimeters required.

A correction has to be made to every number in the table on account of the surface of the mercury assuming a convex form in the tube. During the calibration, the convexity of the mercury is turned towards the open end of the tube (fig. 64), whilst in the measurement of a gas the convexity will be in the opposite direction (fig. 65). It is obvious that the quantity of mercury measured during the calibration, while the eudiometer is inverted, will be less than a volume of gas contained in the tube when the mercury stands at the same division, while the eudiometer is erect. The necessary amount of correction is determined by observing the position of the top of the meniscus, and then introducing a few drops of a solution of corrosive sublimate, which will immediately cause the surface of the mercury to become horizontal (fig. 66), and again measuring.

It will be observed that in fig. 65 the top of the meniscus was at the division 39, whereas in fig. 66, after the addition of corrosive sublimate, the horizontal surface of the mercury stands at 38·7, giving a depression of 0·3 m.m. If the tube were now placed erect, and gas introduced so that the top of the meniscus was at 39, and if it were now possible to overcome the capillarity, the horizontal surface would stand at 39·3. The small cylinder of gas between 38·7 and 39·3, or 0·6 division, would thus escape measurement. This number 0·6 is therefore called the *error of meniscus*, and must be added to all readings of gas in the eudiometer. The difference, therefore, between the two readings is multiplied by two, and the volume represented by the product obtained—the *error of meniscus* —is added to the measurements before finding the corresponding capacities by the table. In the case of the tube, of which the calibration is given above, the difference between the two readings was 0·4 m.m., making the error of meniscus 0·8.



* Fig. 64.



* Fig. 65.

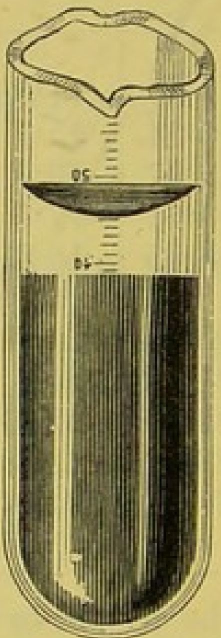


Fig. 66.

All experiments on gas analysis, with the apparatus described,

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* In these the mercury should just touch 39.

should be conducted in a room set apart for the purpose, with the window facing the north, so that the sun's rays cannot penetrate into it, and carefully protected from flues or any source of heat which might cause a change of temperature of the atmosphere. The mercury employed should be purified, as far as possible, from lead and tin, which may be done by leaving it in contact with dilute nitric acid in a shallow vessel for some time, or by keeping it when out of use under concentrated sulphuric acid, to which some mercurous sulphate has been added. This mercury reservoir may conveniently be made of a glass globe with a neck at the top and a stop-cock at the bottom (fig. 67), and which is not filled more than one-half, so as to maintain as large a surface as possible in contact with the sulphuric acid. Any foreign metals (with the exception of silver, gold, and platinum) which may be present are removed by the mercurous sulphate, an equivalent quantity of mercury being precipitated. This process, which was originated by M. Deville, has been in use for many years with very satisfactory results, the mercury being always clean and dry when drawn from the stop-cock at the bottom of the globe. The mouth of the globe should be kept close to prevent the absorption of water by the sulphuric acid.

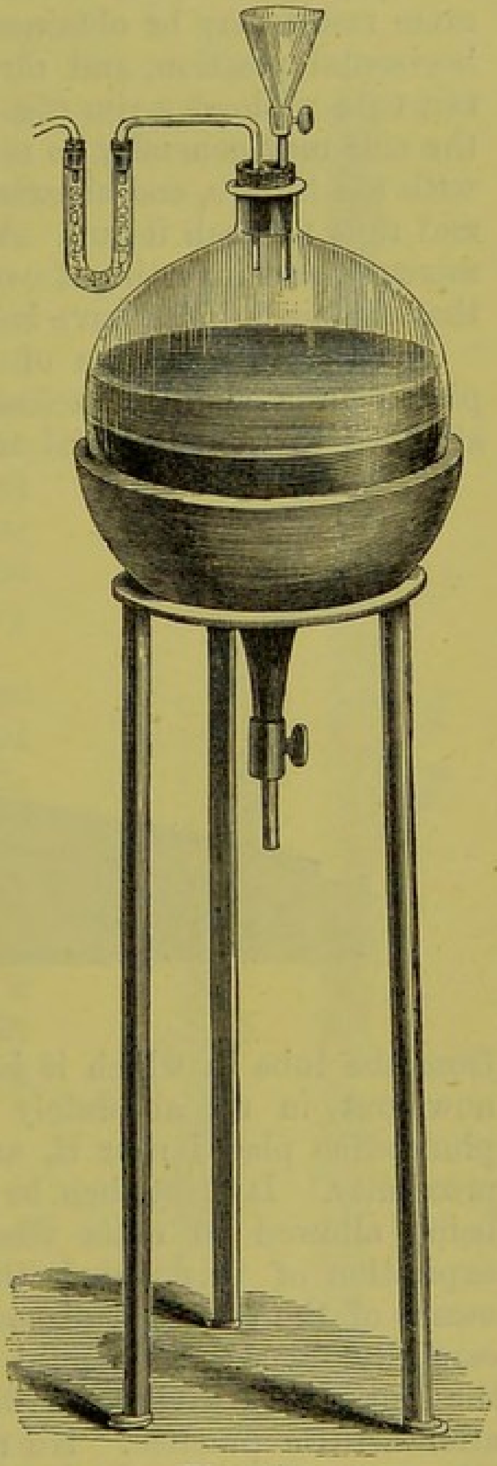

Fig. 67.

In all cases, where practicable, gases should be measured when completely saturated with aqueous vapour: to ensure this, the top of the eudiometer and absorption tubes should be moistened before the introduction of the mercury. This may be done by dipping the end of a piece of iron wire into water, and touching the interior of the closed extremity of the tube with the point of the wire.

In filling the eudiometer, the greatest care must of course be taken to exclude all air-bubbles from the tubes. This may be effected in several ways: the eudiometer may be held in an inverted or inclined position, and the mercury introduced through a narrow glass tube which passes to the end of the eudiometer and communicates, with the intervention of a stop-cock, with a reservoir of mercury (fig. 68). On carefully opening the stop-cock, the mercury slowly flows into the eudiometer, entirely displacing the air. The same result may be obtained by placing the eudiometer nearly in a horizontal position, and carefully introducing the mercury from a test-tube without a rim (fig. 69). Any minute bubbles adhering to the side may generally be removed by closing the mouth of the tube with the thumb, and allowing a small air-bubble to rise in the tube, and thus to wash it out. After filling the eudiometer entirely with mercury, and inverting it over the trough, it will generally be found that the air-bubbles have been removed.

For the introduction of the gases, the eudiometer should be placed in a slightly inclined position, being held by a support attached to the mercurial trough (fig. 70), and the gas transferred from the tube in which it has been collected. The eudiometer is now put in an absolutely vertical position, determined by a plumb-line placed near it, and a thermometer suspended in close proximity. It must then be left for at least half an hour, no one being allowed to enter the room in the meantime. After the expiration of this period, the operator enters the room, and, by means of the telescope placed several feet from the mercury table, carefully observes the height of the mercury in the tube, estimating the tenths of a division with the eye, which can readily be done after a little practice. He next reads the thermometer with the telescope, and finally the height of the mercury in the trough is read off on the tube, for which purpose the trough must have glass sides. The difference between these two numbers is the length of the column of mercury in the eudiometer, and has to be subtracted from the reading of the barometer. It only remains to take the height of the barometer. The most convenient form of instrument for gas analysis is the syphon barometer, with the divisions etched

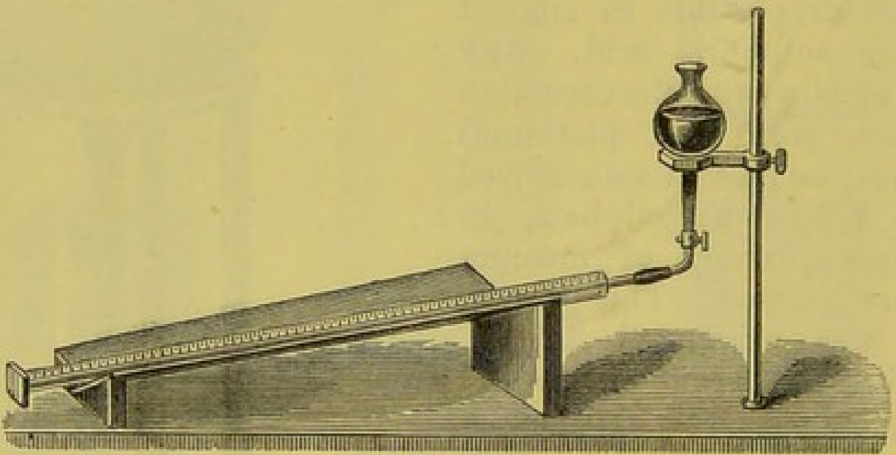
Fig. 68.

on the tube. This is placed on the mercury table, so that it may be read by the telescope immediately after the measurements in the eudiometer. There are two methods of numbering the divisions on the barometer: in one the zero point is at or near the bend of the tube, in which case the height of the lower column must be subtracted from that of the higher; in the other the zero is placed near the middle of the tube, so that the numbers have to be added to obtain the actual height. In cases of extreme accuracy, a correction must be made for the temperature of the barometer, which is determined by a thermometer suspended in the open limb of the instrument, and passing through a plug of cotton wool. Just before observing the height of the barometer, the bulb of the thermometer is depressed for a moment into the mercury in the open limb, thus causing a movement of the mercurial column, which overcomes any tendency that it may have to adhere to the glass.

In every case the volume observed must be reduced to the normal temperature and pressure, in order to render the results comparable. If the absolute volume is required, the normal pressure of 760 m.m. must be employed; but when comparative volumes only are desired, the pressure of 1000 m.m. is generally adopted, as it somewhat simplifies the calculation. In the following formula for correction of the volume of gases—

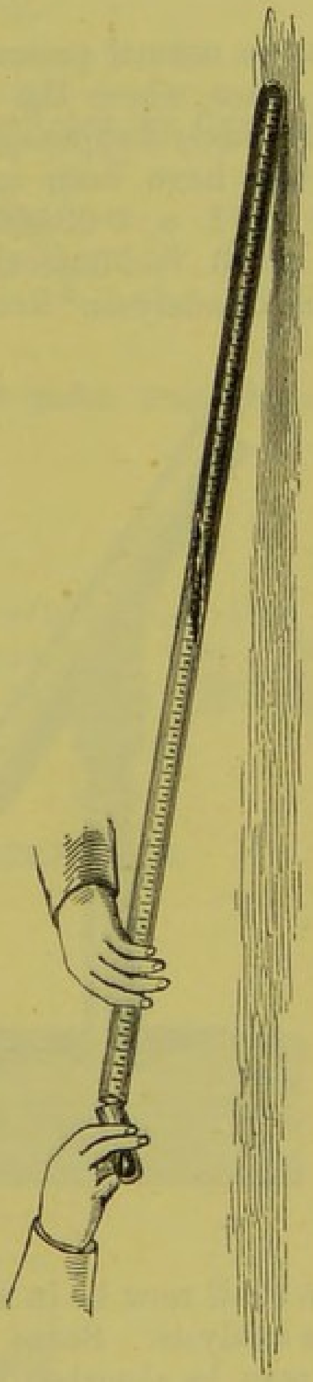

Fig. 69.

$V^1$=the correct volume.

V=the volume found in the table, and corresponding to the observed height of the mercury in the eudiometer, the error of meniscus being, of course, included.

B=the height of the barometer (corrected for temperature, if necessary) at the time of measurement.

$b$=the difference between the height of the mercury in the trough and in the eudiometer.

$t$=the temperature in centigrade degrees.

T=the tension of aqueous vapour in millimeters of mercury at $t°$. This number is, of course, only employed when the gas is saturated with moisture at the time of measurement.

Then

$$V^1 = \frac{V \times (B - b - T)}{760 \times (1 + 0{\cdot}003665t)},$$

when the pressure of 760 m.m. is considered the normal one; or,

$$V = \frac{V \times (B - b - T)}{1000 \times (1 + 0{\cdot}003665t)},$$

when the normal pressure of 1 meter is adopted.

In cases where the temperature at measurement is below 0° (which rarely happens), the factor $1 - 0{\cdot}003665t$ must be used.

Tables have been constructed containing the values of T; of $1000 \times (1 + 0{\cdot}003665t)$, and of $760 \times (1 + 0{\cdot}003665t)$, which very much facilitate the numerous calculations required in this branch of analysis.*

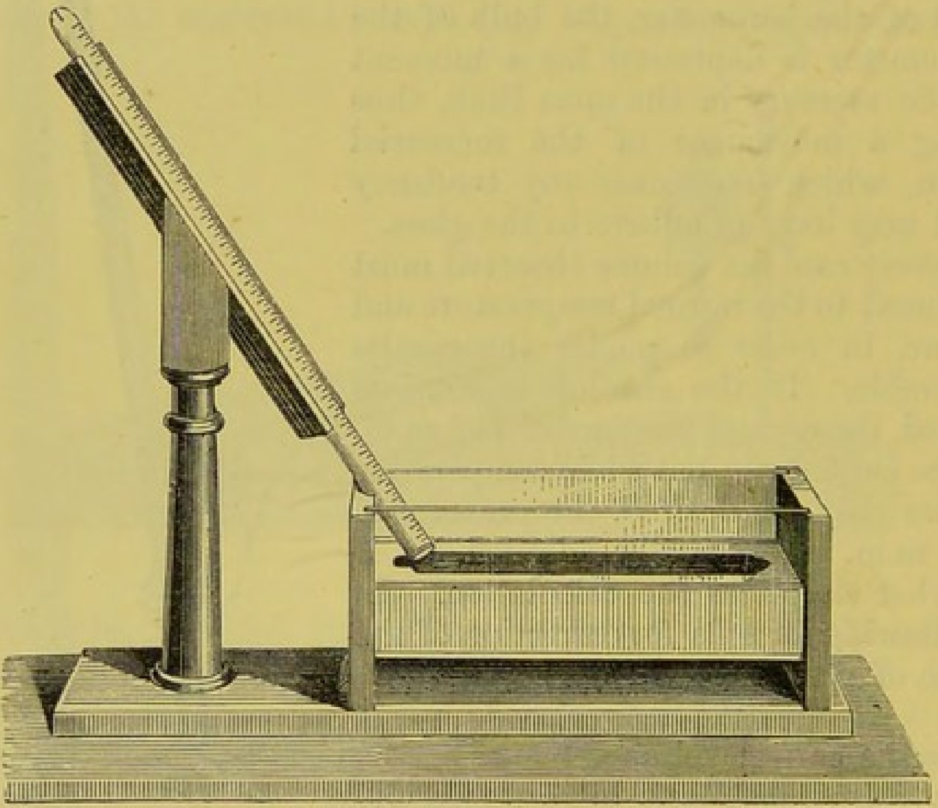

Fig. 70.

We shall now be in a position to examine the methods employed in gas analysis. Some gases may be estimated directly; that is, they may be absorbed by certain re-agents, the diminution of the volume indicating the quantity of the gas present. Some are determined indirectly; that is, by exploding them with other gases, and measuring the quantities of the products. Some gases may be estimated either directly or indirectly, according to the circumstances under which they are found.

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* Mr. Sutton will forward a copy of these Tables, printed separately for laboratory use, to any one desiring them, on receipt of the necessary address.

§ 94.

## 1. GASES ESTIMATED DIRECTLY.

### A. Gases Absorbed by Crystallized Sodic Phosphate and Potassic Hydrate:—

Hydrochloric acid,
Hydrobromic acid,
Hydriodic acid.

### B. Gases Absorbed by Potassic Hydrate, and not by Crystallized Sodic Phosphate:—

Carbonic anhydride,
Sulphurous anhydride,
Hydrosulphuric acid.

### C. Gases Absorbed by neither Crystallized Sodic Phosphate nor Potassic Hydrate:—

Oxygen,
Nitric oxide,
Carbonic oxide,
Hydrocarbons of the composition $Cn\ H^{2}n$,
Hydrocarbons of the formula $(Cn\ H^{2}n+1)^{2}$,
Hydrocarbons of the formula $Cn\ H^{2}n+2$,
except Marsh gas.

## 2. GASES ESTIMATED INDIRECTLY.

Hydrogen,
Carbonic oxide,
Marsh gas,
Methyl,
Ethylic hydride,
Ethyl,
Propylic hydride,
Butylic hydride,
Nitrogen.

## DIRECT ESTIMATIONS.

### Group A, containing Hydrochloric, Hydrobromic, and Hydriodic Acids.

§ 95. In Bunsen's method the re-agents for absorption are generally used in the solid form, in the shape of bullets. To make the bullets of sodic phosphate, the end of a piece of platinum wire, of about one foot in length, is coiled up and fixed in the centre of a pistol-bullet mould. It is well to bend the handles of the mould, so that when it is closed the handles are in contact, and may be fastened together by a piece of copper wire (fig. 71). The usual practice is to place the platinum wire in the hole through which the mould is filled; but it is more convenient to file a small notch in one of the faces of the open mould, and place the wire in the notch before the mould is closed. In this manner the wire is not in the way during the casting, and it is subsequently more easy to trim the bullet. Some ordinary crystallized sodic phosphate is fused in a platinum crucible (or better, in a small piece of wide glass tube, closed at one end, and with a spout at the other, and held by a copper-wire handle), and poured into the bullet mould (fig. 72). When quite cold, the mould is first gently warmed in a gas-flame, opened, and the bullet removed. If the warming of the mould is omitted, the bullet is frequently broken in consequence of its adhering to the metal. Some chemists recommend the use of sodic sulphate instead of phosphate, which may be made into balls by dipping the coiled end of a piece of platinum wire into the salt fused in its water of crystallization. On removing the wire, a small quantity of the salt will remain attached to the wire. When this has solidified, it is again introduced for a moment and a larger quantity will collect; and this is repeated until the ball is sufficiently large. The balls must be quite smooth, in order to prevent the introduction of any air into the eudiometer. When the bullets are made in a mould, it is necessary to remove the short cylinder which is produced by the orifice through which the fused salt has been poured.

Fig. 71.

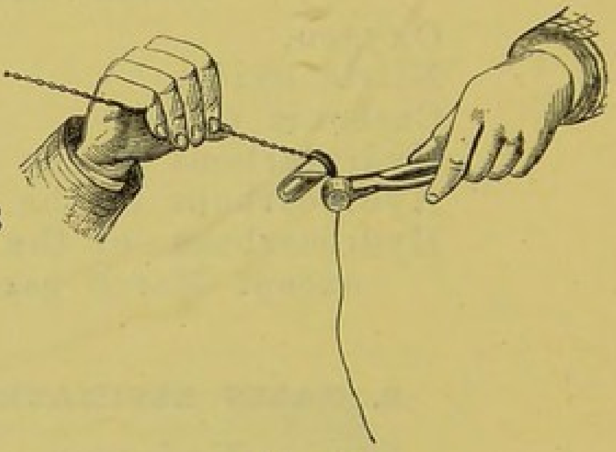

Fig. 72.

In the estimation of these gases, it is necessary that they should be perfectly dry. This may be attained by introducing a bullet of fused calcic chloride. After the lapse of about an hour, the bullet may be removed, the absorption tube placed in a vertical position, with thermometer, etc., arranged for the reading, and left for half an hour to assume the temperature of the air. When the reading has been taken, one of the bullets of sodic phosphate or sodic sulphate is depressed in the trough, wiped with the fingers while under the mercury in order to remove any air that it might have carried down with it, and introduced into the absorption tube, which for this purpose is inclined and held in one hand, while the bullet is passed into the tube with the other. Care must be taken that the whole of the platinum wire is covered with mercury while the bullet remains in the gas, otherwise there is a risk of air entering the tube between the mercury and the wire (fig. 73).

After standing for an hour, the bullet is withdrawn from the absorption tube. This must be done with some precaution, so as to prevent any gas being removed from the tube. It is best done by drawing down the bullet by a brisk movement of the wire, the gas being detached from the bullet during the rapid descent of the latter into the mercury. The bullet may then be more slowly removed from the tube. As sodic phospate and sodic sulphate contain water of crystallization, and a corresponding proportion of this is liberated for every equivalent of sodic chloride formed, care must be taken that the bullets are not too small, else the water set free will soil the sides of the eudiometer, especially if there is a large volume of gas to be absorbed. As a further precaution, drive off some of the water of crystallization before casting the bullet. When the bullet has been removed, the gas must be dried as before with calcic chloride and again measured. If two or more of the gases are present in the mixture to be analyzed, the sodic phosphate ball must be dissolved in water, and the chlorine, bromine, and iodine determined by the ordinary analytical methods. If this has to be done, care must be taken that the sodic phosphate employed is free from chlorine.

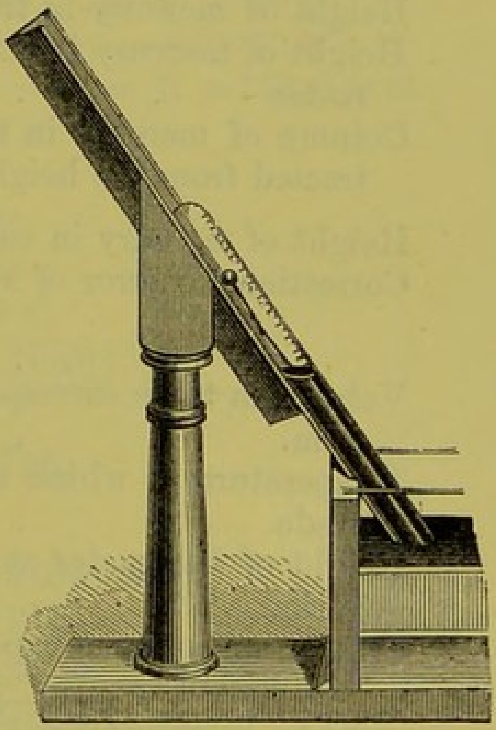
Fig. 73.

### Group B. Gases absorbed by Potassic Hydrate, but not by Sodic Phosphate.

Carbonic anhydride, sulphuretted hydrogen, and sulphurous anhydride.

§ 96. If the gases occur singly, they are determined by means of a bullet of caustic potash made in the same manner as the sodic phosphate balls. The caustic potash employed should contain sufficient water to render the bullets so soft that they may be marked with the nail when cold. Before use the balls must be slightly moistened with water; and if large quantities of gas have to be absorbed, the bullet must be removed after some hours, washed with water, and returned to the absorption tube. The absorption may extend over twelve or eighteen hours. In order to ascertain if it is completed, the potash ball is removed, washed, again introduced, and allowed to remain in contact with the gas for about an hour. If no diminution of volume is observed the operation is finished.

The following analyses of a mixture of air and carbonic anhydride will serve to show the mode of recording the observations and the methods of calculation required.

### Analysis of a Mixture of Air and Carbonic Anhydride.

#### 1. Gas Saturated with Moisture.

Height of mercury in trough . = 171·8 m.m.
Height of mercury in absorption eudiometer . . . = 89·0 m.m.
Column of mercury in tube, to be subtracted from the height of barometer = $b$ = 82·8 m.m.

Height of mercury in eudiometer = 89·0 m.m.
Correction for error of meniscus = 0·8 m.m.
89·8 m.m.

Volume in table corresponding to 89·8 m.m. . . . = V = 96·4
Temperature at which the reading was made . . . = $t$ = 12·2°
Height of barometer at time of observation . . . = B = 765·25 m.m.
Tension of aqueous vapour at 12·2° = T = 10·6 m.m.

$$V^1 = \frac{V \times (B - b - T)}{1000 \times (1 + 0\cdot003665t)} = \frac{96\cdot4 \times (765\cdot25 - 82\cdot8 - 10\cdot6)}{1000 \times [1 + (0\cdot003665 \times 12\cdot2)]} = \frac{96\cdot4 \times 671\cdot85}{1000 \times 1\cdot044713} = 61\cdot994$$

$$\begin{array}{rl} \log.\ 96\cdot4 & = 1\cdot98408 \\ \log.\ 671\cdot85 & = \underline{2\cdot82727} \\ & \phantom{=}\ 4\cdot81135 \\ \log.\ (1000 \times 1\cdot044713) & = \underline{3\cdot01900} \\ & \phantom{=}\ 1\cdot79235 = \log.\ 61\cdot994 = V^1 \end{array}$$

Corrected volume of air and CO$^2$ = $V^1$ = 61·994.

After absorption of carbonic anhydride by bullet of potassic hydrate.

Gas Dry.

Height of mercury in trough . = 172·0 m.m.
Height of mercury in absorption eudiometer . . . = 62·5 m.m.
Column of mercury in eudiometer = $b$ = 109·5 m.m.

Height of mercury in eudiometer = 62·5 m.m.
Correction for error of meniscus = 0·8 m.m.
63·3 m.m.

Volume in table corresponding to 63·3 m.m. . . . = V = 69·35
Temperature . . . = $t$ = 10·8°
Barometer . . . = B = 766·0 m.m.

$$V^1 = \frac{V \times (B - b)}{1000 \times (1 + 0{\cdot}003665t)} =$$

$$\frac{69{\cdot}35 \times (766{\cdot}0 - 109{\cdot}5)}{1000 \times [1 + (0{\cdot}003665 \times 10{\cdot}8)]} =$$

$$\frac{69{\cdot}35 \times 656{\cdot}5}{1000 \times 1{\cdot}039582} = 43{\cdot}795$$

$$\begin{aligned} \log.\ 69{\cdot}35 &= 1{\cdot}84105 \\ \log.\ 656{\cdot}5 &= \underline{2{\cdot}81723} \\ &\phantom{=}\ 4{\cdot}65828 \\ \log.\ (1000 \times 1{\cdot}039582) &= \underline{3{\cdot}01686} \\ &\phantom{=}\ \underline{\underline{1{\cdot}64142}} = \log.\ 43{\cdot}795 = V^1 \end{aligned}$$

Corrected volume of air = 43·795
Air + $CO^2$ = 61·994
Air = 43·795
$CO^2$ = 18·199

61·994 : 18·199 : : 100 : $x$ = percentage of $CO^2$

$$x = \frac{18{\cdot}199 \times 100}{61{\cdot}995} = 29{\cdot}355$$

Percentage of $CO^2$ in mixture of air and gas = 29·355.

Gas Moist.

Height of mercury in trough . = 174·0 m.m.
Height of mercury in eudiometer = 98·0 m.m.
Column of mercury in tube . = $b$ = 76·0 m.m.

Height of mercury in eudiometer = 98·0 m.m.
Correction for error of meniscus = 0·8 m.m.
98·8 m.m.

Volume in table, corresponding to 98·8 m.m. . . . = V = 105·6
Temperature . . . = $t$ = 12·5°
Barometer . . . = B = 738·0 m.m.
Tension of aqueous vapour at 12·5° = T = 10·8 m.m.
Corrected volume of air and carbonic anhydride . . . = 65·754

After absorption of $CO^2$.

Gas Dry.

Height of mercury in trough . = 173·0 m.m.
Height of mercury in absorption eudiometer . . . = 70·3 m.m.
Column of mercury in tube . = $b$ = 102·7 m.m.

Height of mercury in eudiometer = 70·3 m.m.
Correction for error of meniscus = 0·8 m.m.
71·1 m.m.

Volume in table corresponding to 71·1 m.m. . . . = V = 77·4
Temperature . . . = $t$ = 14·1°
Barometer . . . = B = 733·5 m.m.

Corrected volume of air = 46·425
Air + $CO^2$ = 65·754
Air = 46·425
$CO^2$ = 19·329

65·754 : 19·329 : : 100 : 29·396.

| | I. | II. |
|---|---|---|
| Percentage of $CO^2$ in mixture of air and gas | 29·355 | 29·396 |

If either sulphurous anhydride or sulphuretted hydrogen occurs together with carbonic anhydride, one or two modes of operation may be followed. Sulphuretted hydrogen and sulphurous anhydride are absorbed by manganic peroxide and by ferric oxide, which may be formed into bullets in the following manner. The oxides are made into a paste with water, and introduced into a bullet mould, the interior of which has been oiled, and containing the coiled end of a piece of platinum wire; the mould is then placed on a sand-bath till the ball is dry. The oxides will now be left in a porous condition, which would be inadmissible for the purpose to which they are to be applied; the balls are therefore moistened several times with a sirupy solution of phospheric acid, care being taken that they do not become too soft, so as to render it difficult to introduce them into the eudiometer. After the sulphuretted hydrogen or sulphurous anhydride has been removed, the gas should be dried by means of calcic chloride. The carbonic anhydride can now be determined by means of the bullet of potassic hydrate.

The second method is to absorb the two gases by means of a ball of potassic hydrate containing water, but not moistened on the exterior, then to dissolve the bullet in dilute acetic acid which has been previously boiled and allowed to cool without access of air, and to determine the amount of sulphuretted hydrogen or sulphurous anhydride by means of a standard solution of iodine. This process is especially applicable when rather small quantities of sulphuretted hydrogen have to be estimated.

**Group C. This group contains the gases not absorbed by Potassic Hydrate or Sodic Phosphate, and consists of Oxygen, Nitric Oxide, Carbonic Oxide, Hydrocarbons of the formulæ $\mathrm{CnH^2n}$ $\mathrm{(Cn^2H^2n+1)^2}$, and $\mathrm{CnH^2n+{}^2}$, except Marsh gas.**

Oxygen was formerly determined by means of a ball of phosphorus, but it is difficult subsequently to free the gas from the phosphorous acid produced, and which exerts some tension, and so vitiates the results; besides which, the presence of some gases interferes with the absorption of oxygen by phosphorus; and if any potassic hydrate remains on the side of the tube, from the previous absorption of carbonic anhydride, there is a possibility of the formation of phosphoretted hydrogen, which would, of course, vitiate the analysis. A more convenient re-agent is a freshly prepared alkaline solution of potassic pyrogallate introduced into the gas in a bullet of papier-maché. The balls of papier-maché are made by macerating filter-paper in water, and forcing as much of it as possible into a bullet mould into which the end of a piece of platinum wire has been introduced. In order to keep the mould from opening while it is being filled, it is well to tie the handles together with a piece of string or wire, and when charged it is placed on a sand-bath. After the mass is dry the mould may be opened, when a large absorbent bullet will have been produced. The absorption of oxygen by the alkaline pyrogallate is not very rapid, and it may be necessary to remove the ball once or twice during the operation, and to charge it freshly.

Nitric oxide cannot be readily absorbed in an ordinary absorption tube; it may, however, be converted into nitrous anhydride and nitric peroxide by addition of excess of oxygen, absorbing the oxygen compounds with potassic hydrate, and the excess of oxygen by potassic pyrogallate. The diminution of the volume will give the quantity of nitric oxide. This process is quite successful when the nitric oxide is mixed with olefiant gas and ethylic hydride, but it is possible that other hydrocarbons might be acted on by the nitrous compounds.

Carbonic oxide may be absorbed by two re-agents. If carbonic anhydride and oxygen be present they must be absorbed in the usual manner, and afterwards a papier-maché ball saturated with a concentrated solution of cuprous chloride in dilute hydrochloric acid introduced. A ball of caustic potash is subsequently employed to remove the hydrochloric acid given off by the previous re-agent, and to dry the gas. Carbonic oxide may also be absorbed by introducing a ball of potassic hydrate, placing the absorption tube in a beaker of mercury, and heating the whole in a water bath to 100° for 60 hours. The carbonic oxide is thus converted into potassic formate and entirely absorbed.

Olefiant Gas and other Hydrocarbons of the formula $CnH^2n$ are absorbed by Nordhausen sulphuric acid, to which an additional quantity of sulphuric anhydride has been added. Such an acid may be obtained by heating some Nordhausen acid in a retort connected with a receiver containing a small quantity of the same acid. This liquid is introduced into the gas by means of a dry coke bullet. These bullets are made by filling the mould, into which the usual platinum wire has been placed, with a mixture of equal weights of finely powdered coke and bituminous coal. The mould is then heated as rapidly as possible to a bright red heat, and opened after cooling; a hard porous ball will have been produced, which may be employed for many different re-agents. It is sometimes difficult to obtain the proper mixture of coal and coke, but when once prepared, the bullets may be made with the greatest ease and rapidity. The olefiant gas will be absorbed by the sulphuric acid in about an hour, though they may be left in contact for about two hours with advantage. If, on removing the bullet, it still fumes strongly in the air, it may be assumed that the absorption is complete. The gas now contains sulphurous, sulphuric, and perhaps carbonic anhydrides; these may be removed by a manganic peroxide ball, followed by one of potassic hydrate, or the former may be omitted, the caustic potash alone being used. The various members of the $CnH^2n$ group cannot be separated directly, but by the indirect method of analysis their relative quantities in a mixture may be determined.

The hydrocarbons $(CnH^2n+^1)^2$ and $CnH^2n+^2$ may be absorbed by absolute alcohol, some of which is introduced into the absorption tube, and agitated for a short time with the gas.

Correction has then to be made for the weight of the column of alcohol on the surface of the mercury, and for the tension of the alcohol vapour. This method only gives approximate results, and can only be employed in the presence of gases very slightly soluble in alcohol.

The time required in the different processes of absorption just described is considerable; perhaps it might be shortened by surrounding the absorption eudiometer with a wider tube, similar to the external tube of a Liebig's condenser, and through which a current of water is maintained. By means of a thermometer in the space between the tubes the temperature of the gas would be known, and the readings might be taken two or three minutes after the withdrawal of the re-agents. Besides this advantage, the great precaution necessary for maintaining a constant temperature in the room might be dispensed with. A few experiments made some years ago in this direction gave satisfactory results.

## INDIRECT DETERMINATIONS.

§ 97. Gases which are not absorbed by any re-agents that are applicable in eudiometers over mercury, must be determined in an indirect manner, by exploding them with other gases, and noting either the change of volume or the quantity of their products of decomposition; or lastly, as is most frequently the case, by a combination of these two methods. Thus, for example, oxygen may be determined by exploding with excess of hydrogen, and observing the contraction; hydrogen may be estimated by exploding with excess of oxygen, and measuring the contraction; and marsh gas by exploding with oxygen, measuring the contraction, and also the quantity of carbonic anhydride generated.

The operation is conducted in the following manner:—The long eudiometer furnished with explosive wires is filled with mercury (after a drop of water has been placed at the top of the tube by means of an iron wire, as before described), and some of the gas to be analyzed is introduced from the absorption eudiometer. This gas is then measured with the usual precautions, and an excess of oxygen or hydrogen (as the case may be) introduced. These gases may be passed into the eudiometer directly from the apparatus in which they are prepared; or they may be previously collected in lipped tubes of the form of absorption tubes, so as to be always ready for use.

For the preparation of the oxygen a bulb is used, which is blown at the closed end of a piece of combustion tube. The bulb is about half filled with dry powdered potassic chlorate, the neck drawn out, and bent to form a delivery tube. The chlorate is fused, and the gas allowed to escape for some time to ensure the expulsion of the atmospheric air; the end of the delivery tube is then brought under the orifice of the eudiometer, and the necessary quantity of gas admitted. When it is desired to prepare the oxygen beforehand, it may be collected directly from the bulb; or, another method to obtain the gas free from air may be adopted by those who are provided with the necessary appliances. This is, to connect a bulb containing potassic chlorate with a Sprengel's mercurial air-pump, and, after heating the chlorate to fusion, to produce a vacuum in the apparatus. The chlorate may be again heated until oxygen begins to pass through the mercury at the end of the Sprengel, the heat then withdrawn, and a vacuum again obtained. The chlorate is once more heated, and the oxygen collected at the bottom of the Sprengel. Of course the usual precautions for obtaining an air-tight joint between the bulb and the Sprengel must be taken, such as surrounding the caoutchouc connector with a tube filled with mercury.

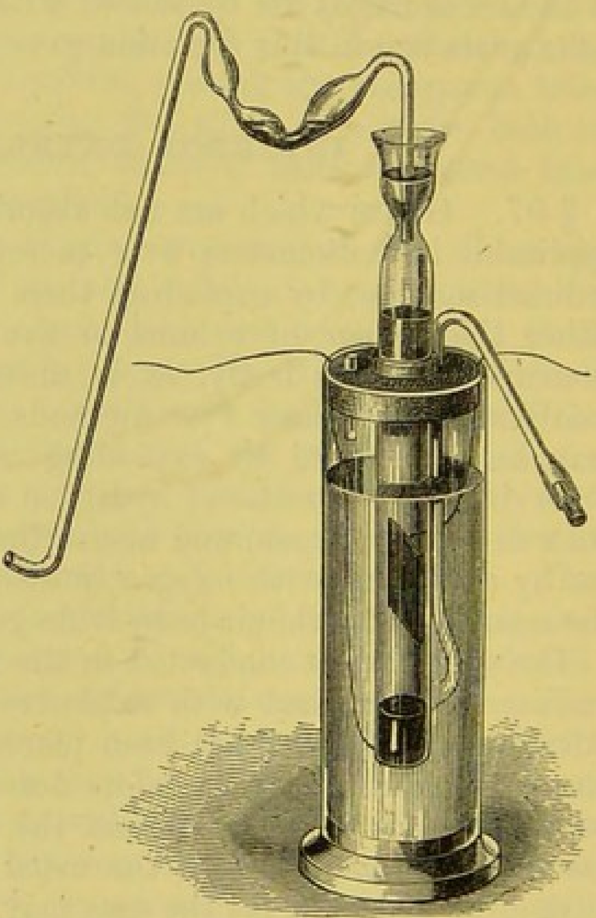

Fig. 74.

The hydrogen for these experiments must be prepared by electrolysis, since that from other sources is liable to contamination with impurities which would vitiate the analysis. The apparatus employed by Bunsen for this purpose (fig. 74) consists of a glass tube, closed at the lower end, and with a funnel at the other, into which a delivery tube is ground, the funnel acting as a water-joint. A platinum wire is sealed into the lower part of the tube; and near the upper end another wire, with a platinum plate attached, is fused into the glass. Some amalgam of zinc is placed into the tube so as to cover the lower platinum wire, and the apparatus filled nearly to the neck with water, acidulated with sulphuric acid. On connecting the platinum wires with a battery of two or three cells, the upper wire being made the negative electrode, pure hydrogen is evolved from the platinum plate, and, after the expulsion of the air, may be at once passed into the eudiometer, or, if preferred, collected in tubes for future use. Unfortunately, in this form of apparatus, the zinc amalgam soon becomes covered with a saturated solution of zinc sulphate, which puts a stop to the electrolysis. In order to remove this layer, Bunsen has a tube fused into the apparatus at the surface of the amalgam; this is bent upwards parallel to the larger tube, and curved downwards just below the level of the funnel. The end of the tube is closed with a caoutchouc stopper. On removing the stopper, and pouring fresh acid into the funnel, the saturated liquid is expelled.

Another form of apparatus for preparing electrolytic hydrogen may readily be constructed. A six-ounce wide-mouth bottle is fitted with a good cork, or better, with a caoutchouc stopper. In the stopper four tubes are fitted (fig. 75). The first is a delivery tube, provided with a U-tube, containing broken glass and sulphuric acid, to conduct the hydrogen to the mercurial trough. The second tube, about 5 centimeters long, and filled with mercury, has fused into its lower end a piece of platinum wire carrying a strip of foil, or the wire may be simply flattened. The third tube passes nearly to the bottom of the bottle, the portion above the cork is bent twice at right angles, and cut off, so that the open end is a little above the level of the shoulder of the bottle; a piece of caoutchouc tube, closed by a compression cock, is fitted to the end of the tube. The fourth tube is a piece of combustion tube about 30 centimeters in length, and which may with advantage be formed into a funnel at the top. This tube reaches about one-third down the bottle, and inside it is placed a narrower glass tube, attached at its lower end by a piece of caoutchouc connector to a rod of amalgamated zinc. The tube is filled with mercury to enable the operator readily to connect the zinc with the battery; some zinc amalgam is placed at the bottom of the bottle; and dilute sulphuric acid is poured in through the wide tube until the bottle is nearly filled with liquid. To use the apparatus, the delivery tube is dipped into mercury, the wire from the positive pole of the battery placed into the mercury in the tube to which the zinc is attached, and the negative pole connected by means of mercury with the platinum plate. The current, instead of passing between the amalgam at the bottom of the vessel and the platinum

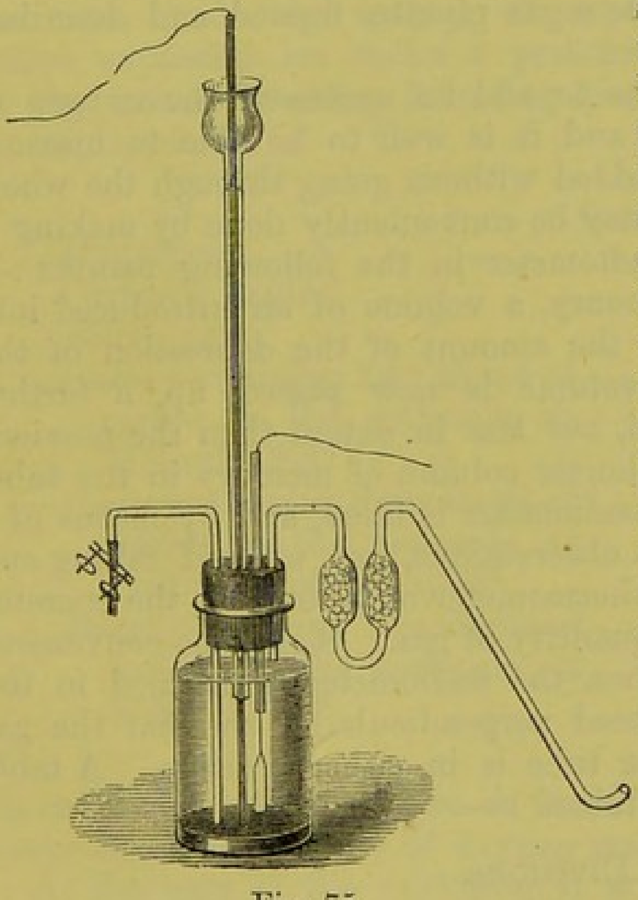

Fig. 75.

plate, as in Bunsen's apparatus, travels from the rod of amalgamated zinc to the platinum, consequently the current continues to pass until nearly the whole of the liquid in the bottle has become saturated with zinc sulphate. As soon as the hydrogen is evolved, of course a column of acid is raised in the funnel until the pressure is sufficient to force the gas through the mercury in which the delivery tube is placed. Care must be taken that the quantity of acid in the bottle is sufficient to prevent escape of gas through the funnel tube, and also that the delivery tube does not pass too deeply into the mercury so as to cause the overflow of the acid. When the acid is exhausted, the compression cock on the bent tube is opened and fresh acid poured into the funnel; the dense zinc sulphate solution is thus replaced by the lighter liquid, and the apparatus is again ready for use.

A very convenient apparatus for transferring oxygen and hydrogen into eudiometers is a gas pipette, figured and described (fig. 47, page 354).

It is necessary in all cases to add an excess of the oxygen or hydrogen before exploding, and it is well to be able to measure approximately the amount added without going through the whole of the calculations. This may be conveniently done by making a rough calibration of the eudiometer in the following manner:—The tube is filled with mercury, a volume of air introduced into it from a small tube, and the amount of the depression of the mercury noted; a second volume is now passed up, a further depression will be produced, but less in extent than the previous one, in consequence of the shorter column of mercury in the tube. This is repeated until the eudiometer is filled, and by means of a table constructed from these observations, but without taking any notice of the variations of thermometer or barometer, the operator can introduce the requisite quantity of gas. It may be convenient to make this calibration when the eudiometer is inclined in the support, and also when placed perpendicularly, so that the gas may be introduced when the tube is in either position. A table like the following is thus obtained:—

DIVISIONS.

| Measures. | Tube Inclined. | Tube Perpendicular. |
|---|---|---|
| 1 | 27 | 45 |
| 2 | 45 | 69 |
| 3 | 61 | 87 |
| 4 | 75 | 102 |
| 5 | 88 | 116 |
| 6 | 100 | 128 |
| 7 | 109 | 138 |
| &c. | &c. | &c. |

In explosions of hydrocarbons with oxygen, it is necessary to have a considerable excess of the latter gas in order to moderate the violence of the explosion. The same object may be attained by diluting the gas with atmospheric air, but it is found that sufficient oxygen serves equally well. If the gas contains nitrogen, it is necessary subsequently to explode the residual gas with hydrogen; and if oxygen only has been used for diluting the gas, a very large quantity of hydrogen must be added, which may augment the volume in the eudiometer to an inconvenient extent. When atmospheric air has been employed, this inconvenience is avoided. After the introduction of the oxygen, the eudiometer is restored to its vertical position, allowed to stand for an hour, and the volume read off.

The determination of the quantity of oxygen which must be added to combustible gases so as to prevent the explosion from being too violent, and at the same time to ensure complete combustion, has been made the subject of experiment. When the gases before explosion are under a pressure equal to about half that of the atmosphere, the following proportions of the gases must be employed:—

| | Volume of Combustible Gas. | Volume of Oxygen. |
|---|---|---|
| Hydrogen . . . . | 1 | 1·5 |
| Carbonic oxide . . . | 1 | 1·5 |
| Marsh gas . . . . | 1 | 5 |
| Gases containing two atoms of carbon in the molecule, as Methyl, $C^2H^6$ . . . | 1 | 10 |
| Gases containing three atoms of carbon in the molecule, as Propylic hydride, $C^3H^8$ . | 1 | 18 |
| Gases containing four atoms of carbon in the molecule, as Ethyl, $C^4H^{10}$ . . . | 1 | 25 |

In cases of mixtures of two or more combustible gases, proportionate quantities of oxygen must be introduced.


Fig. 76.

At the time of the explosion, it is necessary that the eudiometer should be carefully closed to prevent the loss of gas by the sudden expansion. For this purpose a thick plate of caoutchouc, three or four centimeters wide, is cemented on a piece of cork by means of marine glue, or some similar substance, and the lower surface of the cork cut so as to lie firmly at the bottom of the mercurial trough (fig. 76). It is, however, preferable to have the caoutchouc firmly fixed in the trough. As the mercury does not adhere to the caoutchouc, there is some risk of air entering the eudiometer after the explosion; this is obviated by rubbing the plate with some solution of corrosive sublimate before introducing it into the mercury, which causes the metal to wet the caoutchouc and removes all air from its surface. When the caoutchouc is not fixed in the trough, the treatment with the corrosive sublimate has to be repeated before every experiment, and this soils the surface of the mercury to an inconvenient extent. The cushion is next depressed to the bottom of the trough, and the eudiometer placed on it and firmly held down (fig. 77). If this is done with the hands, the tube must be held by that portion containing the mercury, for it is found that when eudiometers burst (which, however, only happens when some precaution has been neglected) they invariably give way just at the level of the mercury within the tube, and serious accidents might occur if the hands were at this point. The cause of the fracture at this point is the following :—Though the gas is at a pressure below that of the atmosphere before the explosion, yet at the instant of the passage of the spark, the expansion of the gas at the top of the tube condenses the layer just below it; this on exploding increases the density of the gas further down the tube, and by the time the ignition is communicated to the lowest quantity of gas, it may be at a pressure far above that of the atmosphere. It may be thought that the explosion is so instantaneous that this explanation is merely theoretical, but on exploding a long column of gas, the time required for the complete ignition is quite perceptible, and sometimes the flash may be observed to be more brilliant at the surface of the mercury. Some experimenters prefer to fix the eudiometer by means of an arm from a vertical stand, the arm being hollowed out on the under side, and the cavity lined with cork.

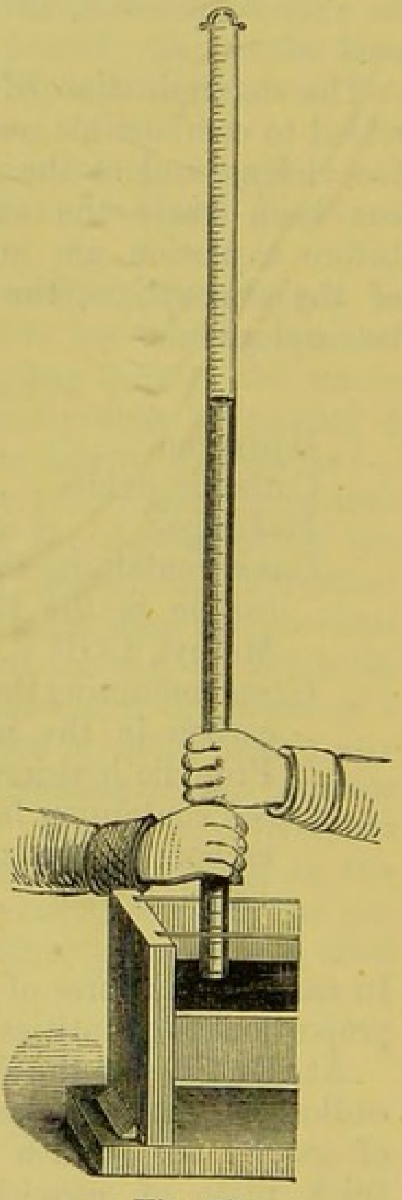

Fig. 77.

If a large quantity of incombustible gas is present, the inflammability of the mixture may be so much reduced that either the explosion does not take place at all, or, what may be worse, only a partial combustion ensues. To obviate this, some explosive mixture of oxygen and hydrogen, obtained by the electrolysis of water, must be introduced. The apparatus used by Bunsen for this purpose is shown in figure 78. The tube in which the electrolysis takes place is surrounded by a cylinder containing alcohol, in order to prevent the heating of the liquid. A convenient apparatus for the preparation of this gas is made by blowing a bulb of about four centimeters in diameter on the end of a piece of narrow glass tube, sealing two pieces of flattened platinum wire into opposite sides of the globe, and bending the tube so as to form a delivery tube. Dilute sulphuric acid, containing about one volume of acid to twenty of water, is introduced into the globe, either before bending the tube, by means of a funnel with a fine long stem, or, after the bending, by warming the apparatus, and plunging the tube into the acid. Care must be taken that the acid is dilute, and that the battery is not too strong, in order to avoid the formation of ozone, which would attack the mercury, causing the sides of the eudiometer to be soiled, at the same time producing a gas too rich in hydrogen.

The spark necessary to effect the explosion may be obtained from several sources. An ordinary electrical machine or electrophorus may be used, but these are liable to get out of order by damp. Bunsen uses a porcelain tube, which is rubbed with a silk rubber, coated with electrical amalgam; by means of this a small Leyden jar is charged. A still more convenient apparatus is an induction coil large enough to produce a spark of half an inch in length.

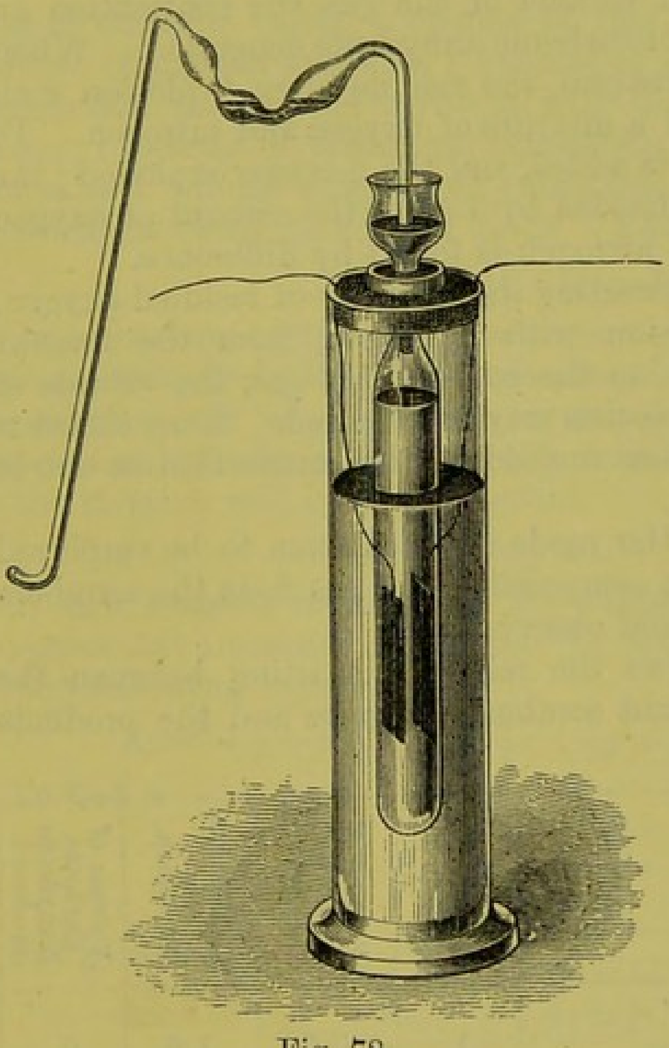

Fig. 78.

After the explosion the eudiometer is slightly raised from the caoutchouc plate to allow the entrance of mercury. When no more mercury rushes in, the tube is removed from the caoutchouc plate, placed in a perpendicular position, and allowed to remain for at least an hour before reading. After measuring the contraction, it is generally necessary to absorb the carbonic anhydride formed by the combustion by means of a potash ball, in the way previously described. In some rare instances the amount of water produced in the explosion with oxygen must be measured. If this has to be done, the eudiometer, the mercury, the original gas, and the oxygen must all be carefully dried. After the explosion the eudiometer is transferred to a circular glass vessel containing mercury, and attached to an iron-wire support, by which the entire arrangement can be suspended in a glass tube adapted to the top of an iron boiler, from which a rapid current of steam may be passed through the glass tube, so as to heat the eudiometer and mercury to an uniform temperature of 100°. From the measurements obtained at this temperature the amount of water produced may be calculated. If three combustible gases are present, the only data required for calculation are, the original volume of the gas, the contraction on explosion, and the amount of carbonic anhydride generated. When the original gas contains nitrogen, the residue after explosion with excess of oxygen consists of a mixture of oxygen and nitrogen. To this an excess of hydrogen is added, and the mixture exploded; the contraction thus produced divided by 3 gives the amount of oxygen in the residual gas, and the nitrogen is found by difference.

It is obvious that, by subtracting the quantity of residual oxygen, thus determined by explosion with hydrogen, from the amount added, in the first instance, to the combustible gas, the volume of oxygen consumed in the explosion may be obtained. Some chemists prefer to employ this number instead of the contraction as one of the data for the calculation.

We must now glance at the mode of calculation to be employed for obtaining the percentage composition of a gas from the numbers arrived at by the experimental observations.

The following table shows the relations existing between the volume of the more important combustible gases and the products of the explosion :—

| Name of Gas. | Volume of Combustible Gas. | Volume of Oxygen Consumed. | Contraction after Explosion. | Volume of Carbonic Anhydride produced. |
|---|---|---|---|---|
| Hydrogen, $H$ | 1 | 0·5 | 1·5 | 0 |
| Carbonic Oxide, $CO$ | 1 | 0·5 | 0·5 | 1 |
| Methylic Hydride, $CH^3H$ | 1 | 2 | 2 | 1 |
| Acetylene, $C^2H^2$ | 1 | 2·5 | 1·5 | 2 |
| Olefiant Gas, $C^2H^4$. | 1 | 3 | 2 | 2 |
| Methyl, $CH^3, CH^3$. | 1 | 3·5 | 2·5 | 2 |
| Ethylic Hydride, $C^2H^5H$ | 1 | 3·5 | 2·5 | 2 |
| Propylene, $C^3H^6$ | 1 | 4·5 | 2·5 | 3 |
| Propylic Hydride, $C^3H^7H$ | 1 | 5 | 3 | 3 |
| Butylene, $C^4H^8$ | 1 | 6 | 3 | 4 |
| Ethyl, $C^2H^5, C^2H^5$. | 1 | 6·5 | 3·5 | 4 |
| Butylic Hydride, $C^4H^9H$ | 1 | 6·5 | 3·5 | 4 |

As an example, we may take a mixture of hydrogen, carbonic oxide, and marsh gas, which gases may be designated by $x$, $y$, and $z$ respectively. The original volume of gas may be represented by A, the contraction by C, and the amount of carbonic anhydride by D.

A will, of course, be made up of the three components, or

$$A = x + y + z.$$

C will be composed as follows :—When a mixture of hydrogen and oxygen is exploded, the gas entirely disappears. One volume of hydrogen combining with half a volume of oxygen, the contraction will be $1\frac{1}{2}$ times the quantity of hydrogen present, or $1\frac{1}{2}x$. In the case of carbonic oxide, 1 volume of this gas uniting with half its volume of oxygen produces 1 volume of carbonic anhydride, so the contraction due to the carbonic will be half its volume, or $\frac{1}{2}y$. Lastly, 1 volume of marsh gas combining with 2 volumes of oxygen generates 1 volume of carbonic anhydride, so the contraction in this case will be twice its volume, or $2z$. Thus we have—

$$C = 1\tfrac{1}{2}x + \tfrac{1}{2}y + 2z.$$

Since carbonic oxide on combustion forms its own volume of carbonic anhydride, the amount produced by the quantity present in the mixture will be $y$. Marsh gas also generates its own volume of carbonic anhydride, so the quantity corresponding to the marsh gas in the mixture will be $z$. Therefore

$$D = y + z.$$

It now remains to calculate the values of $x$, $y$, and $z$ from the experimental numbers A, C, and D, which is done by the help of the following equations :—

$$A = x + y + z\,. \quad C = 1\tfrac{1}{2}x + \tfrac{1}{2}y + 2z\,. \quad D = y + z\,.$$

To find $x$—

$$\begin{array}{r}
x + y + z = A\,, \\
y + z = D\,, \\
\hline
x \qquad\quad = A - D\,. \\
\hline
\end{array}$$

For $y$ we have—

$$\begin{array}{rl}
4y + 4z & = 4D\,, \\
3x + \;\; y + 4z & = 2C\,, \\
\hline
-\,3x + 3y \qquad & = 4D - 2C\,, \\
3x \qquad\qquad & = 3A - 3D\,, \\
\hline
3y \qquad & = 3A - 2C + D\,, \quad \text{or} \\
y & = \dfrac{3A - 2C + D}{3}\,. \\
\hline
\end{array}$$

The value of $z$ is thus found—

$$\begin{array}{l}
D = y + z \;\therefore \\
z = D - y = \\
\qquad D - \dfrac{3A - 2C + D}{3}\,, \quad \text{or} \\
z = \dfrac{2C - 3A + 2D}{3}\,. \\
\hline
\end{array}$$

By replacing the letters A, C, and D by the numbers obtained by experiment, the quantities of the three constituents in the volume A may easily be calculated by the three formulæ:—

$$x = A - D \quad = \text{hydrogen},$$

$$y = \frac{3A - 2C + D}{3} = \text{carbonic oxide},$$

$$z = \frac{2C - 3A + 2D}{3} = \text{marsh gas}.$$

The percentage composition is, of course, obtained by the simple proportions—

$$A : x : : 100 : \text{per-cent. of hydrogen},$$

$$A : y : : 100 : \text{per-cent. of carbonic oxide},$$

$$A : z : : 100 : \text{per-cent. of marsh gas}.$$

If the gas had contained nitrogen, it would have been determined by exploding the residual gas, after the removal of the carbonic anhydride, with excess of hydrogen. The contraction observed, divided by 3, would give the volume of oxygen in the residue, and this, deducted from the residue, would give the amount of nitrogen. If A again represents the original gas, and $n$ the amount of nitrogen it contains, the expression $A - n$ would have to be substituted for A in the above equations.

It may be as well to develop the formula for obtaining the same results by observing the volume of oxygen consumed instead of the contraction. If B represent the quantity of oxygen, we shall have

$$B = \tfrac{1}{2}x + \tfrac{1}{2}y + 2z,$$

the values of A and D remaining as before, $x = A - D$.

$z$ is thus found—

$$\begin{aligned} x + y + 4z &= 2B, \\ x + y + z &= A, \\ \hline 3z &= 2B - A, \quad \text{or} \\ z &= \frac{2B - A}{3}. \end{aligned}$$

For $y$—

$$\begin{aligned} D &= y + z \\ y &= D - z = \\ & D - \frac{2B - A}{3}, \quad \text{or} \\ y &= \frac{3D - 2B + A}{3} \end{aligned}$$

Thus we have—

$$x=A-D$$
$$y=\frac{3D-2B+A}{3}$$
$$z=\frac{2B-A}{3}$$

---

Having thus shown the mode of calculation of the formulæ, it will be well to give some examples of the formulæ employed in some of the cases which most frequently present themselves in gas analysis. In all cases—

A=original mixture ,
C=contraction ,
D=carbonic anhydride produced.

### 1. Hydrogen and Nitrogen.

$$H=x\,;\ N=y.$$

Excess of oxygen is added, and the contraction on explosion observed :—

$$x=\frac{2C}{3}\,,$$
$$y=\frac{3A-2C}{3}\,,\ \text{or}\ A-x\,.$$

### 2. Carbonic Oxide and Nitrogen.

$$CO=x\,;\ N=y.$$

The gas is exploded with excess of oxygen, and the amount of carbonic anhydride produced is estimated :—

$$x=D\,,$$
$$y=A-D\,.$$

### 3. Hydrogen, Carbonic Oxide, and Nitrogen.

$$H=x\,;\ CO=y\,;\ N=z.$$

In this case the contraction and the quantity of carbonic anhydride are measured :—

$$x=\frac{2C-D}{3}\,,$$
$$y=D\,,$$
$$z=\frac{3A-2C-2D}{3}$$

### 4. Hydrogen, Marsh Gas, and Nitrogen.

$\mathrm{H}=x$ ; $\mathrm{CH}^4=y$ ; $\mathrm{N}=z$.

$$x=\frac{2\mathrm{C}-4\mathrm{D}}{3},$$

$$y=\mathrm{D},$$

$$z=\frac{3\mathrm{A}-2\mathrm{C}+\mathrm{D}}{3}.$$

### 5. Carbonic Oxide, Marsh Gas, and Nitrogen.

$\mathrm{CO}=x$ ; $\mathrm{CH}^4=y$ ; $\mathrm{N}=z$.

$$x=\frac{4\mathrm{D}-2\mathrm{C}}{3},$$

$$y=\frac{2\mathrm{C}-\mathrm{D}}{3},$$

$$z=\mathrm{A}-\mathrm{D}.$$

### 6. Hydrogen, Methyl (or Ethylic Hydride), and Nitrogen.

$\mathrm{H}=x$ ; $\mathrm{C}^2\mathrm{H}^6=y$ ; $\mathrm{N}=z$.

$$x=\frac{4\mathrm{C}-5\mathrm{D}}{6},$$

$$y=\frac{\mathrm{D}}{2},$$

$$z=\frac{3\mathrm{A}-2\mathrm{C}+\mathrm{D}}{3}.$$

### 7. Carbonic Oxide, Methyl (or Ethylic Hydride), and Nitrogen.

$\mathrm{CO}=x$ ; $\mathrm{C}^2\mathrm{H}^6=y$ ; $\mathrm{N}=z$.

$$x=\frac{5\mathrm{D}-4\mathrm{C}}{3},$$

$$y=\frac{2\mathrm{C}-\mathrm{D}}{3},$$

$$z=\frac{3\mathrm{A}-4\mathrm{D}+2\mathrm{C}}{3}.$$

8. Hydrogen, Carbonic Oxide, and Marsh Gas.

$$H=x\ ;\ CO=y\ ;\ CH^4=z.$$

$$x=A-D\ ,$$

$$y=\frac{3A-2C+D}{3}\ ,$$

$$z=\frac{2C-3A+2D}{3}\ .$$

9. Hydrogen, Carbonic Oxide, and Ethylic Hydride (or Methyl).

$$H=x\ ;\ CO=y\ ;\ C^2H^6=z.$$

$$x=\frac{3A+2C-4D}{6}\ ,$$

$$y=\frac{3A-2C+D}{3}\ ,$$

$$z=\frac{2C-3A+2D}{6}\ .$$

10. Carbonic Oxide, Marsh Gas, and Ethylic Hydride (or Methyl).

$$CO=x\ ;\ CH^4=y\ ;\ C^2H^6=z.$$

$$x=\frac{3A-2C+D}{3}\ ,$$

$$y=\frac{3A+2C-4D}{3}\ ,$$

$$z=D-A\ .$$

11. Hydrogen, Marsh Gas, and Acetylene.

$$H=x\ ;\ CH^4=y\ ;\ C^2H^2=z.$$

$$x=\frac{5A-2C-D}{2}\ ,$$

$$y=2C-3A\ ,$$

$$z=\frac{D-2C+3A}{2}\ .$$

12. Hydrogen, Marsh Gas, and Ethylic Hydride (or Methyl).

$$H=x\ ;\ CH^4=y\ ;\ C^2H^6=z.$$

This mixture cannot be analyzed by indirect determination, since a mixture of two volumes of hydrogen with two volumes of ethylic hydride (or methyl) has the same composition as four volumes of marsh gas—

$$C^2H^6+H^2=2CH^4\ ;$$

and, consequently, would give rise to the same products on combustion with oxygen as pure marsh gas—

$$C^2H^6+H^2+O^8=2CO^2+4OH^2\ ;$$
$$2CH^4+O^8=2CO^2+4OH^2.$$

In this case it is necessary to estimate by direct determination the ethylic hydride (or methyl) in a separate portion of the gas by absorption with alcohol, another quantity of the mixture being exploded with oxygen, and the amount of carbonic anhydride produced and measured. If the quantity absorbed by alcohol$=$E, then

$$x=A-D+E\ ,$$
$$y=D-2E\ ,$$
$$z=E\ .$$

### 13. Hydrogen, Carbonic Oxide, Propylic Hydride.

$$H=x\ ;\ CO=y\ ;\ C^3H^8=z.$$

$$x=\frac{3A+4C-5D}{9}\ ,$$
$$y=\frac{3A-2C+D}{3}\ ,$$
$$z=\frac{2C-3A+2D}{9}\ .$$

### 14. Carbonic Oxide, Marsh Gas, and Propylic Hydride.

$$CO=x\ ;\ CH^4=y\ ;\ C^3H^8=z.$$

$$x=\frac{3A-2C+D}{3}\ ,$$
$$y=\frac{3A+4C-5D}{6}\ ,$$
$$z=\frac{D-A}{2}\ .$$

### 15. Carbonic Oxide, Ethylic Hydride (or Methyl), and Propylic Hydride.

$$CO=x\ ;\ C^2H^6=y\ ;\ C^3H^8=z.$$

$$x=\frac{3A-2C+D}{3}\ ,$$
$$y=\frac{3A+4C-5D}{3}\ ,$$
$$z=\frac{4D-3A-2C}{3}\ .$$

### 16. Marsh Gas, Ethylic Hydride (or Methyl), and Propylic Hydride.

$$CH^4 = x\ ;\ C^2H^6 = y\ ;\ C^3H^8 = z.$$

As a mixture of two volumes of marsh gas and two of propylic hydride has the same composition as four of ethylic hydride (or methyl)—

$$CH^4 + C^3H^8 = 2C^2H^6\ ,$$

the volume absorbed by alcohol, and which consists of ethylic hydride (or methyl) and propylic hydride, must be determined, and another portion of the gas exploded, and the contraction measured. If E represents the volume absorbed—

$$\begin{aligned} x &= A - E\ , \\ y &= 4A - 2C + 2E\ , \\ z &= 2C - 4A - E\ . \end{aligned}$$

### 17. Hydrogen, Carbonic Oxide, and Ethyl (or Butylic Hydride).

$$H = x\ ;\ CO = y\ ;\ C^4H^{10} = z.$$

$$\begin{aligned} x &= \frac{A + 2C - 2D}{4}\ , \\ y &= \frac{3A - 2C + D}{3}\ , \\ z &= \frac{2C + 2D - 3A}{12}\ . \end{aligned}$$

### 18. Nitrogen, Hydrogen, Carbonic Oxide, Ethylic Hydride (or Methyl), and Butylic Hydride (or Ethyl).

$$N = n\ ;\ H = w\ ;\ CO = x\ ;\ C^2H^6 = y\ ;\ C^4H^{10} = z.$$

In one portion of the gas the ethylic hydride (or methyl) and the butylic hydride (or ethyl) are absorbed by alcohol; the amount absorbed = E.

A second portion of the original gas is mixed with oxygen and exploded, the amount of contraction and of carbonic anhydride being measured.

The residue now contains the nitrogen and the excess of oxygen; to this an excess of hydrogen is added, the mixture exploded, and the contraction measured. From this the quantity of nitrogen is thus obtained. Let—

$G$ = excess of oxygen and nitrogen,
$v$ = excess of oxygen,
$n$ = nitrogen,
$C'$ = contraction on explosion with hydrogen.

Then—

$$G = v + n\,,$$
$$C' = 3v\,,$$
$$3v = C'$$
$$v = \frac{C'}{3}\,,$$
$$n = G - v = G - \frac{C'}{3} = \frac{3G - C'}{3}\,.$$

From these data the composition of the mixture can be determined—

$$w = \frac{2C - D - 3E}{3}\,,$$
$$x = \frac{3A - 2C + D - 3n}{3}\,,$$
$$y = \frac{3A - 2C - 2D + 12E - 3n}{6}\,,$$
$$z = \frac{2C - 3A + 2D - 6E + 3n}{6}\,.$$

## MODIFICATIONS AND IMPROVEMENTS UPON THE FOREGOING PROCESSES.

§ 98. In the method of gas analysis that we have been considering, the calculations of results are somewhat lengthy, as will be seen by a reference to the example given of the analysis of a mixture of air and carbonic anhydride (page 420). Besides this, the operations must be conducted in a room of uniform temperature, and considerable time allowed to elapse between the manipulation and the readings in order to allow the eudiometers to acquire the temperature of the surrounding air; and, lastly, the absorption of gases by solid re-agents is slow. These disadvantages are to a great extent counterbalanced by the simplicity of the apparatus, and of the manipulation.

From time to time various chemists have proposed methods by which the operations are much hastened and facilitated, and the calculations shortened. It will be necessary to mention a few of these processes, which, however, require special forms of apparatus.

Williamson and Russell have described (*Proceedings of the Royal Society*, ix. 218) an apparatus, by means of which the gases in the eudiometers are measured under a constant pressure, the correction for temperature being eliminated by varying the column of mercury in the tube so as to compensate for the alteration of volume observed in a tube containing a standard volume of moist air. In this case solid re-agents were employed in the eudiometers.

In 1864 they published (*J. C. S.* xvii. 238) a further development of this method, in which the absorptions were conducted in a separate laboratory vessel, by which means the re-agents could be employed in a pasty condition and extended over a large surface.

And in 1868 Russell improved the apparatus, so that liquid re-agents could be used in the eudiometers, and the analysis rapidly executed. A description of this last form of instrument may be found in *J. C. S.* xxi. 128.

The gutta-percha mercury trough employed is provided with a deep well, into which the eudiometer can be depressed to any required extent, and on the surface of the mercury a wide glass cylinder, open at both ends and filled with water, is placed. The eudiometer containing the gas to be examined is suspended within the cylinder of water by means of a steel rod passing through a socket attached to a stout standard firmly fixed to the table. In a similar manner, a tube containing moist air is placed by the side of the eudiometer. The clamp supporting this latter tube is provided with two horizontal plates of steel, at which the column of the mercury is read off. When a volume of gas has to be measured, the pressure tube containing the moist air is raised or lowered, by means of an ingeniously contrived fine adjustment, until the mercury stands very nearly at the level of one of the horizontal steel plates. The eudiometer is next raised or lowered until the column of mercury within it is at the same level. The final adjustment to bring the top of the meniscus exactly to the lower edge of the steel bar is effected by sliding a closed wide glass tube into the mercury trough. Thus we have two volumes of gas under the same pressure and temperature, and both saturated with moisture. If the temperature of the water in the cylinder increased, there would be a depression of the columns in both tubes; but by lowering the tubes, and thus increasing the pressure until the volume of air in the pressure tube was the same as before, it would be found that the gas in the eudiometer was restored to the original volume. Again, if the barometric pressure increased, the volumes of the gases would be diminished; but, by raising the tubes to the necessary extent, the previous volumes would be obtained. Therefore, in an analysis, it is only necessary to measure the gas at a pressure equal to that which is required to maintain the volume of moist air in the pressure tube constant. The re-agents are introduced into the eudiometer in the liquid state by means of a small syringe made of a piece of glass tube about one-eighth of an inch in diameter. For this purpose the eudiometer is raised until its open end is just below the surface of the mercury, and the syringe, which is curved upwards at the point, is depressed in the trough, passed below the edge of the water-cylinder, and the extremity of the syringe introduced into the eudiometer. When a sufficient quantity of the liquid has been injected, the eudiometer is lowered and again raised, so as to moisten the sides of the tube with the liquid, and thus hasten the absorption. Ten minutes was found to be a sufficient time for the absorption of carbonic anhydride when mixed with air.

To remove the liquid re-agent, a ball of moistened cotton wool is employed. The ball is made in the following manner:—A piece of steel wire is bent into a loop at one end, and some cotton wool tightly wrapped round it. It is then dipped in water and squeezed with the hand under the liquid until the air is removed. The end of the steel wire is next passed through a piece of glass tube, curved near one end, and the cotton ball drawn against the curved extremity of the tube. The ball, saturated with water, is now depressed in the mercury trough, and, after as much of the water as possible has been squeezed out of it, it is passed below the eudiometer, and, by pushing the wire, the ball is brought to the surface of the mercury in the eudiometer and rapidly absorbs all the liquid re-agent, leaving the meniscus clean. The ball is removed with a slight jerk, and gas is thus prevented from adhering to it. It is found that this mode of removing the liquid can be used without fear of altering the volume of the gas in the eudiometer.

Carbonic anhydride may be absorbed by a solution of potassic hydrate, and oxygen by means of potassic hydrate and pyrogallic acid. The determination of ethylene is best effected by means of fuming sulphuric acid on a coke ball, water and dilute potassic hydrate being subsequently introduced and removed by the ball of cotton wool.

Doubtless this mode of using the liquid re-agents might be employed with advantage in the ordinary process of analysis to diminish the time necessary for the absorption of the gases. By this process of Russell's the calculations are much shortened and facilitated, the volumes read off being comparable among themselves; this will be seen by an example taken from the original memoir of the determination of oxygen in air—

| | | Volume in Table corresponding to reading. |
|---|---|---|
| Volume of air taken . . . | 130·3 | 132·15 |
| Volume after absorption of oxygen by potassic hydrate and pyrogallic acid . . . . | 103·5 | 104·46 |

132·15
104·46
27·69 volumes of oxygen in 132·15 of air.

132·15 : 27·69 : : 100 : 20·953 percentage of oxygen in air.

Russell has also employed his apparatus for the analysis of carbonates (*J. C. S.* [N. S.] vi. 310). For this purpose he adapted a graduated tube, open at both ends, to a glass flask by means of a thick piece of caoutchouc tube. Into the flask a weighed quantity of a carbonate was placed, together with a vessel containing dilute acid. The position of the mercury in the graduated tube was first read off, after which the flask was shaken so as to bring the acid and carbonate in contact, and the increase in volume was due to the carbonic anhydride evolved. The results thus obtained are extremely concordant.

In eight experiments with sodic carbonate the percentage of carbonic anhydride found varied from 41·484 to 41·607, theory requiring 41·509.

Thirteen experiments with calc-spar gave from 43·520 to 43·858, the theoretical percentage being 44·0; and in nine other analyses from 43·581 to 43·901 were obtained.

Two experiments were made with manganic peroxide, oxalic acid and sulphuric acid, and gave 58·156 and 58·101 per cent. of carbonic anhydride.

Some determinations of the purity of magnesium were also performed by dissolving the metal in hydrochloric acid and measuring the resulting hydrogen. Four operations gave numbers varying between 8·255 and 8·282. The metal should yield 8·333.

Russell has also employed this process for the determination of the combining proportions of nickel and cobalt (*J. C. S.* [N. S.] vii. 294).

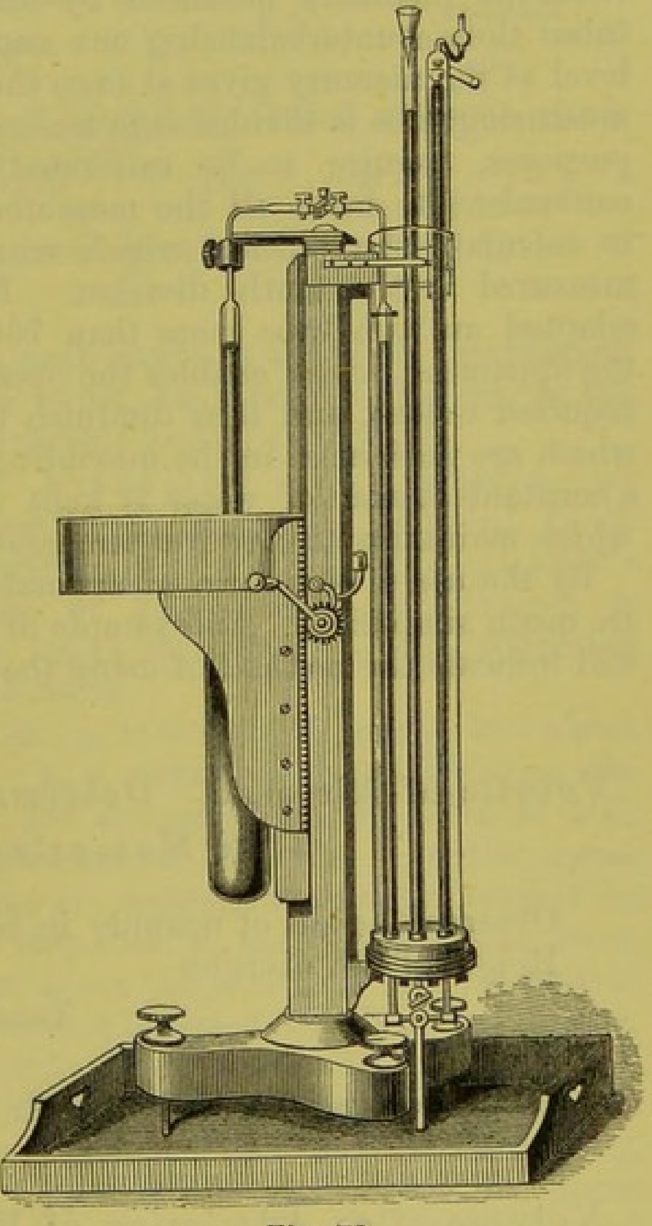

Fig. 79.

Regnault and Reiset described (*Ann. Chim. Phys.* [3] xxvi. 333) an apparatus by which absorptions could be rapidly conducted by means of liquid re-agents brought in contact with the gases in a laboratory tube. The measurements are made in a graduated tube, which can be placed in communication with the laboratory tube by means of fine capillary tubes provided with stop-cocks, the lower end of the measuring tube being connected by an iron socket and stop-cock with another graduated tube in which the pressure to which the gas is subjected is measured. The measuring and pressure tubes are surrounded by a cylinder of water. An apparatus similar in principle to this has recently been constructed by Frankland, and is fully described in the section on Water Analysis (§ 88, page 348).

Frankland and Ward (*J. C. S.* vi. 197) made several important improvements in the apparatus of Regnault and Reiset. They introduced a third tube (fig. 79), closed at the top with a stopper, and which is made to act as a barometer, to indicate the tension of the gas in the measuring tube, thus rendering the operation entirely independent of variations of atmospheric pressure. The correction for aqueous vapour is also eliminated, by introducing a drop of water into the barometer as well as into the measuring tube, the pressures produced by the aqueous vapour in the two tubes thus counterbalancing one another, so that the difference of level of the mercury gives at once the tension of the dry gas. The measuring tube is divided into ten equal divisions (which, for some purposes, require to be calibrated), and in one analysis it is convenient to make all the measurements at the same division, or to calculate the tension which would be exerted by the gas if measured at the tenth division. Frankland and Ward also adapted an iron tube more than 760 m.m. long at the bottom of the apparatus, which enables the operator to expand the gas to any required extent, and thus diminish the violence of the explosions which are performed in the measuring tube. During the operation a constant stream of water is kept flowing through the cylinder, which maintains an uniform temperature.

By the use of this form of apparatus the calculations of analyses are much simplified. An example of an analysis of atmospheric air will indicate the method of using the instrument.

### Volume of Air used. Determined at 5th Division on the Measuring Tube.

| | m.m. |
|---|---|
| Observed height of mercury in barometer . | 673·0 |
| Height of 5th division . . . . . . | 383·0 |
| Tension of gas . | 290·0 |
| | 0·5 |
| Corrected tension of gas at 10th division . . | 145·00 |

### Volume after Admission of Hydrogen. Determined at 6th Division.

| | m.m. |
|---|---|
| Observed height of mercury in barometer . | 772·3 |
| Height of 6th division . . . . . . | 304·0 |
| Tension of gas . | 468·3 |
| | 0·6 |
| Corrected tension at 10th division . . . . | 280·98 |

Volume after Explosion. Determined at 5th Division.

| | |
|---|---|
| | m.m. |
| Observed height of mercury in barometer . | 763·3 |
| Height of 5th division . . . . . | 383·0 |
| Tension of gas . | 380·3 |
| | 0·5 |
| Corrected tension at 10th division . . . . | 190·15 |
| Tension of air with hydrogen . . . . . | 280·98 |
| Tension of gas after explosion . . . . . | 190·15 |
| Contraction on explosion . . . . . | 90·83 |

of which one-third is oxygen.

$$\frac{90\cdot83}{3}=30\cdot276=\text{volumes of oxygen in }145\cdot0\text{ volumes of air}$$

$$145\cdot0 \;:\; 30\cdot276 \;::\; 100 \;:\; x$$

$$x=\frac{30\cdot276\times100}{145\cdot0}=20\cdot88=\text{percentage of oxygen in air.}$$

If all the measurements had been made at the same division, no correction to the tenth division would have been necessary, as the numbers would have been comparable among themselves.

Another modification of Frankland and Ward's, or Regnault's apparatus has been designed by McLeod (*J. C. S.* [N.S.] vii. 313), in which the original pressure tube of Regnault's apparatus, or the filling tube of Frankland and Ward, is dispensed with, the mercury being admitted to the apparatus through the stop-cocks at the bottom.

The measuring tube A (fig. 80) is 900 m.m. in length, and about 20 m.m. in internal diameter. It is marked with ten divisions, the first at 25 m.m. from the top, the second at 50, the third at 100, and the remaining ones at intervals of 100 m.m. In the upper part of the tube, platinum wires are sealed, and it is terminated by a capillary tube and fine glass stop-cock, *a*, the capillary tube being bent at right angles at 50 m.m. above the junction. At the bottom of the tube, a wide glass stop-cock *b* is sealed, which communicates, by means of a caoutchouc joint surrounded with tape and well wired to the tubes, with a branch from the barometer tube B. This latter tube is 5 m.m. in width, and about 1200 m.m. long, and is graduated in millimeters from bottom to top. At the upper extremity a glass stop-cock *d* is joined, the lower end being curved and connected by caoutchouc with a stop-cock and tube C, descending through the table to a distance of 900 m.m. below the joint. It is advisable to place washers of leather at the end of the plugs of the stop-cocks *c* and *b*, as the pressure of the mercury which is afterwards to be introduced has a tendency to force them out; and if this should happen, the washers prevent any great escape of mercury.

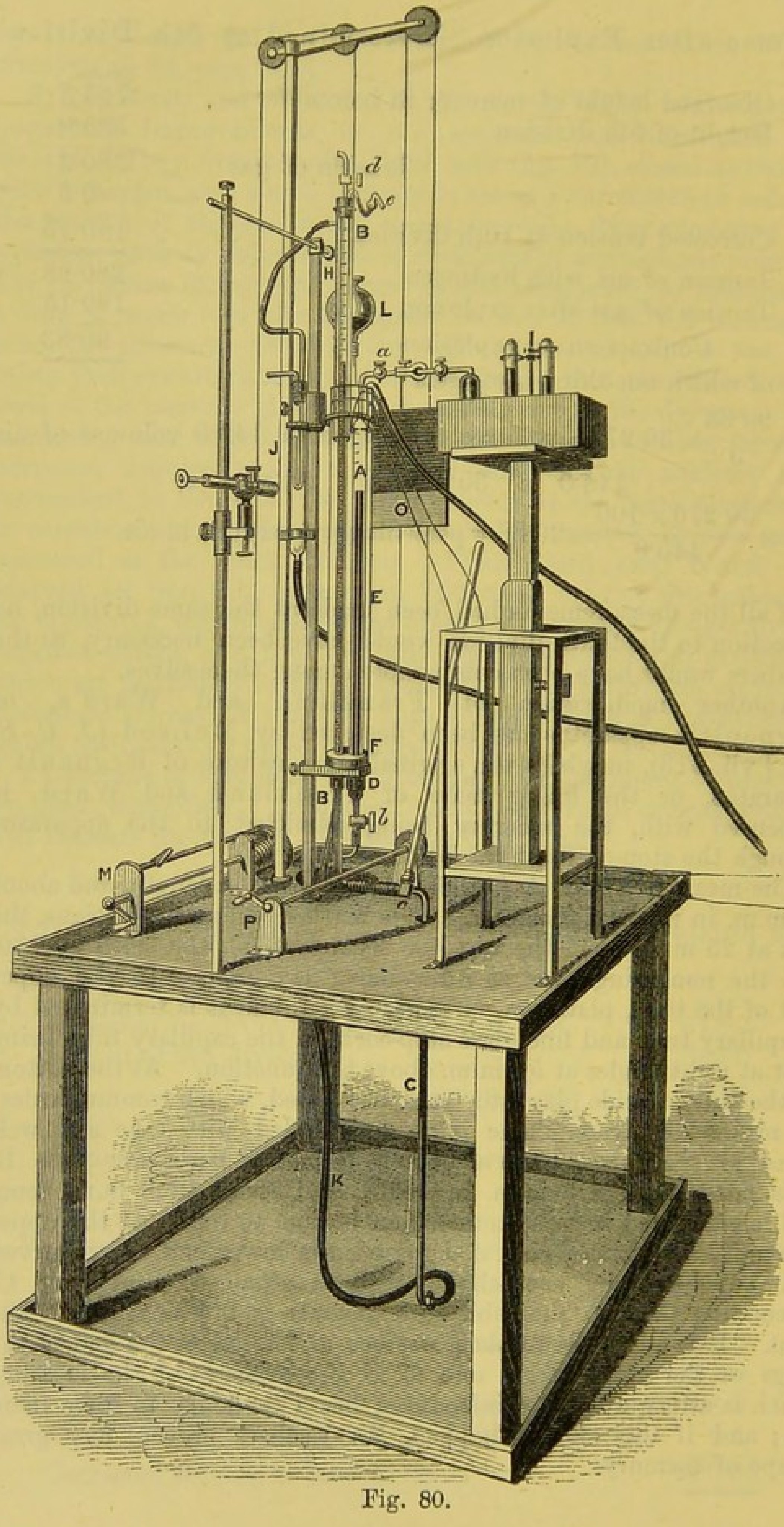

Fig. 80.

The two tubes are firmly held by a clamp D, on which rests a wide cylinder E, about 55 m.m. in diameter, surrounding the tubes, and adapted to them by a water-tight caoutchouc cork F. The cylinder is maintained in an upright position by a support at its upper end G, sliding on the same rod as the clamp. Around the upper part of the barometer tube a syphon H is fixed by means of a perforated cork, through which the stop-cock *d* passes. A small bulb-tube *e*, containing some mercury, is also fitted in this cork, so as to allow of the air being entirely removed from the syphon. The syphon descends about 100 m.m. within the cylinder, and has a branch at the top communicating by caoutchouc with a bent tube contained in a wider one J affixed to the support. A constant current of water is supplied to the cylinder through a glass tube, which passes to the bottom, and escapes through the syphon and tubes to the drain.

To the end of the narrow tube C is fastened a long piece of caoutchouc tube K, covered with tape, by which a communication is established with the mercurial reservoir L, suspended by a cord, so that by means of the winch M, it may be raised above the level of the top of the barometer tube. As the mercury frequently forces its way through the pores of the caoutchouc tube, it is advisable to surround the lower part with a piece of wide flexible tube; this prevents the scattering of the mercury, which collects in a tray placed on the floor. Into the bottom of the tray a screw must be put, to which the end of the glass tube is firmly attached by wire. The capillary stop-cock *a* is provided with a steel cap, by means of which it may be adapted to a short and wide laboratory tube capable of holding about 150 c.c., and identical in form with the one described in the section on Water Analysis (§ 88). The mercurial trough for the laboratory tube is provided with a stand with rings, for the purpose of holding two tubes containing gases that may be required.

The apparatus is used in the same way as Frankland and Ward's, except that the mercury is raised and lowered in the tubes by the movement in the reservoir L, instead of pouring it into the centre supply-tube.

To arrange the apparatus for use, the reservoir L is lowered to the ground, and mercury poured into it. The laboratory tube being removed, the stop-cocks are all opened, and the reservoir gradually raised. When the tube A is filled, the stop-cock *a* is closed, and the reservoir elevated until mercury flows through the stop-cock *d* at the top of the barometer. It is convenient to have the end of the tube above the stop-cock so bent that a vessel can be placed below to receive the mercury. This bend must, of course, be so short that, when the plug of the stop-cock is removed, the syphon will pass readily over. When the air is expelled from the barometer tube, the stop-cock is closed. A few drops of water must next be introduced into the barometer: this is accomplished by lowering the reservoir to a short distance below the top of the barometer, and gently opening the stop-cock *d*, while a small pipette, from which water is dropping, is held against the orifice, the stop-cock being closed when a sufficient amount of water has penetrated into the tube. In the same manner, a small quantity of water is passed into the measuring tube. In order to get rid of any bubbles of air which may still linger in the tubes, the reservoir is lowered to the ground so as to produce a vacuum in the apparatus; in this manner the interior surfaces of the tubes become moistened. The reservoir is now gently raised, thus refilling the tubes with mercury. Great care must be taken that the mercury does not rush suddenly against the tops of the measuring and barometer tubes, which might cause their destruction. This may be avoided by regulating the flow of mercury by means of the stop-cock *c*, which may be conveniently turned by a long key of wood, resting against the upper table of the sliding stand of the mercurial trough. When the reservoir has again been elevated above the top of the barometer, the stop-cocks of the measuring and barometer tubes are opened, and the air and water which have collected allowed to escape.

The heights of the mercurial columns in the barometer, corresponding to the different divisions of the measuring tube, have now to be determined. This is done by running out all the mercury from the tubes, and slowly readmitting it until the meniscus of the mercury just touches the lowest division in the measuring tube. This may be very conveniently managed by observing the division through a small telescope of short focus, and sufficiently close to the apparatus to permit of the key of the stop-cock *c* being turned, while the eye is still at the telescope. When a reading is taken, the black screen O behind the apparatus must be moved by means of the winch P, until its lower edge is about a millimeter above the division. The telescope is now directed to the barometer tube, and the position of the mercury carefully noted. As the tubes only contain aqueous vapour, and are both of the same temperature, the columns in the two tubes are those which exactly counterbalance one another, and any difference of level that may be noticed is due to capillarity.

The same operation is now repeated at each division of the tube. The measuring tube next requires calibration, an operation performed in a manner perfectly similar to that described in § 88 (page 351), namely, by filling the measuring tube with water, and weighing the quantities contained between every two divisions. The eudiometer being filled with water, and the stop-cock *b* closed, the reservoir is raised and the mercury allowed to rise to the top of the barometer. The capillary stop-cock *a* having been opened, the cock *b* is gently turned, and the water allowed to flow out until the mercury reaches the lowest division of the tube. A carefully weighed flask is now supported just below the steel cap, the stop-cock *b* again opened, until the next division is reached, and the quantity of water is weighed, the temperature of the water in the wide cylinder being observed. The same operation is repeated at each division, and by calculation the exact contents of the tube in cubic centimeters may be found.

In this manner, a table, such as the following, is obtained:—

| Division on measuring tube. | Height of Mercury in Barometer tube corresponding to division. | Contents. | |
|---|---|---|---|
| | | Cubic Centimeters. | Log. |
| 1 | 756·9 | 8·6892 | 0·9389814 |
| 2 | 706·7 | 18·1621 | 1·2591664 |
| 3 | 606·8 | 36·9307 | 1·5673880 |
| 4 | 506·5 | 55·7344 | 1·7461232 |
| 5 | 406·8 | 74·4299 | 1·8717477 |
| 6 | 306·8 | 93·3306 | 1·9700244 |
| 7 | 206·9 | 112·4165 | 2·0508303 |
| 8 | 107·0 | 131·6335 | 2·1193666 |
| 9 | 7·1 | 151·1623 | 2·1794435 |

When a gas is to be analyzed, the laboratory tube is filled with mercury, either by sucking the air out through the capillary stop-cock, while the open end of the tube stands in the trough, or much more conveniently, by exhausting the air through a piece of flexible tube passed under the mercury to the top of the laboratory tube, the small quantity of air remaining in the stop-cock and at the top of the wide tube being very readily withdrawn. The face of one of the steel pieces is greased with a small quantity of resin cerate, and, the measuring apparatus being full of mercury, the clamp is adjusted.

Before the introduction of the gas, it is advisable to ascertain if the capillary tubes are clear, as a stoppage may arise from the admission of a small quantity of grease into one of them. For this purpose the globe L is raised above the level of the top of the measuring tube, and the capillary stop-cocks opened ; if a free passage exists, the mercury will be seen to flow through the tubes. The stop-cock of the laboratory tube is now closed. When all is properly arranged, the gas is transferred into the laboratory tube, and the stop-cock opened, admitting a stream of mercury. The cock *c* is gently turned, so as just to arrest the flow of mercury through the apparatus, and the reservoir lowered to about the level of the table, which is usually sufficient. By carefully opening the cock *c*, the gas is drawn over into the measuring tube, and when the mercury has reached a point in the capillary tube of the laboratory tube, about midway between the bend and the stop-cock, the latter is quickly closed. It is necessary that this stop-cock should be very perfect.

This is attained by grinding the plug into the socket with fine levigated rouge and solution of sodic or potassic hydrate. By this means the plug and socket may be polished so that a very small quantity of resin cerate and a drop of oil renders it perfectly gas-tight. In grinding, care must be taken that the operation is not carried on too long, otherwise the hole in the plug may not coincide with the tubes. If this stop-cock is in sufficiently good order, it is unnecessary to close the stop-cock *a* during an analysis.

The mercury is allowed to flow out of the apparatus until its surface is a short distance below the division at which the measurements are to be made. The selection of the division depends on the quantity of gas and the kind of experiment to be performed with it. A saving of calculation is effected if all the measurements in one analysis are carried on at the same division. When the mercury has descended below the division, the cock *c* is closed, the reservoir raised, and the black screen moved until its lower edge is about a millimeter above the division, and the telescope placed so that the image of the division coincides with the cross-wires in the eye-piece. The stop-cock *c* is now gently opened until the meniscus just touches the division; the cock is closed and the height of the mercury in the barometer is measured by means of the telescope. The difference between the reading of the barometer, and the number in the table corresponding to the division at which the measurement is taken, gives in millimeters the tension of the gas. The volume of the gas is found in the same table, and with the temperature, which is read off at the same time as the pressure, all the data required for the calculation of the volume of the gas at 0° and 760 m.m. are obtained. No correction is required for tension of aqueous vapour; the measuring tube and barometer tube being both moist, the tensions in the tubes are counterbalanced. Absorptions are performed with liquid re-agents by introducing a few drops of the liquid into the laboratory tube, transferring the gas into it, and allowing the mercury to drop slowly through the gas for about five minutes. The gas is then passed over into the measuring tube, and the difference of tension observed corresponds to the amount of gas absorbed. It is scarcely necessary to add, that the greatest care must be taken to prevent any trace of the re-agent passing the stop-cock. If such an accident should occur, the measuring tube must be washed out several times with distilled water at the conclusion of the analysis. If the re-agent is a solution of potassic hydrate it may be got rid of by introducing into the tube some distilled water, to which a drop of sulphuric acid has been added. If this liquid is found to be acid on removing it from the tube, it may be presumed that all the alkali has been neutralized.

When explosions are to be performed in the apparatus, the gas is first measured and then returned to the laboratory tube. A quantity of oxygen or hydrogen, as the case may be, which is judged to be the proper volume, is transferred into the laboratory tube, and some mercury is allowed to stream through the gases so as to mix them thoroughly. The mixture is next passed into the eudiometer and measured. If a sufficient quantity of the second gas has not been added, more can readily be introduced. After the measurement, it may be advisable to expand the mixture, in order to diminish the force of the explosion. This is done by allowing mercury to flow out from the tube into the reservoir. When the proper amount of expansion has been reached, the stop-cocks *a* and *b* are closed. To enable the electric spark to pass between the wires, it is necessary to lower the level of the water in the cylinder. For this purpose, the bent glass tube at the extremity of the syphon is made to slide easily through the cork which closes the top of the wide tube J. By depressing the bent tube, the water flows out more rapidly than before, and the level consequently falls. When the surface is below the eudiometer wires, a spark from an induction-coil is passed, exploding the gas. The syphon tube is immediately raised, and, when the water in the cylinder has reached its original level, the gas is cool enough for measurement. 900 c.c. of mercury are amply sufficient for the whole apparatus ; and as there is no cement used to fasten the wide tubes into iron sockets, a great difficulty in the original apparatus is avoided.

The following details of an analysis, in which absorptions only were performed, will show the method employed. The gas was a mixture of nitrogen, oxygen, and carbonic anhydride, and the measurements were all made at division No. 1 on the eudiometer, which has been found to contain 8·6892 c.c.

### Original Gas.

| | mm. |
|---|---|
| Temperature of water in cylinder, 15·4°. | |
| Height of mercury in barometer tube . . . . . . | 980·5 |
| „ „ corresponding to Division No. 1 (see Table) . . . . . . . . . . . | 756·9 |
| Pressure of the gas . . . . . . . . . . | 223·6 |

After absorption of the carbonic anhydride by solution of potassic hydrate—

| | |
|---|---|
| Height of mercury in barometer tube . . . . . | 941·7 |
| „ „ corresponding to Division No. 1 | 756·9 |
| Pressure of the gas after removal of carbonic anhydride | 184·8 |
| Pressure of original gas . . . . . . . . | 223·6 |
| „ gas after removal of carbonic anhydride . | 184·8 |
| Tension of carbonic anhydride . . . . . . . | 38·8 |

After absorption of the oxygen by potassic pyrogallate—

| | |
|---|---|
| Height of mercury in barometer tube . . . . . | 885·4 |
| „ „ corresponding to Division No. 1 | 756·9 |
| Pressure of nitrogen . . . . . . . . . | 128·5 |

| | |
|---|---|
| Pressure of oxygen and nitrogen | 184·8 |
| „ nitrogen | 128·5 |
| „ oxygen | 56·3 |

These measurements, therefore, give us the following numbers :—

| | m.m. |
|---|---|
| Pressure of nitrogen | 128·5 |
| „ oxygen | 56·3 |
| „ carbonic anhydride | 38·8 |
| „ original gas | 223·6 |

If the percentage composition of the gas is required, it is readily obtained by a simple proportion, the temperature having remained constant during the experiment :—

$$\begin{array}{ccccccccl}
\text{m.m.} & & \text{m.m.} & & & & & & \text{m.m.} \\
223{\cdot}6 & : & 128{\cdot}5 & :: & 100 & : & & & 57{\cdot}469 \text{ per cent. N} \\
223{\cdot}6 & : & 56{\cdot}3 & :: & 100 & : & & & 25{\cdot}179 \text{ per cent. O} \\
223{\cdot}6 & : & 38{\cdot}8 & :: & 100 & : & & & 17{\cdot}352 \text{ per cent. CO}^2 \\
 & & & & & & & & \overline{100{\cdot}000}
\end{array}$$

If, however, it is necessary to calculate the number of cubic centimeters of the gases at 0° and 760 m.m., it is done by the following formulæ :—

$$\frac{8{\cdot}6892 \times 128{\cdot}5}{760 \times [1 + (0{\cdot}003665 \times 15{\cdot}4)]} = 1{\cdot}3906 \text{ c.c. of nitrogen.}$$

$$\frac{8{\cdot}6892 \times 56{\cdot}3}{760 \times [1 + (0{\cdot}003665 \times 15{\cdot}4)]} = 0{\cdot}6093 \text{ c.c. of oxygen.}$$

$$\frac{8{\cdot}6892 \times 38{\cdot}8}{760 \times [1 + (0{\cdot}003665 \times 15{\cdot}4)]} = 0{\cdot}4199 \text{ c.c. of carbonic anhydride.}$$

$$\frac{8{\cdot}6892 \times 223{\cdot}6}{760 \times [1 + (0{\cdot}003665 \times 15{\cdot}4)]} = 2{\cdot}4198 \text{ c.c. of the original gas.}$$

If many of the calculations are to be done, they may be very much simplified by constructing a table containing the logarithms of the quotients obtained by dividing the contents of each division of the tube by $760 \times (1 + 0{\cdot}003665t)$. The following is a very short extract from such a table :—

| T°. | Division No. 1.<br>$\text{Log.} \frac{8{\cdot}6892}{760 \times (1 + \delta t)}$. | Division No. 2.<br>$\text{Log.} \frac{18{\cdot}1621}{760 \times (1 + \delta t)}$. |
|---|---|---|
| 15·0 | $\bar{2}{\cdot}03492$ | $\bar{2}{\cdot}35511$ |
| ·1 | $\bar{2}{\cdot}03477$ | $\bar{2}{\cdot}35496$ |
| ·2 | $\bar{2}{\cdot}03462$ | $\bar{2}{\cdot}35481$ |
| ·3 | $\bar{2}{\cdot}03447$ | $\bar{2}{\cdot}35466$ |
| ·4 | $\bar{2}{\cdot}03432$ | $\bar{2}{\cdot}34451$ |

By adding the logarithms of the tensions of the gases to those in the above table, the logarithms of the quantities of gases are obtained; thus:—

| | |
|---|---|
| Log. corresponding to Division No. 1, and 15·4° . . . . . . | $\bar{2}$·03432 |
| Log. 128·5 = pressure of nitrogen . | $\bar{2}$·10890 |
| Log. of quantity of nitrogen . . | 0·14322 = log. 1·3906 |
| Volume of nitrogen at 0° and 760 m.m. . . . . | 1·3906 c.c. |
| | $\bar{2}$·03432 |
| Log. 56·3 = pressure of oxygen . | 1·75051 |
| Log of quantity of oxygen . . | $\bar{1}$·78483 = log. 0·6093 |
| Volume of oxygen at 0° and 760 m.m. . . . . | 0·6093 c.c. |
| | $\bar{2}$·03432 |
| Log. 38·8 = pressure of carbonic anhydride . . . . . . . | 1·58883 |
| Log. of quantity of carbonic anhydride . . . . . . | $\bar{1}$·62315 = log. 0·4199 |
| Volume of carbonic anhydride at 0° and 760 m.m. . . . | 0·4199 c.c. |
| | $\bar{2}$·03432 |
| Log. 223·6 = pressure of original gas | 2·34947 |
| Log. of quantity of original gas . | 0·38379 = log. 2·4198 |
| Volume of original gas at 0° and 760 m.m. . . . . | 2·4198 c.c. |

| | | | |
|---|---|---|---|
| Nitrogen . . . | 1·3906 | or | 1·391 c.c. |
| Oxygen . . . | 0·6093 | or | 0·609 c.c. |
| Carbonic anhydride . | 0·4199 | or | 0·420 c.c. |
| Total . . | 2·4198 | or | 2·420 c.c. |

The following example of an analysis of coal gas will show the mode of working with this apparatus, and the various operations to be performed in order to determine the carbonic anhydride, oxygen, hydrocarbons absorbed by Nordhausen sulphuric acid, hydrogen, marsh gas, carbonic oxide, and nitrogen.

The measuring tube and laboratory tube were first filled with mercury, some of the gas introduced into the laboratory tube, and passed into the apparatus.

The gas was measured at the second division.

| | |
|---|---|
| Height of mercury in the barometer tube . | 989·0 |
| ,, ,, ,, measuring tube . | 706·8 |
| Pressure of the gas at 16·6° | 282·2 |

Two or three drops of a solution of potassic hydrate were now placed in the laboratory tube, and the gas passed from the measuring tube, the mercury being allowed to drop through the gas for ten minutes. On measuring again—

Height of mercury in barometer . . . . 984·0

Some saturated solution of pyrogallic acid was introduced into the laboratory tube, and the gas left in contact with the liquid for ten minutes. On measuring—

Height of mercury in barometer . . . . 983·6

| | |
|---|---|
| Height of mercury when measuring original gas | 989·0 |
| ,, ,, after absorption of $CO^2$ . | 984·0 |
| Pressure of $CO^2$ | 5·0 |
| ,, ,, after absorption of $CO^2$ . | 984·0 |
| ,, ,, after absorption of O . | 983·6 |
| Pressure of O | 0·4 |

The volumes of the gases being proportional to their pressures, it is simple to obtain the percentages of carbonic anhydride and oxygen in the original gas.

| Original gas. | | $CO^2$ | | | | |
|---|---|---|---|---|---|---|
| 282·2 | : | 5·0 | : : | 100 | : | 1·772 per cent. $CO^2$ |
| **Original gas.** | | O | | | | |
| 282·2 | : | 0·4 | : : | 100 | : | 0·142 per cent. O |
| | | | | | | 1·914 |

By subtracting 1·914 from 100, we obtain the remainder, 98·086, consisting of the hydrocarbons absorbed by Nordhausen sulphuric acid, hydrogen, carbonic oxide, marsh gas, and nitrogen ; thus :—

| | |
|---|---|
| Original gas . . . . . . . . | 100·000 |
| O and $CO^2$ . . . . . . . . | 1·914 |
| $CnH^2n$. H. CO. $CH^4$. N . . . . . | 98·086 |

While the gas remains in the measuring tube, the laboratory tube is removed, washed, dried, filled with mercury, and again attached to the apparatus. Much time is saved by replacing the laboratory tube by a second, which was previously ready. As a minute quantity of gas is lost in this operation, in consequence of the amount between the stop-cocks being replaced by mercury, it is advisable to pass the gas into the laboratory tube, then transfer it to the eudiometer, and measure again.

| | |
|---|---|
| On remeasuring, the mercury in the barometer stood at . . . . . . . . . | 983·3 |
| The mercury in the measuring tube . . . . | 706·8 |
| Pressure of $CnH^2n$. H. CO. $CH^4$. N | 276·5 |

The gas is again passed into the laboratory tube, and a coke ball, soaked in fuming sulphuric acid, left in contact with the gas for an hour; the bullet is then withdrawn, and some potassic hydrate introduced and left in the tube for ten minutes, in order to remove the vapours of sulphuric anhydride, and the sulphurous and carbonic anhydrides formed during the action of the Nordhausen acid on the gas. The gas is now measured again.

| | |
|---|---|
| Height of mercury in barometer tube . . | 969·3 |
| " " " before absorbing $CnH^{2}n$ . . . . . . . . | 983·3 |
| " " " after . | 969·3 |
| Pressure of $CnH^{2}n$ | 14·0 |

The percentage of these hydrocarbons is thus formed :—

Gas containing $CnH^{2}n$. H. CO. $CH^{4}$. N.

$$276·5 \; : \; \overset{CnH^{2}n,}{14·0} \; :: \; 98·086 \; : \; \underline{4·966} \text{ per cent. } CnH^{2}n$$

It now remains to determine the hydrogen, carbonic oxide, marsh gas, and nitrogen in a portion of the residual gas. The laboratory tube is therefore removed, some of the gas allowed to escape, and another laboratory tube adapted to the apparatus. The portion of gas remaining is expanded to a lower ring (in this special case to the third division), and the tension measured :—

| | |
|---|---|
| Height of mercury in the barometer tube . . | 642·2 |
| " " measuring tube . . | 606·7 |
| Pressure of residue | 35·5 |

An excess of oxygen has now to be added. For this purpose the gas is passed into the laboratory tube, and about five times its volume of oxygen introduced from a test tube or gas pipette. The necessary quantity of oxygen is conveniently estimated by the aid of rough graduations on the laboratory tube, which are made by introducing successive quantities of air from a small tube in the manner previously described for the calibration of the eudiometers.

After the introduction of the oxygen, the mixed gases are passed into the eudiometer and measured.

| | |
|---|---|
| Height of mercury in the eudiometer after addition of O . . . . . . . . . | 789·5 |

The mixture has now to be exploded, and when the pressure is considerable, it is advisable to expand the gas so as to moderate the violence of the explosion. When sufficiently dilated, the stop-cock at the bottom of the eudiometer is closed, the level of the water lowered beneath the platinum wires by depressing the syphon, and the spark passed. The explosion should be so powerful that it should be audible, and the flash visible in not too bright daylight.

The stop-cock at the bottom of the eudiometer is now opened, and the gas measured.

| | |
|---|---|
| Height of mercury in barometer after explosion . | 732·5 |

The difference between this reading and the previous one gives the contraction produced by the explosion :—

| | |
|---|---|
| Height of mercury in barometer before explosion | 789·5 |
| ,, ,, ,, after ,, | 732·5 |
| Contraction = C | 57·0 |

It is now necessary to estimate the amount of carbonic anhydride formed. This is done by absorbing with potassic hydrate as before described.

| | |
|---|---|
| Height of mercury in barometer tube after absorbing $CO^2$ . . . . . . . | 715·8 |

This number deducted from the last reading gives the carbonic anhydride.

| | |
|---|---|
| Height of mercury in barometer after exploding . | 732·5 |
| ,, ,, ,, after absorbing $CO^2$ | 715·8 |
| Carbonic anhydride = D | 16·7 |

It now remains to determine the quantity of oxygen which was not consumed in the explosion, and which excess now exists mingled with the nitrogen. For this purpose, a volume of hydrogen about three times as great as that of the residual gas is added, in the same way as the oxygen was previously introduced, and the pressure of the mixture determined.

| | |
|---|---|
| Height of mercury in barometer after adding H | 1031·3 |

This mixture is exploded and another reading taken.

| | |
|---|---|
| Height of mercury in barometer after exploding with H . . . . . . . . | 706·7 |

This number subtracted from the former, and the difference divided by 3, gives the excess of oxygen.

| | |
|---|---|
| Height of mercury in barometer before exploding with H . . . . . . . . | 1031·3 |
| Height of mercury in barometer after exploding with H . . . . . . . . | 706·7 |
| | 3) 324·6 |
| Excess of oxygen | 108·2 |

In order to obtain the quantity of nitrogen in the gas analyzed, this number has to be deducted from the volume of gas remaining after the explosion with oxygen and the removal of the carbonic anhydride.

| | |
|---|---|
| Height of mercury in barometer after absorbing $CO^2$ | 715·8 |
| ″ ″ in eudiometer at division No. 3 | 606·7 |
| Nitrogen and excess of oxygen | 109·1 |
| Excess of oxygen | 108·2 |
| Nitrogen | 0·9 |

We have now all the data necessary for the calculation of the composition of the coal gas. It is first requisite to calculate the proportion of the combustible gas present in the coal gas, which is done by deducting the sum of the percentages of gas determined by absorption from 100.

| | |
|---|---|
| Percentage of carbonic anhydride | 1·772 |
| ″ oxygen | 0·142 |
| ″ $CnH^2n$ | 4·966 |
| $CO^2$. O. $CnH^2n$ | 6·880 |
| Original gas | 100·000 |
| $CO^2$. O. $CnH^2n$ | 6·880 |
| H. CO. $CH^4$. N | 93·120 |

The formulæ for the calculation of the analysis of a mixture of hydrogen, carbonic oxide, and marsh gas, are (see page 437)—

$$\text{Hydrogen} = x = A - D$$

$$\text{Carbonic oxide} = y = \frac{3A - 2C + D}{3}$$

$$\text{Marsh gas} = z = \frac{2C - 3A + 2D}{3}$$

$$A = 35{\cdot}5 - 0{\cdot}9 = 34{\cdot}6$$
$$C = 57{\cdot}0$$
$$D = 16{\cdot}7$$

$$\begin{array}{rr} A = & 34{\cdot}6 \\ D = & 16{\cdot}7 \\ \hline & 17{\cdot}9 \end{array} = x = \text{Hydrogen in } 35{\cdot}5 \text{ of the gas exploded with oxygen.}$$

$$\begin{array}{rr} A = & 34{\cdot}6 \\ & 3 \\ \hline 3A = & 103{\cdot}8 \\ D = & 16{\cdot}7 \\ \hline 3A + D = & 120{\cdot}5 \\ 2C = & 114{\cdot}0 \\ \hline 3) & 6{\cdot}5 \end{array} = 3A + D - 2C \qquad \begin{array}{rr} C = & 57{\cdot}0 \\ & 2 \\ \hline 2C = & \underline{114{\cdot}0} \end{array}$$

$$\frac{3A + D - 2C}{3} = \underline{2{\cdot}167} = y = \text{Carbonic oxide in } 35{\cdot}5 \text{ of the gas.}$$

$$
\begin{array}{rr}
D = & 16{\cdot}7 \\
 & 2 \\
\hline
2D = & 33{\cdot}4 \\
2C = & 114{\cdot}0 \\
\hline
2D + 2C = & 147{\cdot}4 \\
3A = & 103{\cdot}8 \\
\hline
 & 3)\ 43{\cdot}6 = 2D + 2C - 3A
\end{array}
$$

$$\frac{2D + 2C - 3A}{3} = \underline{14{\cdot}533} = z = \text{Marsh gas in } 35{\cdot}5 \text{ of the gas.}$$

These numbers are readily transformed into percentages, thus :—

35·5 : 17·9 : : 93·12 : 46·952 per cent. of Hydrogen.
35·5 : 2·167 : : 93·12 : 5·684 per cent. of Carbonic oxide.
35·5 : 14·533 : : 93·12 : 38·122 per cent. of Marsh gas.
35·5 : 0·9 : : 93·12 : 2·361 per cent. of Nitrogen.

This completes the calculations, the results of which are as follows :—

| | |
|---|---|
| Hydrogen . . . . | 46·952 |
| Marsh gas . . . . | 38·122 |
| $CnH^2n$ . . . . . | 4·966 |
| Carbonic oxide . . . | 5·684 |
| Carbonic anhydride . . | 1·772 |
| Oxygen . . . . | 0·142 |
| Nitrogen . . . . | 2·361 |
| | 99·999 |

It is obvious that this analysis is not quite complete, since it does not give any notion of the composition of the hydrocarbons absorbed by the Nordhausen acid. To determine this, some of the original gas, after the removal of carbonic anhydride and oxygen, is exploded with oxygen, and the contraction and carbonic anhydride produced are measured. The foregoing experiments have shown the effect due to the hydrogen, carbonic oxide, and marsh gas, the excess obtained in the last explosion being obviously caused by the hydrocarbons dissolved by the sulphuric acid, and from these data the composition of the gas may be calculated.

It may be remarked that analyses of this kind were performed with the apparatus at the rate of two a day when working for seven hours.

It may be useful to show how this analysis appears in the laboratory note-book :—

## *Analysis of Coal Gas.*

989·0
706·8
282·2 (16·6°) original gas

984·0 Aft. absorb. $CO^2$

983·6 Aft. absorb. O

983·3 Remeasured

969·3 Aft. absorb. $CnH^2n$

642·2
606·7
35·5 Portion of Residue

789·5 with O

732·5 Aft. expl.
715·8 Aft. absorb. $CO^2$

1031·3 with H
706·7 Aft. expl.

989·0
984·0
5·0 = $CO^2$

984·0
983·6
0·4 = O

282·2 : 5·0 : : 100 : 1·772 $CO^2$
282·2 : 0·4 : : 100 : 0·142 O
1·914

100·000
1·914 $CO^2$. O
98·086 $CnH^2n$. H. CO. $CH^4$. N

983·3
706·8
276·5

983·3
969·3
14·0 $CnH^2n$

276·5 : 14·0 : : 98·086 : 4·966 $CnH^2n$

$CO^2$ = 1·772
O = 0·142
$CnH^2n$ = 4·966
6·880

35·5 = H. CO. $CH^4$. N
0·9 = N
34·6 = H. CO. $CH^4$ = A

789·5
732·5
57·0 = contraction = C

732·5
715·8
16·7 = $CO^2$ = D

1031·3
706·7
3) 324·6
108·2 = O

715·8
606·7
109·1 = N + O
108·2 = O
0·9 = N

$$H = x = A - D = 17·9$$

$$CO = y = \frac{3A - 2C + D}{3} = 2·167$$

$$CH^4 = z = \frac{2C - 3A + 2D}{3} = 14·533$$

34·600

34·6 = A
16·7 = D
17·9 = $x$ = H

57·0 = C
2
114·0 = 2C

34·6 = A
3
103·8 = 3A
16·7 = D
120·5 = 3A + D
114·0 = 2C
3) 6·5 = 3A + D - 2C
2·167 = $y$ = CO

16·7 = D
2
33·4 = 2D
114·0 = 2C
147·4 = 2C + 2D
103·8 = 3A
3) 43·6 = 2D + 2C - 3A
14·533 = $z$ = $CH^4$

100·000
6·880 CO. O. $CnH^2n$
93·120 H. CO. $CH^4$. N

35·5 : 17·9 : : 93·12 : 46·952 H
35·5 : 2·167 : : 93·12 : 5·684 CO
35·5 : 14·533 : : 93·12 : 38·122 $CH^4$
35·5 : 0·9 : : 93·12 : 2·361 N

H = 46·952
$CH^4$ = 38·122
$CnH^2n$ = 4·966
CO = 5·684
$CO^2$ = 1·772
O = 0·142
N = 2·361

99·999

It is assumed in the above example, that the temperature of the water in the cylinder remained constant throughout the period occupied in performing the analysis. As this very rarely happens, the temperature should be carefully read off after every measurement of the gas and noted, in order that due correction be made for any increase or decrease of volume which may result in consequence.

## THOMAS'S IMPROVED GAS APPARATUS.

In the *Chemical Society's Journal* for May, 1879, Thomas described an apparatus for gas analysis which has the closed pressure tube of Frankland and Ward, and is supplied with mercury by means of the flexible caoutchouc tube arrangement of Mc Leod. The manner in which this apparatus is filled with mercury and got into order for working is so similar to that already described, that no further reference need be made thereto.

The eudiometer is only 450 m.m. long from shoulder to shoulder, and the laboratory tube and mercury trough are under the command of the operator from the floor level. The eudiometer has divisions 20 m.m. apart, excepting the uppermost, which is placed as close beneath the platinum wires as is convenient to obtain a reading. The method explained in sequel of exploding combustible gases under reduced pressure, without adding excess of gas to modify the force of the explosion, permits the shortening of the eudiometer as above, and enables the apparatus to be so erected, that a long column of the barometer tube shall stand above the summit of the eudiometer. By means of such an arrangement a volume of gas may be measured under nearly atmospheric pressure, and as this pressure is equal to more than 700 m.m., plus aqueous tension, the sensitiveness of the apparatus is considerably augmented. The barometer tube is 1000 m.m. in length, having about 700 m.m. lines above Division 2 on the eudiometer. The steel clamp and facets forming the connections between the eudiometer and detachable laboratory tube of the apparatus previously described are dispensed with, as in this form the eudiometer and laboratory vessels are united by a continuous capillary tube, 12 m.m. (outside) diameter, and one three-way glass tap is employed in lieu of the two stop-cocks. The arrangement is simple. The glass tap is hollow in the centre, and through this hollow a communication is made with the capillary, by means of which either the laboratory tube or the eudiometer can be washed out. As the laboratory vessel is not disconnected for the removal of the re-agent used in an absorption, it is supported by a clamp, as shown in the drawing; and when it requires washing out the mercury trough is turned aside, in order that an enema syringe may be used for injecting a stream of water. A few drops of water are let fall into the hollow of the tap, and blown through the capillary tube three times in succession, so as to get rid of the absorbent remaining in the capillary, then the syringe is brought into play once more, the excess of water removed by wiping, and the trough turned back into position. The laboratory tube may be refilled with mercury as described on page 449; but it will be found much more serviceable if a double-acting syringe, connected to a bulb apparatus (to catch any mercury that may come over), and then to the orifice of the hollow in the tap by a ground perforated stopper be used, as this will obviate the destructive effect of heavy suction upon the gums and teeth. The mercury trough is supported upon a guide which travels over the upright U, and is turned aside for the purpose of washing out the laboratory vessel in the following manner:--The spiral spring is depressed by means of the tension rods until the slot is brought below the stud fixed in the upright U; and the top ferrule holding the guide rods being movable, the trough can be turned round out of the way, but is prevented from coming in contact with the glass water-cylinder by an arrangement in the top of the guide, which comes against the stud in the upright. The height of the trough can be accurately adjusted by the screw in the top of the lever guide. When the trough is in position, the clamp holding the laboratory vessel may be loosed when necessary.

The eudiometer and barometer tubes pass through an india-rubber cork, as in Mc Leod's apparatus, but are not supported by the clamp C, which here simply bears the water-cylinder. No glass stop-cocks are used, or glass-work of any kind employed in the construction of the lower portion of the apparatus. The lower end of the eudiometer has a neck of the same outside diameter as the barometer tube (9·5 m.m.), and both tubes are fixed into the steel block X, without rigidity, by the usual steam cylinder-gland arrangement, small india-rubber rings being used to form the packing. The steel block is fixed to the table by a nut screwed upon the ⅜-inch hydraulic iron tube, which runs to the bottom of the table. The tap in the steel block is so devised that it first cuts off connection with the barometer tube, in order that the gas may be drawn over from the laboratory vessel into the eudiometer without risking the fracture of the upper end of the barometer tube by any sudden action of the mercury. This precaution is necessary, as during the transferring of the gas the mercury in the barometer tube is on the point of lowering, to leave a vacuous space in the summit of the tube. By moving the handle a little further on the quadrant a communication is made with both tubes and the reservoir for the purpose of bringing the gas into position, so as to take a reading; then the handle is drawn a little further to cut off

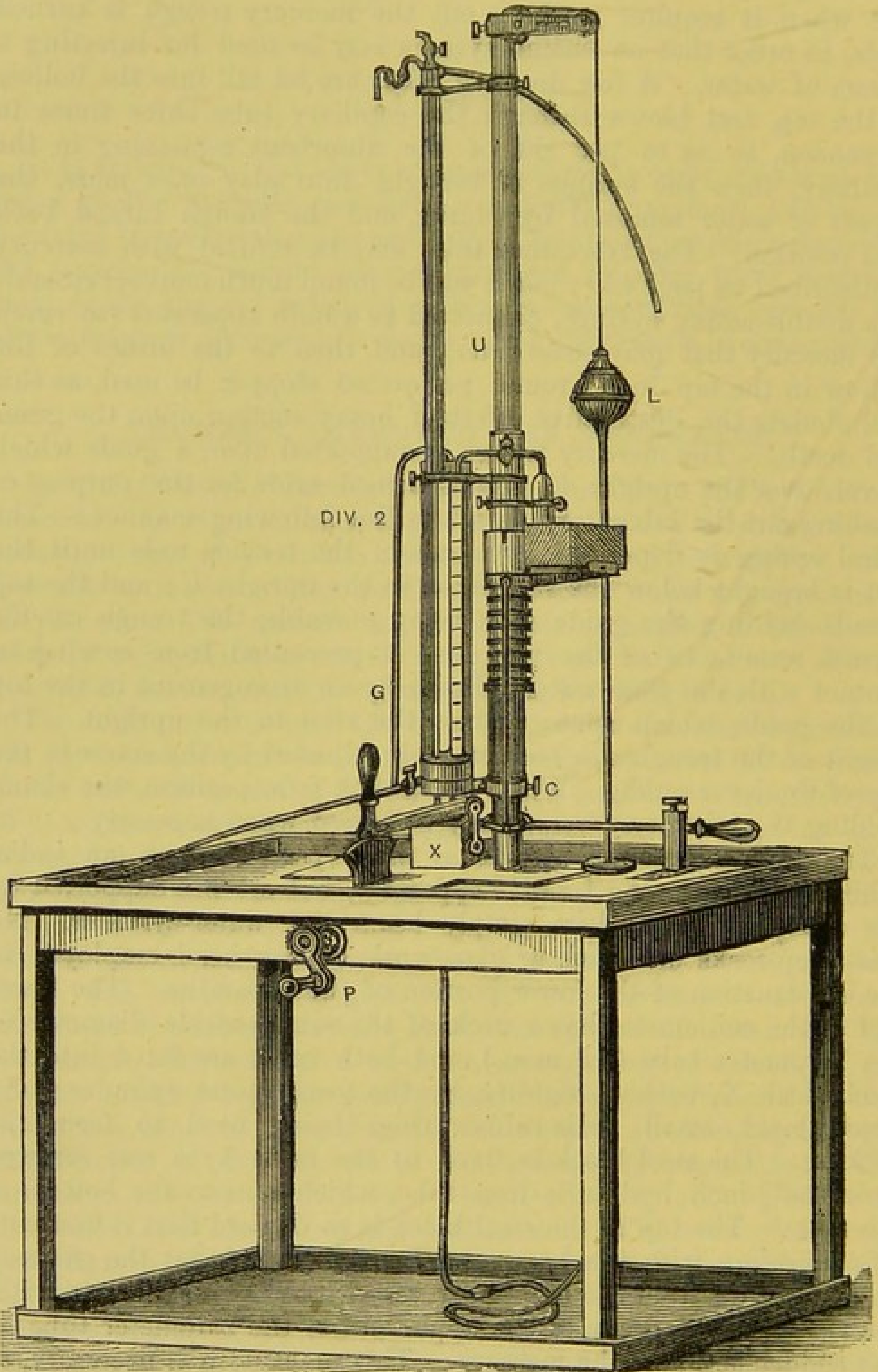

Fig. 81.

the reservoir supply, whilst there is a way still left between the eudiometer and barometer tubes, and if the handle be drawn forward a little more, all communication is cut off for the purpose of exploding.

The windlass P, for raising and lowering the mercury reservoir L, is placed beneath the table, in order that it may be under command from a position opposite the laboratory vessel, and it is furnished with a spring ratchet motion, so as to be worked by one hand. The water-cylinder should be four inches in diameter, and the casing tube of the barometer as wide as practicable, so that the temperature of the apparatus may be maintained as constant as possible. To attain an accurate result it is as essential to keep the barometer tube of uniform temperature as the eudiometer, since the tension of aqueous vapour varies proportionally. The stream of water from the service main is run into the casing tube at the upper end of the barometer, and, whilst the water-cylinder is filling, the tap at the bottom is opened slightly, so that water may run out very slowly. When the water-cylinder is full, the upright tube G acts as a syphon, and sucks out the excess of water from the top of the cylinder, thus keeping up the circulation at the point where it is most required. For a further detailed description of the apparatus see *J. C. S.*, May, 1879.

There are only two working taps upon this apparatus;—the three-way glass tap between the eudiometer and laboratory tube, and the steel tap at the lower ends of the barometer and eudiometer. The steel tap is greased with a little beef-tallow (made from clean beef-suet), or with real Russian tallow; it will last for twelve months without further attention. A moderately thick washer of india-rubber, placed between the steel washer and the nut at the end of the steel tap, adds greatly to the steady working of the needle on the quadrant. Moderately soft resin cerate is best for the glass tap.

When filling the laboratory vessel with mercury, suction is maintained until the mercury has reached some height in the hollow of the three-way tap. The remainder of the hollow space is replenished by pouring the mercury from a small crucible; any water that may be present is then removed, and the small stopper inserted. When the laboratory vessel has to be washed out after an absorption, the gas is transferred to the eudiometer until the absorbent gets within a quarter of an inch of the stop-cock. The mechanical arrangement should be so manageable that this nicety of adjustment can be accomplished with ease. Much depends, of course, upon the care bestowed in cerating the tap, so that the capillary is not carelessly blocked up. As soon as the gas has passed over to the extent required, turn the three-way tap until the through-way is at right angles to the capillary, and the way to the hollow of the tap is in communication with the laboratory vessel, then take out the little stopper from the hollow, so that the mercury shall flow out, and allow the laboratory vessel to become emptied whilst the reading of the volume of the gas is being taken. The best arrangement for washing out the laboratory tube is a "syphon enema" (Dr. Higginson's principle, which may be obtained of any druggist), adapting in the place of the usual nozzle a bent glass tube. This syringe is constant in its action, as it fills itself when the pressure is released, if the tube at the lower end is placed in a vessel of water. The laboratory vessel can be washed out and refilled in a very little time, as it is already connected, and for all ordinary absorptions it is sufficient to wipe the vessel out once by passing up a fine towel twisted on a round stick. When $CnH^2n$ gases are to be absorbed by fuming sulphuric acid, the water should be carefully blown out of the capillary tube into the laboratory vessel, which must be repeatedly dried. A few drops of strong sulphuric acid were at first run into the hollow of the tap and then through the capillary whilst the laboratory vessel was full of mercury, in order to remove any moisture remaining, but it has since been found unnecessary, as the drying can be performed thoroughly without.

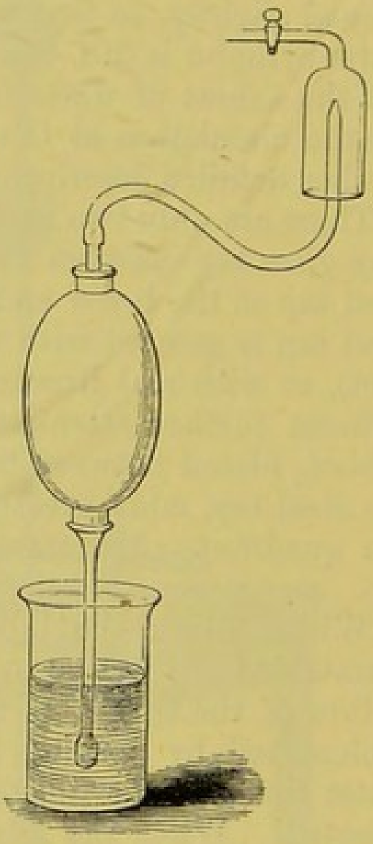

Fig. 82.

To calibrate the eudiometer with water, introduce the quantity required through the hollow in the stopper, then remove the latter, and collect the water in a light flask from the bottom of the tap-socket.

In the same paper (*J. C. S.*, May, 1879), Thomas pointed out that it was not essential to add excess of either oxygen or hydrogen for the purpose of modifying the force of the explosion when combustible gases were under analysis, and it is necessary to take advantage of this when working with so short an eudiometer. The method is, however, applicable to all gas apparatus having a reasonable length of barometer column above the eudiometer; in fact, the exploding pressures were first worked out and employed in an apparatus on McLeod's model. When the percentage of oxygen in a sample of air has to be determined by explosion, only one-half its volume of hydrogen is required, and the pressure need not be reduced below 400 m.m. If much more than one-half volume of hydrogen has been added by accident, explode under atmospheric pressure. When the excess of oxygen used in an analysis has to be determined, add 2·5 times its volume of hydrogen, and reduce the pressure to 180 m.m. of mercury before exploding. After adding the hydrogen and the reading has been taken, the gas is expanded by lowering the mercurial reservoir until a column of mercury, measuring the number of m.m.'s in length just referred to and in the following table, stands above the meniscus of the mercury in the eudiometer. This column can be read off quite near enough by the eye, as there is no risk of breaking the apparatus by the force of the explosion if the pressure is 20 m.m. greater than that given; but if the gas under analysis is all combustible, it is better to explode at a slightly less pressure than to exceed that recommended.

| Name of Gas. | Volume of Combustible Gas. | Volume of Oxygen to be added. | Pressure of mixture before exploding. |
|---|---|---|---|
| Hydrogen - - - - | 1 | 1 | 200 m.m. |
| Carbonic Oxide - - - | 1 | 1 | 200 m.m. |
| Marsh Gas - - - | 1 | 2·5 | 170 m.m. |
| Acetylene - - - | 1 | 3 | 150 m.m. |
| Olefiant Gas - - - | 1 | 3·5 | 145 m.m. |
| Methyl and Hydride of Ethyl | 1 | 4 | 140 m.m. |
| Propyl - - - - | 1 | 5 | 135 m.m. |
| Hydride of Propyl - - | 1 | 5·5 | 130 m.m. |
| Butyl - - - - | 1 | 6 | 125 m.m. |
| Ethyl and Hydride of Butyl | 1 | 7 | 120 m.m. |

It follows, naturally, that the exploding pressure will depend upon the proportion of combustible gas introduced; and experience alone can enable one to determine with any degree of exactness what that pressure must be, as no general law can be laid down. For instance, if more than three volumes of hydrogen were added to one of oxygen, the exploding pressure should exceed 200 m.m.; and if much nitrogen or other gas were present that did not take a part in the reaction, the pressure should be still more increased. As a consequence, the same experience is necessary when dealing with explosive gases by the other method, because the addition of too much inert gas, with a view to modify the force of the explosion, may lead to imperfect combustion, inasmuch as the cooling effect of the tube and gas can reduce the temperature below that required. In all instances, when the approximate composition of the gas is known, it is not difficult to determine the quantity of oxygen or hydrogen, as the case may be, which is required for explosion, or the pressure under which the gas should be exploded. In order to do this systematically, it is always well to remember certain points observed during the stages of the analysis. The gas in the laboratory vessel, before being transferred to the eudiometer, occupies a certain volume in a position between (or otherwise) the calibration divisions. After transferring and reading off, bear in mind the number of m.m.'s which the volume represents; and calculate, as the gas is being re-transferred to the laboratory vessel to be mixed with that employed in the explosion, the height at which the mercury should stand in the barometer tube when measuring the mixed gases, and how much of the laboratory vessel was occupied on a previous occasion when a similar reading was obtained. If this is done, one can realize at once, after reading off the volume of the mixed gases, the proportion of combustible gas added, and the pressure under which the gas has been measured. Another glance at the volume which the gas occupies in the eudiometer, with a comparison of the pressure recorded upon the barometer tube, enables one, after a little practice, to at once expand the mixture to the point at which it will explode with satisfactory results. It is not expedient to place too much reliance upon the marks showing equal volumes upon the laboratory vessel, especially when dealing with small quantities of gas; and a comparison of the volumes obtained in reading before and after the addition of oxygen or hydrogen is always prudent, in order to see that sufficient gas has been added, as well as to enable one to judge the pressure under which the gas should be exploded.

NOTE.—**Meyer** and **Seubert** (*Z. a. C.* xxiv. 414) have designed a gas apparatus similar in many respects to that of **McLeod** and **Thomas**, but of simpler construction, and especially adapted for explosions under diminished pressure.

### Keiser's Portable Gas Apparatus.

This apparatus is based on the principle of determining the volume of a gas from the weight of mercury which it may be made to displace at a known temperature and pressure. It dispenses entirely with the long graduated tubes and other vessels common to the apparatus previously described, without any sacrifice of accuracy.

The following description occurs in the *Amer. Chem. Journ.*, 1886 (but is reproduced here from *The Analyst*, xi. 106):—

Fig. 83 shows the construction of the measuring apparatus and the absorption pipette. A is the measuring apparatus, B is the absorption pipette; *a* and *b* are glass bulbs of about 150 c.c. capacity. They are connected at the bottom by a glass tube of 1 m.m. bore, carrying the three-way stop-cock *d*. The construction of the key of the stop-cock is shown in the margin. One hole is drilled straight through the key, and by means of this the vessels *a* and *b* may be made to communicate. Another opening is drilled at right angles to the first, which communicates with an opening extending through the handle, but does not communicate with the first opening. By means of this, mercury contained in either *a* or *b* may be allowed to flow out through the handle *d* into a cup placed beneath. The bulb *b* is contracted at the top to an opening 20 m.m. in diameter. This is closed by a rubber stopper carrying a bent glass tube, to which is attached the rubber pump *c*. To a second glass tube passing through the stopper, a short piece of rubber tubing with a pinch-cock is attached. By means of the pump *e* air may be forced into or withdrawn from *b*, as one or the other end of the pump is attached to the glass tube. The bulb *a* terminates at the top in a narrow glass tube, to which is fused the three-way stop-cock *c*. The construction of the key of this stop-cock is also shown in the cut. By means of it the vessel *a* may be allowed to communicate with the outside air, or with the tube passing to the absorption pipette, or with the gauge *g*. The gauge *g* is a glass tube having a bore 1 m.m. in diameter and bent, as shown in the figure. By pouring a few drops of water into the open end of this tube a column of water several centimeters high in both limbs of the tube is obtained. This serves as a manometer, and enables the operator to know when the pressure of the gas equals the atmospheric pressure. To secure a uniform temperature, the bulbs *a* and *b* are surrounded by water contained in a glass vessel. This vessel for holding water is merely an inverted bottle of clear glass from which the bottom has been removed. The handle of the stop-cock *d* passes through a rubber stopper in the neck of the bottle. A thermometer graduated to $\frac{1}{5}^\circ$ is placed in the water near the bulb *a*. The whole apparatus is supported upon a vertical wooden stand.

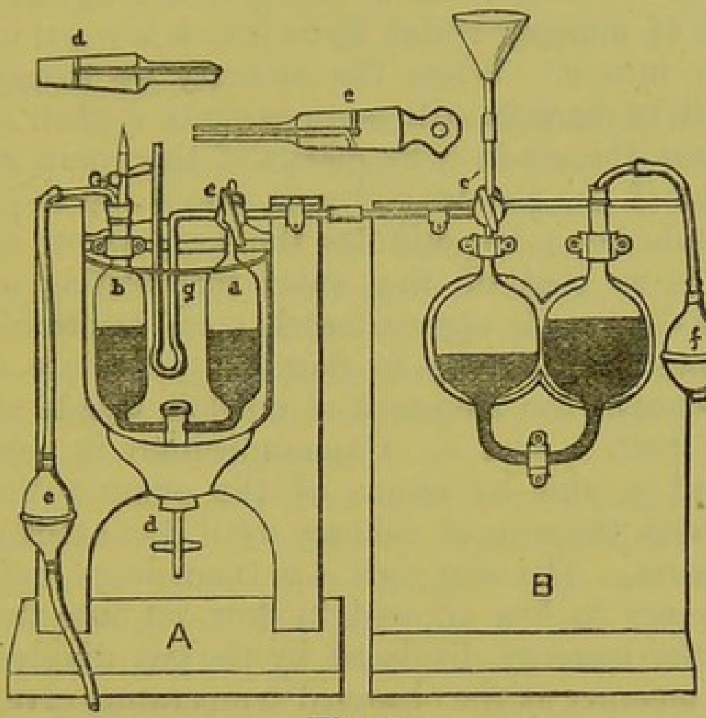

Fig. 83.

The absorption pipette B consists of two nearly spherical glass bulbs of about 300 c.c. capacity. They communicate at the bottom by means of a glass tube, 3 m.m. inside diameter. *c′* is a two-way stop-cock. The holes in the key are drilled at right angles, so that the tube which connects with the measuring apparatus may be put in communication either with the funnel or with the absorption bulb. The funnel is of service in removing air from the tube which connects the measuring apparatus with the absorption pipette. By pouring mercury or water into the funnel and turning the stop-cocks *c′* and *c* in the proper directions all the air is readily removed. *f* is a rubber pump used in transferring gas from B to A. The lower part of the pipette contains mercury, which protects the reagent from the action of the air.

To measure the volume of a gas, the vessel *a* is filled completely with pure mercury. This is easily accomplished by pouring the mercury into *b*, and then, after turning *c* until *a* communicates with the outside air, forcing it into *a* by means of the pump *e*. Any excess of mercury in *b* is then allowed to flow out through the stop-cock *d*. When *a* and *b* are now placed into communication the mercury will flow from *a* to *b*, and gas will be drawn in through the stop-cock *c*. The volume of mercury which flows into *b* is equal to the volume of gas drawn into *a*. When the mercury no longer rises in *b*, and it is desired to draw in still more gas into *a*, then it is only necessary to exhaust the air in *b* by means of the pump *e*. After the desired quantity of gas has been drawn into *a* the stop-cock *c* is closed. After standing a few minutes the temperature of the gas becomes the same as that of the water surrounding *a*. The pressure of the gas is then made approximately equal to atmospheric pressure by allowing the mercury to flow out of *b* into a weighed beaker placed beneath the stop-cock *d* until it stands at nearly the same level in both *a* and *b*. Communication is now established between *a* and *g*, and by means of the pump *e* the pressure can be adjusted with the utmost delicacy until it is exactly equal to atmospheric pressure. The stop-cock *d* is then closed, and the remainder of the mercury in *b* is allowed to flow out into the beaker. The weight of the mercury displaced by the gas divided by the specific gravity of mercury at the observed temperature gives the volume of the gas in cubic centimeters.

If it is desired to remove any constituent of the gas by absorption, a pipette B, containing the appropriate reagent, is attached to the measuring apparatus. All the air in the connecting tube is expelled by pouring mercury into the funnel and turning the stop-cocks *c′* and *c* so that the mercury flows out through *c*. A little more than enough mercury to expel the gas in the vessel *a* is poured into *b*. The small quantity of air which is confined in the tube connecting *b* with the stop-cock is removed by allowing a few drops of mercury to run out through *b*. Then *a* and *b* are placed in communication. The stop-cocks *c* and *c′* are turned so that the gas may pass into the pipette, the mercury which filled the connecting tube passes into the absorbing reagent and unites with that which is already at the bottom of the pipette. The transfer is facilitated by the pump *e*. After absorption the residual volume is measured in the same way that the original volume was measured. *a* is completely filled with mercury from the upper to the lower stop-cock, and all the mercury in *b* is allowed to run out; the gas is then drawn back into the measuring apparatus, the last portion remaining in the connecting tube being displaced by means of mercury from the funnel. The volume is then determined as before.

The calculation of the results of an analysis is very simple. If the temperature and pressure remain the same during an analysis, as is frequently the case, then the weights of mercury obtained are in direct proportion to the gas volumes, and the percentage composition is at once obtained by a simple proportion.

If the temperature and pressure are different when the measurements are made, it is necessary to reduce the volumes to 0° and 760 m.m. The following formula is then used :—

$$V' = \frac{W\,(H - h)}{D\,(1 + 0{\cdot}00367 \times t)\;760},$$

in which

$W$ = weight of mercury obtained (in grams),
$D$ = specific gravity of mercury at $t°$,
$t$ = temperature at which the gas is measured,
$H$ = height of the barometer,
$h$ = tension of aqueous vapour,
$V'$ = reduced gas volume (in cubic centimeters).

In all the measurements made with the apparatus the gas is saturated with aqueous vapour, because it comes in contact with the water in the manometer $g$.

The following experiments were made to test the accuracy of the instrument. A quantity of air was drawn into the measuring bulb and its volume determined. The air was then transferred to an absorption pipette which contained only mercury and no reagent. It was then brought back again into the measuring apparatus and its volume redetermined. The following results were obtained :—

I.

| | Volume at 0°–760 m.m. |
|---|---|
| Volume of air taken | 57·558 c.c. |
| „ after first transfer | 57·567 |
| „ „ second transfer | 57·570 |

II.

| | At 0°–760 m.m. |
|---|---|
| Volume taken | 93·216 c.c. |
| „ after transferring | 93·229 |

III.

| | At 0°–760 m.m. |
|---|---|
| Volume taken | 133·473 c.c. |
| „ after transferring | 133·490 |

IV.

| | At 0°–760 m.m. |
|---|---|
| Volume taken | 92·275 c.c. |
| „ after transferring | 92·260 |

V.

| | At 0°–760 m.m. |
|---|---|
| Volume taken | 109·025 c.c. |
| „ after transferring | 109·020 |

VI.

| | At 0°–760 m.m. |
|---|---|
| Volume taken | 103·970 c.c. |
| „ after first transfer | 103·955 |
| „ „ second transfer | 103·980 |

The apparatus was also tested by making analyses of atmospheric air. It has been shown both by Winkler and Hempel that the composition of the air varies from day to day. This variation is sometimes as much as 0·5 per cent. The causes which produce these fluctuations in the composition of the atmosphere are at present but imperfectly understood. It is therefore desirable to have some simple instrument by means of which the composition of the air may be determined rapidly and yet with great accuracy.

The following analyses show that the apparatus here described is well adapted to this purpose. The reagent used to absorb the oxygen and carbon dioxide was an alkaline solution of pyrogallol, prepared by mixing one volume of a 25 per cent. solution of pyrogallol with six volumes of a 60 per cent. solution of potassic hydrate.

*Analysis of Air taken from the Laboratory.*

I.

| | W | H | t | V′ | Per cent. $O+CO^2$. |
|---|---|---|---|---|---|
| Air taken | 1738·53 | 743·37 | 15·8 | 116·435 c.c. | ... |
| Vol. of nitrogen | 1377·62 | 743·37 | 15·8 | 92·264 | 20·760 |
| „ „ | 1376·40 | 743·55 | 15·75 | 92·255 | 20·771 |

Per cent of O and $CO^2$, 20·765.

II.

| | W | H | t | V′ | Per cent. $O+CO^2$. |
|---|---|---|---|---|---|
| Vol. of air | 1708·01 | 748·08 | 15·0 | 115·546 c.c. | ... |
| „ nitrogen | 1356·04 | 747·33 | 15·2 | 91·564 | 20·755 |

Per cent. of O and $CO^2$ found, 20·755

The following analyses were made with a sample of atmospheric air collected on a subsequent day:—

I.

| | W | H | t | V′ | Per cent. $O+CO^2$. |
|---|---|---|---|---|---|
| Vol. of air | 1704·81 | 754·92 | 12·2 | 117·814 c.c. | ... |
| „ nitrogen | 1348·33 | 754·78 | 12·08 | 93·216 | 20·877 |
| „ „ | 1344·71 | 755·92 | 11·7 | 93·229 | 20·868 |

Per cent. of O and $CO^2$, 20·872.

II.

| | W | H | t | V′ | Per cent. $O+CO^2$. |
|---|---|---|---|---|---|
| Vol. of air | 1669·39 | 756·30 | 10·15 | 116·584 c.c. | ... |
| „ nitrogen | 1323·24 | 755·49 | 10·05 | 92·260 | 20·863 |
| „ „ | 1322·38 | 755·30 | 10·00 | 92·252 | 20·870 |

Per cent. of O and $CO^2$, 20·866

The apparatus described in the preceding pages was made for the author, in most excellent manner, by Mr. Emil Griener, 79, Nassau Street, New York.

## SIMPLER METHODS OF GAS ANALYSIS.

§ 99. All the sets of apparatus previously described are adapted to secure the greatest amount of accuracy, regardless of speed or the time occupied in carrying out the various intricate processes involved.

For industrial and technical purposes the demand for something requiring less time and care, even at the sacrifice of some accuracy, has been met by a large number of designs for apparatus of a simpler class, among which may be mentioned those of Orsat, Bunte, Winkel, Hempel, Stead, Lunge, etc. Many of these are arranged to suit the convenience of special industries, and will not be described here.

The most useful apparatus for general purposes is either that of Hempel or Lunge, both of which will be shortly described. Fuller details as to these and other special kinds of apparatus are contained in Winkler's *Handbook of Technical Gas Analysis*, translated by Lunge.*

The general principles upon which these various sets of apparatus are based, and the calculation of results, are the same as have been described in preceding pages; and of course due regard must be had to tolerable equality of temperature and pressure, and the effects of cold or warm draughts of air upon the apparatus whilst the manipulations are carried on. If the operator is not already familiar with methods of gas analysis, a study of the foregoing sections will be of great assistance in manipulating the apparatus now to be described.

**Simple Titration of Gases.**—Many instances occur in which an absorbable gas can be passed through a solution of known standard in excess, and the measure of the gas being known either by emptying an aspirator of water containing a known volume, or by the use of a gas-meter. The amount of gas absorbed may be found by titration of the standard absorbent residually. Such instances occur in the exit gases of vitriol and chlorine chambers. In the case of vitriol exits the gases are drawn through a standard solution of soda or other alkali contained in Todd's absorption tubes or some similar arrangement, to which is attached a vessel containing a known volume, say exactly $\frac{1}{10}$ of a cubic foot of water. A tap is fixed at the bottom of this vessel, so that when all is tightly fitted and the tap partially opened, a small flow of water is induced, which draws the gases through the absorbent. When the aspirator is empty the flow of gases ceases, and of course the volume of water so run out represents that of the gases passed.

Another way of measuring the gases is to use an india-rubber vessel, which can be compressed by the hand, known as a finger-pump. The volume contents being known by measurement with water or air, the aspirations made by it may be calculated; the aspirated gases are then drawn slowly through the absorbent liquid. In the case of chlorine exits the gases are passed through a solution of potassic iodide in excess, and the amount of liberated iodine subsequently found by titration with standard sodic arsenite. A most convenient vessel is the revolving double glass aspirator, known as Dancer's, or Muencke's.

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* Van Voorst, 1885.

The standard solutions used in these cases are generally so arranged as to avoid calculations, and the result found for legal purposes in England is given in grains per cubic foot, in order to comply with the conditions of the Noxious Vapours Act, which enjoins that not more than 4 grains of $SO^3$, or 2½ grains of Cl, in one cubic foot shall be allowed to pass into the atmosphere.

Sometimes a gas may be estimated by the reaction which takes place when brought in contact with a chemical absorbent, such as the formation of a precipitate, or the change of colour which it produces in an indicator. The gas in this case can be measured by a graduated aspirator, the flow of which is stopped when the peculiar reaction ceases or is manifested.

**Normal Solutions for Gas Analysis.**—In the titration of gases by these methods, particularly on the Continent, the custom is to use special normal solutions, 1 c.c. of which represents 1 c.c. of the absorbable gas in a dry condition, and at 760 m.m. pressure and 0°C. temperature. These solutions must not be confounded with the usual normal solutions used in volumetric analysis of liquids or solids. For instance, a normal gas solution for chlorine would be made by dissolving 4·4288 gm. of $As^2O^3$, with a few grams of sodic bicarbonate to the liter, and a corresponding solution of iodine containing 11·3396 gm. per liter, in order that 1 c.c. of either should correspond to 1 c.c. of chlorine gas. 1 c.c. of the same iodine solution would also represent 1 c.c. of dry $SO^2$, and so on.

A very convenient bottle for the titration of certain gases is adopted by Hesse. It is made in a conical form, like an Erlenmeyer's flask, and has a mark in the short neck, down to which is exactly fitted a caoutchouc stopper having two holes, which will either admit the spit of a burette or pipette, or may be securely closed by solid glass rods. The exact contents of the vessel up to the stopper is ascertained, and a convenient size is about 500 or 600 c.c. The exact volume is marked upon the vessel.

In the case of gases not affected by water, the bottle is filled with that liquid and a portion displaced by the gas, and the stopper with its closed holes inserted. If water cannot be used, the gas is drawn into the empty bottle by means of tubes with an elastic pump. The absorbable constituent of the gas is then estimated with an excess of the standard solution run in from a pipette or burette. During this a volume of the gas escapes equal to the volume of standard solution added, which must of course be deducted from the contents of the absorbing vessel. The gas and liquid are left to react with gentle shaking until complete. The excess of standard solution is then found residually by another corresponding standard solution; and in the case of using gas normal solutions, the difference found corresponds to the volume of the absorbed constituent of the gas in c.c.; and from this, and from the total volume of gas employed, may be calculated the percentage, allowing for the correction mentioned. This arrangement may be used for $CO^2$ in air, using normal gas baric hydrate and a corresponding normal gas oxalic acid with phenolphthalein. The normal oxalic acid should contain 5·6314 gm. per liter, in order that 1 c.c. may represent 1 c.c. of $CO^2$. The baryta solution must correspond, or its relation thereto found by blank experiment at the time. The arrangement is also available for HCl in gases, using a normal gas silver solution containing 4·8233 gm. Ag per liter, as absorbent, with a corresponding solution of thiocyanate (§ 39) and ferric indicator; or the HCl may be absorbed by potash, then acidified with $HNO^3$, and the titration carried out by the same process; or again, an alkaline carbonate may be used, and the titration made with a normal gas silver solution using the chromate indicator (§ 37, 2*b*).

**Hempel's Gas Burette.**—This consists of two tubes of glass on feet, one of which is graduated to 100 c.c. in $\frac{1}{5}$ c.c. (the burette proper), and the other plain (the level tube). They are connected at the feet by an elastic tube, much in the same way as Lunge's nitrometer. The arrangement is shown in fig. 84.

The illustration shows the burette with three-way stop-cock at bottom, which is necessary in the case of gases soluble in water, or where any of the constituents are affected thereby. If this is not the case, a burette without such stop-cock is substituted (fig. 85). The elastic tube should not be in one piece, but connected in the middle by a short length of glass tube to admit of ready disconnection.

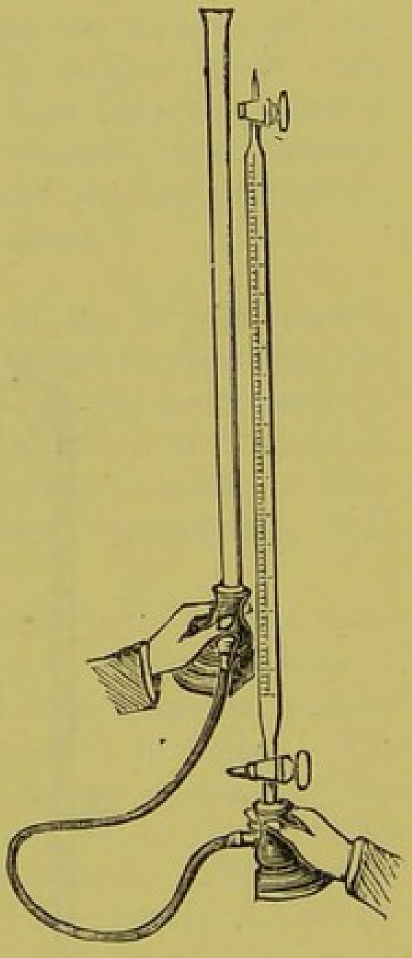

Fig. 84.

Fig. 85 will illustrate not only the original Hempel burette with level tube, but also the method of connection with the gas pipette, and also the way in which the elastic tube is joined by the intervening glass tube.

Hempel, with great ingenuity, has devised special pipettes to be used in connection with the burette, and which render the instrument very serviceable for general gas analysis. The pipette shown in fig. 85 is known as the simple absorption pipette, and serves for submitting the gas originally in the burette to the action of some special absorbent. With a series of these pipettes the gas is submitted to the action of special absorbents, one after another, until the entire composition is ascertained. The connections must in all cases be made of best stout rubber, and bound with wire.

*Collection and measurement of the gas over water.*—Both tubes are filled completely with water (preferably already saturated mechanically with the gas), care being taken that all air is driven out of the elastic tube. The clip is then closed at the top of the burette, and the bulk of the water poured out of the level tube, the elastic tube being pinched meanwhile with the finger and thumb to prevent air entering the burette. The latter is then connected by a small glass tube with the source of the gas to be examined, when, by lowering the level tube, the gas flows in and displaces the water from the burette into the level tube. The pressure is then regulated by

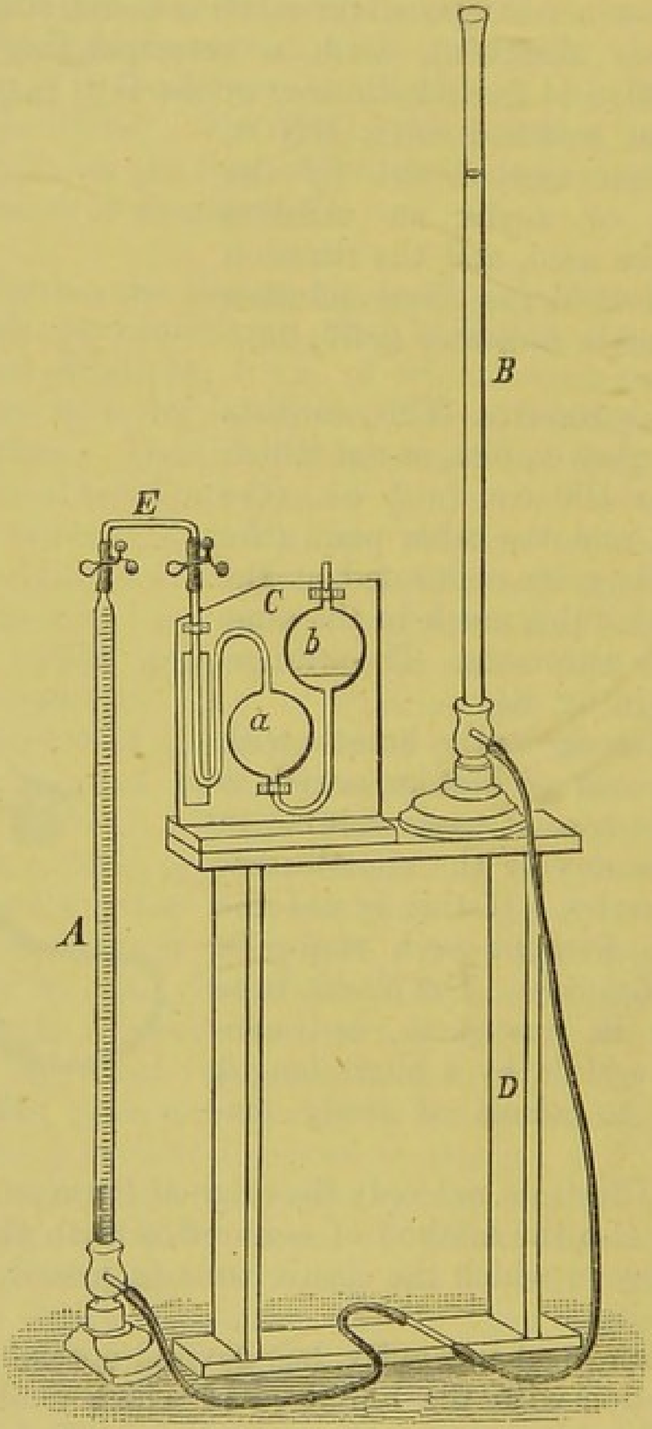

Fig. 85.

raising or lowering either of the tubes until both are level, when the volume of gas is read off. It is convenient of course to take exactly 100 c.c. of gas to save calculation.

*Collection and measurement of the gas without water.*—In this case the three-way tap burette (fig. 84) is dried thoroughly by first washing with alcohol, then ether, and drawing air through it. The three-way tap is then closed, the upper tube connected with the gas supply, and the burette filled either by the pressure of the gas, or by using a small pump attached to the three-way cock to draw out the air and fill the burette with the gas. When full the taps are turned off, and connection made with the level tube, which is then filled with water, the tap opened so that the water may flow into the burette and absorb the soluble gases present. As the burette holds exactly 100 c.c. between the three-way tap and the upper clip, the percentage of soluble gas is shown directly on the graduation.

*The method of absorption.*—In the case of the simple pipette fig. 85, *a* is filled with the absorbing liquid, which reaches into the syphon bend of the capillary tube: the bulb *b* remains nearly empty. In order to fill the instrument, the liquid is poured into *b*, and the air sucked out of *a* by the capillary tube. It is convenient to keep a number of these pipettes filled with various absorbents, well corked, and labelled.

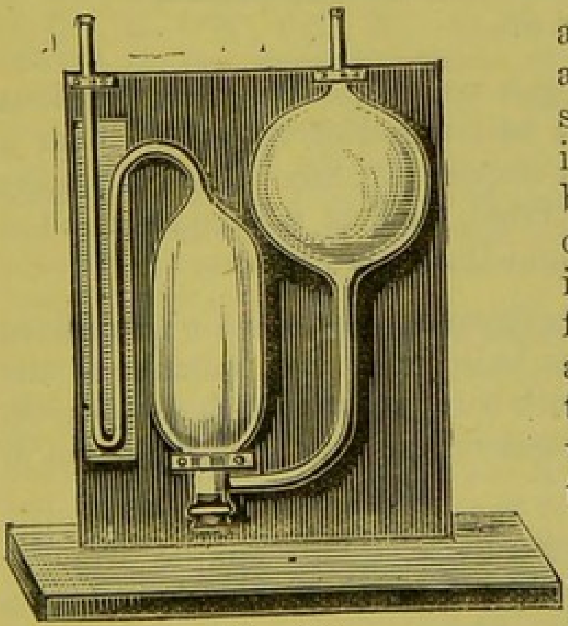

Fig. 86.

Another pipette of similar character is shown in fig. 86, and is adapted for solid re-agents, such as stick phosphorus in water. The instrument has an opening at the bottom, which can be closed with a caoutchouc stopper. This pipette is also used for absorbing $CO^2$ by filling it with plugs of wire gauze and caustic potash solution, so as to expose a large active surface when the liquid is displaced by the gas.

To make an absorption, the capillary U-tube is connected with the burette containing the measured gas by the small capillary tube E (fig. 85), the pinchcock of course being open, then by raising the level tube, the gas is driven over into *a*, where it displaces a portion of the liquid into *b*. When the whole of the gas is transferred, the pinchcock is closed, and the absorption promoted by shaking the gas with the re-agent. When the action is ended, communication with the burette is restored, and the gas syphoned back with the level tube into the burette to be measured.

*The compound gas pipette* shown in fig. 87 is of great utility in preserving absorbents which would be acted on by the air, such for instance as alkaline pyrogallol, cuprous chloride, etc. The bulb next the syphon tube is filled with the absorbent, the next is empty, the third contains water, and the fourth is empty. When the gas is passed in, the intermediate water passes on to the last bulb to make room for the gas, thus shutting off all contact with the atmosphere, except the small amount in the second bulb.

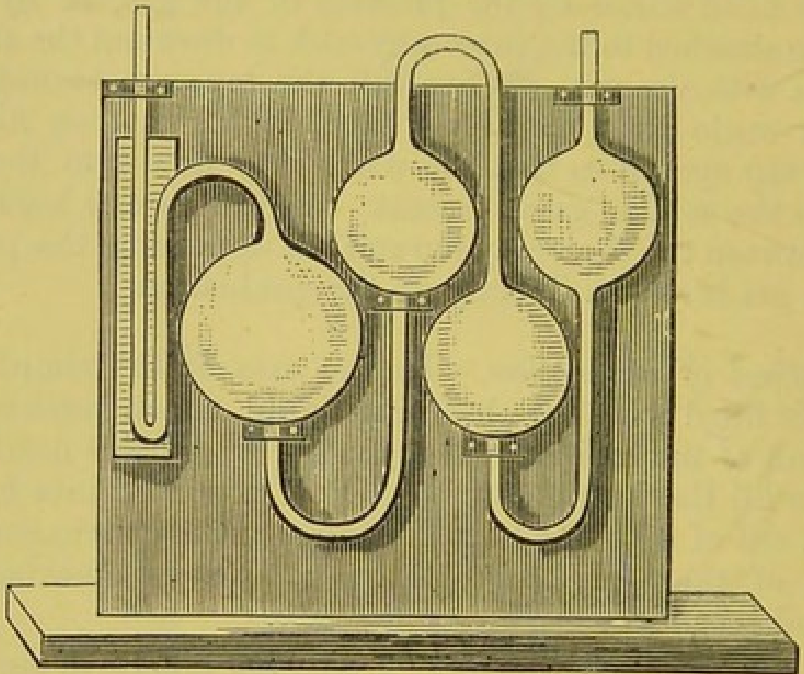

Fig. 87.

*Hydrogen pipette.*—The hydrogen gas necessary for explosions or combustions is produced from a hollow rod of zinc fixed over a glass rod passed through the rubber stopper (fig. 86). The bulb being filled with dilute acid, gas is generated, and as it accumulates the acid is driven into the next bulb and the action ceases.

*Explosion pipette*—Another arrangement provides for explosions by the introduction into a thicker bulb, measured volumes of the gas, of air, and of hydrogen. The bulb being shut off with a stop-cock, a spark is passed through wires sealed into the upper portion of the bulb.

*Pipette with Capillary Combustion Tube.*—This simple arrangement consists of a short glass capillary tube bent at each end in a right angle, into which an asbestos fibre impregnated with finely divided palladium is placed, so as to allow of the passage of the gas.*

---

* To prepare palladium asbestos, dissolve about 1 gm. palladium in *aqua regia*, evaporate to dryness on water-bath to expel all acid. Dissolve in a very small quantity of water, and add 5 or 6 c.c. of saturated solution of sodic formate, then sodic carbonate until strongly alkaline. Introduce into the liquid about 1 gm. soft, long-fibred asbestos, which should absorb the whole liquid. The fibre is then dried at a gentle heat, and finally in the water-bath till perfectly dry; it is then soaked in a little warm water, put into a glass funnel, and all adhering salts washed out carefully without disturbing the palladium deposit. The asbestos so prepared contains about 50 per cent. Pd, and in a perfectly dry state is capable of causing the combination of H and O at ordinary

The gas being mixed with a definite volume of air in the burette, and the measure ascertained (not more than 25 c.c. of gas and 60 or 70 c.c. of air), the asbestos tube is heated gently with a small gas flame or spirit lamp, and the pinchcocks being opened, the mixture is slowly passed through the asbestos and back again, the operation being repeated so long as any combustible gas remains. No explosion need be feared. The residue of gas ultimately obtained is then measured, and the contraction found; from this the volume of gas burned is ascertained either directly, or by the previous removal of $CO^2$ formed by the combustion with the potash pipette. H is very easily burned, CO less easily. Ethylene, benzine, and acetylene require a greater heat and longer time. $CH^4$ is not affected by the method, even though mixed with a large excess of combustible gases.

In order to illustrate the working of the whole set of apparatus, the analysis of a mixture containing most or all of the gases likely to be met with in actual testing is given from a paper contributed by Dr. W. Bott, (*J. S. C. I.* iv. 163). The mixture of gases consists of $CO^2$, O, CO, $C^2H^4$, $CH^4$, H and N. A sample of this gas—say 100 c.c.—is collected and measured in the gas burette. The $CO^2$ is next absorbed by passing the gas into a pipette (fig. 85), containing a solution of 1 part of KHO in 2 parts of water. To ensure a more rapid absorption, the bulb shown in fig. 86 containing the caustic potash may be partly filled with plugs of wire gauze. The absorption of the $CO^2$ is almost instantaneous. It is only necessary to pass the gas into the apparatus and syphon it back again to be measured. The contraction produced gives directly the percentage of $CO^2$, since 100 c.c. were used at starting. The remaining gas contains O, CO, H, $C^2H^4$, $CH^4$, N. The oxygen is next absorbed. This may be effected in two ways—by means of moist phosphorus or by an alkaline solution of pyrogallic acid. The former method is by far the more elegant of the two, but not universally applicable. The absorption is done in a pipette (fig. 86), the corked bulb, of which is filled with thin sticks of yellow phosphorus surrounded by water. The gas to be tested is introduced in the usual manner, and by displacing the water comes into contact with the moist surface of the phosphorus, which speedily absorbs all the oxygen from it. The absorption proceeds best at about 15-20° C., and is complete in ten minutes. The small quantity of $P^2O^3$ formed by the absorption dissolves in the water present, and thus the surface of the phosphorus always remains bright and active. This neat and accurate method is not however universally applicable; the following are the conditions under which it can be used:—The oxygen in the gas must not be more than 50 per cent., and the gas must be free from ammonia, $C^2H^4$ and other hydrocarbons, vapour of alcohol, ether and essential oils. In the instance chosen, the phosphorus method would hence not be applicable, as the mixture contains $C^2H^4$; therefore pyrogallic acid must be used. The absorption is carried out in the compound absorption pipette (fig. 87), the bulb of which is completely filled with an alkaline solution of pyrogallol made by dissolving

temperature, but when used in the capillary tube it is preferable to use heat as mentioned. The capillary combustion tubes are about 1 m.m. bore and 5 m.m. outside diameter, with a length of about 15 c.m. The fibre is placed into them before bending the angles as follows:—Lay a few loose fibres, about 4 c.m. long, side by side on smooth filter paper, moisten with a drop or two of water, then by sliding the finger over them twisted into a kind of thread about the thickness of darning cotton. The thread is taken carefully up with pincers and dropped into the tube held vertically, then by aid of water and gentle shaking moved into position in the middle of the tube. The tube is then dried in a warm place, and finally the ends bent at right angle for a length of 3½ to 4 c.m. Platinum asbestos may be prepared in the same way, using, however, only from half to one-fourth the quantity of metal.

1 part (by volume) of a 25 per cent. pyrogallic acid solution in 6 parts of a 60 per cent. solution of caustic potash. The absorption is complete in about five minutes, but may be hastened by shaking. The remainder of the gas now contains $C^2H^4$, CO, $CH^4$, H, N, and the next step is to absorb the $C^2H^4$ by means of fuming $SO^3$, the $CH^4$ being subsequently determined by explosion. In choosing the latter method a portion, say half, of the residual gas is taken for the estimation of hydrogen. The absorption of the hydrogen is based on the fact that palladium black is capable of completely burning hydrogen when mixed with excess of air, and slowly passed over the metal at the ordinary temperature. About 1½ gm. of palladium black are placed in a small U-tube plunged into a small beaker of cold water, and the gas, mixed with an excess of air (which, of course, must be accurately measured), is passed slowly through the tube two or three times,* the tube at the time being connected with an ordinary absorption pipette filled with water or else with the KOH pipette, which in this case, of course, simply serves as a kind of receiver. Finally the gas is syphoned back into the burette and measured—two-thirds of the contraction correspond to the amount of H originally present in the mixture of gas and air. The $CH^4$ is not attacked by ordinary 30 % $SO^3$ Nordhausen acid during the absorption of the $C^2H^4$. The acid is contained in an absorption pipette (fig. 86), the bulb of which is filled with pieces of broken glass so as to offer a larger absorbing surface to the gas. The absorption is complete in a few minutes, but the remaining gas previous to measuring should be passed into the KOH pipette and back again, so as to free it from fumes of $SO^3$. Residual gas: CO, $CH^4$, H, N. The CO is next absorbed by means of an ammoniacal solution of cuprous chloride in a compound absorption pipette. The gas has to be shaken with the absorbent for about three minutes. It must be borne in mind that $Cu^2Cl^2$ solution also absorbs oxygen, and, according to Hempel, considerable quantities of $C^2H^4$, hence these gases must be removed previously. Residue: $CH^4$, H, N. Both $CH^4$ and H may now be estimated either by exploding with an excess of air in the explosion pipette and measuring (1) the contraction produced, and (2) the amount of $CO^2$ formed (by means of the KOH pipette); or, according to Hempel, absorb the hydrogen first of all as described above—provided the U-tube be kept well cooled with water, inasmuch as that at about 200° C. a mixture of air and $CH^4$ is also acted upon by palladium. The presence of CO, vapours of alcohol, benzine and hydrochloric acid also interfere with the absorption by palladium.

The palladium may be used for many consecutive experiments, but must be kept as dry as possible. After it has been used for several absorptions it may be regenerated by plunging the tube into hot water and passing a current of dry air through it.

Having estimated the hydrogen, the $CH^4$ in the remaining portion of the gas has to be determined. This contains $CH^4$, N and H, the amount of the latter being known from the previous experiment. The gas is mixed with the requisite quantity of air and hydrogen, introduced into the explosion pipette and fired by means of a spark. The water resulting from the combustion condenses in the bulb of the pipette, whilst the $CO^2$ formed is absorbed by the KOH solution present. Hence the total contraction produced corresponds to:

*a.* The hydrogen present in the original gas + ½ its vol. of O (the quantity requisite for complete combustion).

*b.* The known quantity of hydrogen added + ½ its vol. of O.

*c.* The $CH^4$ present + 2 vols. of O requisite for its combustion.

$$\underbrace{\underbrace{CH^4}_{2} + \underbrace{O^4}_{4}}_{} = \underbrace{(CO^2 + 2H^2O)}_{\text{disappears.}}$$

---

* Instead of this the H may be burned in the tube containing the palladium asbestos fibre previously described.

Since $a$ and $b$ are known, or can be readily calculated from the previous data, by subtracting $(a+b)$ from the total contraction it is possible to obtain $C-(a+b)=c$ contraction due to $CH^4$ alone, and one-third of this is equal to the volume of $CH^4$ present, as will be readily seen from the above equation.

The remaining nitrogen is estimated by difference.

**Lunge's Nitrometer.**—This instrument has been incidentally alluded to in § 67 as being useful for the estimation of nitric acid in the form of nitric oxide. It was indeed for this purpose that the instrument was originally contrived, more especially for ascertaining the proportion of nitrogen acids in vitriol.

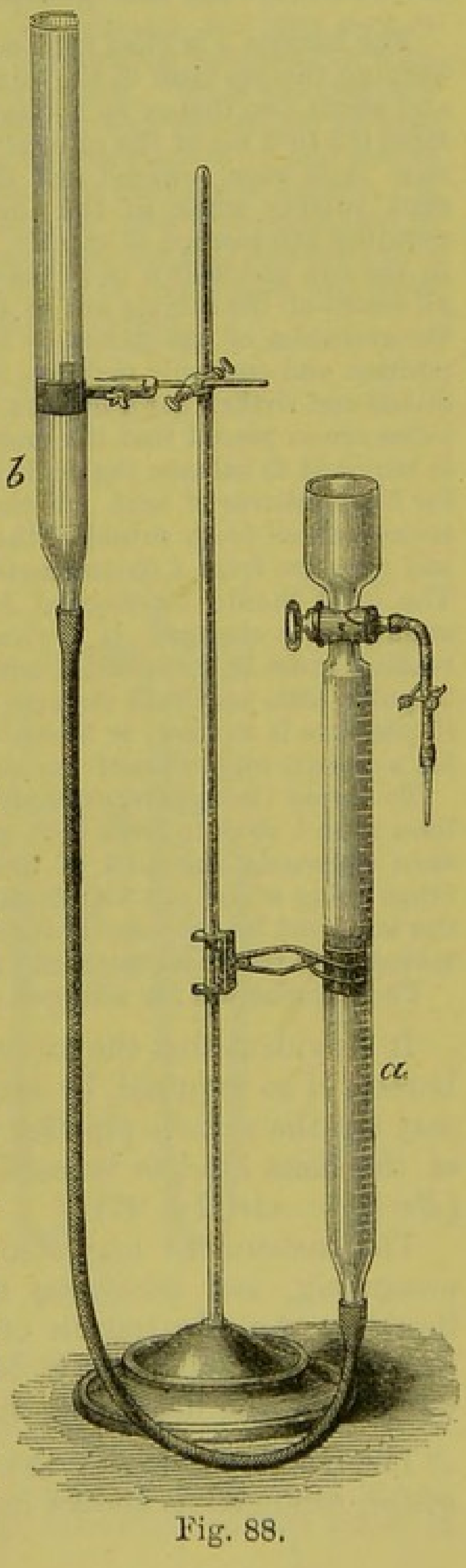

Fig. 88.

The instrument has been found extremely useful also for general technical gas analysis, and for the rapid testing of such substances as manganese peroxide, hydrogen peroxide, bleaching powder, urea, etc. The apparatus in its simplest form is shown in fig. 88, and consists of a graduated measuring tube fitted at the top with a three-way stop-cock, and a glass cup or funnel; the graduation extends from the tap downwards to 50 c.c. usually, and is divided into $\frac{1}{10}$ c.c. The plain tube, known as the pressure or level tube, is about the same size as the burette, and is connected with the latter by means of stout elastic tubing bound securely with wire. Both tubes are held in clamps on a stand, and it is advisable to fix the burette itself into a strong spring clamp, so that it may be removed and replaced quickly.

One great advantage over many other kinds of technical gas apparatus which pertains to this instrument is, that it is adapted for the use of mercury, thus insuring more accurate measurements, and enabling gases soluble in water, etc., to be examined.

Another form of the same instrument is designed by Lunge for the estimation of the nitric acid in saltpetre and nitrate of soda, where a larger volume of nitric oxide is dealt with than occurs in many other cases. In this instrument a bulb is blown on the burette just below the tap, and the volume contents of this bulb being found, the graduation showing its contents begins on the tube at the point where the bulb ends, and thence to the bottom; the level tube also has a bulb at bottom to contain the mercury displaced from the burette. Illustrations of this form of nitrometer may be found in the treatise on technical gas analysis already referred to, and many other places.

The following description of the manipulation required for the estimation of nitrogen acids in vitriol applies to the ordinary nitrometer, and applies equally to the estimation of nitrates in water residues and the like (see page 227):—

The burette *a* is filled with mercury in such quantity that, on raising *b* and keeping the tap open to the burette, the mercury stands quite in the taphole, and about two inches up the tube *b*. The tap is now closed completely, and from 0·5 to 5 c.c. of the nitrous vitriol (according to strength) poured into the cup. *b* is then lowered and the tap cautiously opened to the burette, and shut quickly when all the acid except a mere drop has run in, carefully avoiding the passage of any air. 3 c.c. of strong pure $H^2SO^4$ are then placed in the cup and drawn in as before, then a further 2 or 3 c.c. of acid to rinse all traces of the sample out of the cup. *a* is then taken out of its clamp, and the evolution of gas started by inclining it several times almost to a horizontal position and suddenly righting it again, so that the mercury and acid are well mixed and shaken for a minute or two, until no further gas is evolved. The tubes are so placed that the mercury in *b* is as much higher than that in *a* as is required to balance the acid in *a*; this takes about one measure of mercury for 6·5 measures of acid. When the gas has assumed the temperature of the room, and all froth subsided, the volume is read off, and also the temperature and pressure from a thermometer and barometer near the place of operation. The level should be checked by opening the tap, when the mercury level ought not to change. If it rises, too much pressure has been given, and the reading must be increased a trifle. If it sinks, the reverse. A good plan is to put a little acid into the cup before opening the tap: this will be drawn in if pressure is too low, or blown up if too high. These indications will serve for a correct repetition of the experiment.

To empty the apparatus ready for another trial, lower *a* and open the tap, then raise *b* so as to force both gas and acid into the cup; by opening the tap then outwards, the bulk of the acid can be collected in a beaker, the last drops being wiped out with blotting-paper. It is hardly necessary to say that the tap must be thoroughly tight, and kept so by the use of a little vaseline, taking care that none gets into the bore-hole.

The calculations for nitrogen are given on page 227.

It is evident that the nitrometer can be made to replace Hempel's burette if so required, by attaching to the side opening of the three-way tap the various pipettes previously described, or smaller pipettes of the same kind to be used with mercury, as described by Lunge (*Berichte*, xiv. 14, 92).

The instrument may also be very well employed for collecting, measuring, and analyzing the gases dissolved in water or other liquids. An illustration of this method is given by Lunge and Schmidt (*Z. a. C.* xxv. 309) in the examination of a sample of water from the hot spring at Leuk in Switzerland.

The determination of the dissolved gases was made in the nitrometer, arranged as shown in figs. 89 and 90:—

The flask A is completely filled with the water; an indiarubber plug with a capillary tube ($a$) passing through it, is then inserted in the flask, and the tube is thereby completely filled with water. The whole is then weighed, and the difference between this and the weight of the empty flask and tube gives the amount of water taken. The end of the capillary tube is then connected to the side tube of the nitrometer by the tube $b$. The nitrometer is then completely filled with mercury, and when the tubes are quiet, the flask and measuring tube of the nitrometer are quickly placed in connection, without the introduction of the slightest trace of air. The water in the flask is then slowly heated to boiling. Some water as well as the dissolved gases collect in the measuring tube of the nitrometer. The tube N of the nitrometer should be lowered in order that the boiling may take place under reduced pressure. After boiling for five to ten minutes, the stop-cock is quickly turned through 180°, so that the flask is placed in combination with the cup B, containing mercury, and the flame removed. Since the mercury stands lower in N than in M, it is not possible for any loss of gas to take place at the moment of turning the tap. It is also impossible for any gas or steam to escape through the mercury cup, since the pressure is inward. A small bubble of gas always remains under the stopper; this is brought into M by lowering the tube N as much as possible, and then turning the stop-cock so that the flask and measuring tube are again placed in connection, and when the bubble has passed over, quickly reversing the tap again.

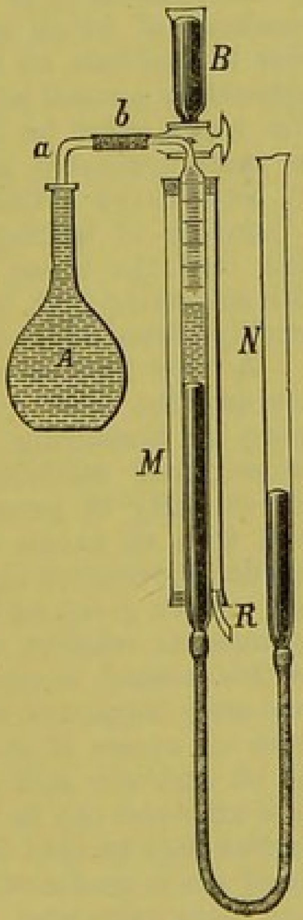

Fig. 89.

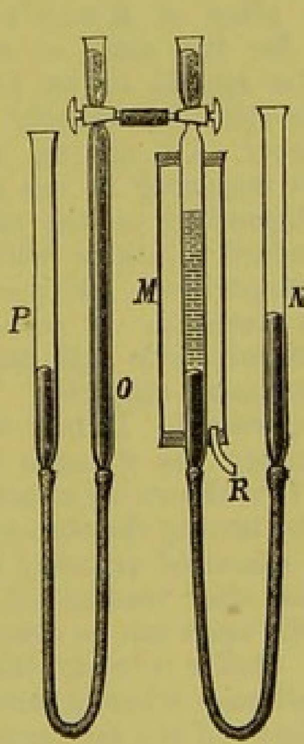

Fig. 90.

When the whole of the gas is collected in the nitrometer, it is connected with a second instrument O P, quite full of mercury. The gas is then transferred by placing the tap in such a position that it is closed in all directions, and the tube M is heated by passing steam through the tube R. When it is quite hot the tube N is lowered, causing the water in M to boil, in order to expel every trace of dissolved gas. The taps are then placed in connection and the gas passes over. It can then be cooled, measured, and submitted to analysis. Two experiments gave 505 gm. water taken, gas evolved 5·06 c.c.,=10·02 per 1000 gm.; 502 gm. water taken, gas evolved 4·94 c.c.,=9·84 per 1000 gm.

The numerous ways in which the nitrometer may be usefully employed for accurate as well as mere technical purposes, have been pointed out by Allen (*J. S. C. I.* iv. 178), and by Lunge himself (*Berichte*, viii. 161), which may be summarized as follows :—

The nitrometer is well adapted for determining the insolubility of gases in certain liquids under variable pressure and temperature. Another application of the same apparatus is for reducing volumes of gas to normal pressure and temperature. Lunge has also by adding an outside decomposing vessel adapted the instrument for the estimation of urea in urine by hypobromite. A small 50 c.c. conical flask, fitted with a perforated indiarubber cork, is connected by a small piece of strong indiarubber tubing with the nose of the three-way tap of the nitrometer, which is filled with mercury (Allen fills the instrument designed by himself with a saturated solution of salt or sodic or magnesic sulphate, which, however together with brine, glycerine, and similar vehicles are all discouraged in favour of mercury by Lunge except in testing nitrous ether). The flask, which should be of strong glass, contains a small glass or ebonite tube (the contents of which may be easily upset), provided with a loop of platinum wire to facilitate its insertion and withdrawal. Or, again, the flask may be replaced by a small bottle, containing an inside tube fused to the bottom. The whole must be light enough to be hung on the nitrometer-tap. The same apparatus may be made to take the place of Knop's azotometer, Scheibler's $CO^2$ apparatus, or be used for the assay of commercial peroxide of hydrogen. In the latter case the sample to be tested is filled into the inner tube, while permanganate solution, strongly acidified with sulphuric acid, is placed into the bottle proper. On mixing, oxygen is readily given off, and the volume of the gas is measured in the nitrometer. A very interesting and novel application depending on the same principle and the same reaction is for titrating standard solutions without weighing or measuring a substance of known composition. Supposing a permanganate solution has to be tested for its strength. A certain measured quantity of permanganate is acidified with sulphuric acid, and decomposed with an excess of hydrogen peroxide of unknown strength. The complete decolourisation shows whether an excess was present. If now the volume of oxygen given off be measured in the nitrometer, the strength of the permanganate solution can be easily calculated. It is shown by experiments that this method is accurate as well as quick. For testing the strength of standard acids (sulphuric, hydrochloric acid, etc.), a measured quantity is treated with an excess of sodic or calcic carbonate, and after reading off the volume of carbonic acid evolved, the strength of the acids can be computed. These examples can be increased by many more. Suffice it to say, that the nitrometer may be used for analytical purposes in all cases where a certain quantity of gas is produced, which after measuring allows of the decomposed substance being calculated. Of course, the gas must not be soluble in the liquid employed for decomposing, nor must it attack mercury. Bleaching powder solution acts on hydrogen peroxide like permanganate (see page 139). By means of bleaching powder solution in excess, the strength of hydrogen peroxide can therefore be estimated and *vice versâ*. Potassic ferricyanide in alkaline solution liberates the oxygen of hydrogen peroxide, and may therefore be titrated in the same manner. The nitrometer further serves in analytical operations for absorbing gases. The determination of indigotin and indigo-red in commercial indigo by reduction to indigo-white and measuring the amount of oxygen absorbed, belongs to this class of operations. Another very convenient application is for absorbing gases evolved in manufacturing processes, inasmuch as the nitrometer combines the advantages of Bunte's and Hempel's gas burettes with the possibility of manipulating the gases over mercury. If it be required to test burner-gases for $CO^2$ and oxygen, which is all that is necessary in most cases, the gases are aspirated into the nitrometer-tube, and after cutting off the further supply of the gases, potassic hydrate solution is introduced through the cup into the measuring tube. After shaking, the percentage of $CO^2$ can be read off. Then some concentrated pyrogallic acid solution is added, and the oxygen estimated. If analyses of gases have to be performed where reagents must be applied which act on each other, the nitrometer is combined with several of Hempel's gas-pipettes in the way before described (*J. S. C. I.* iv. 495).

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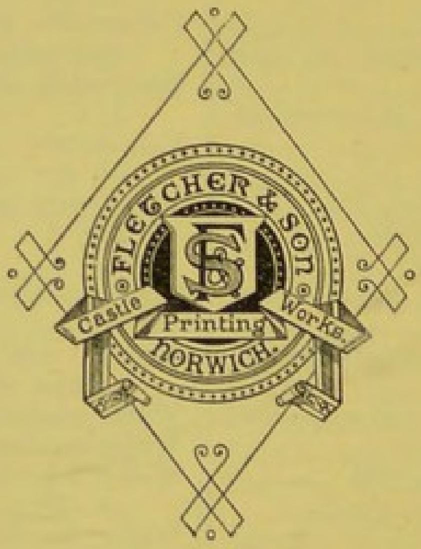
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