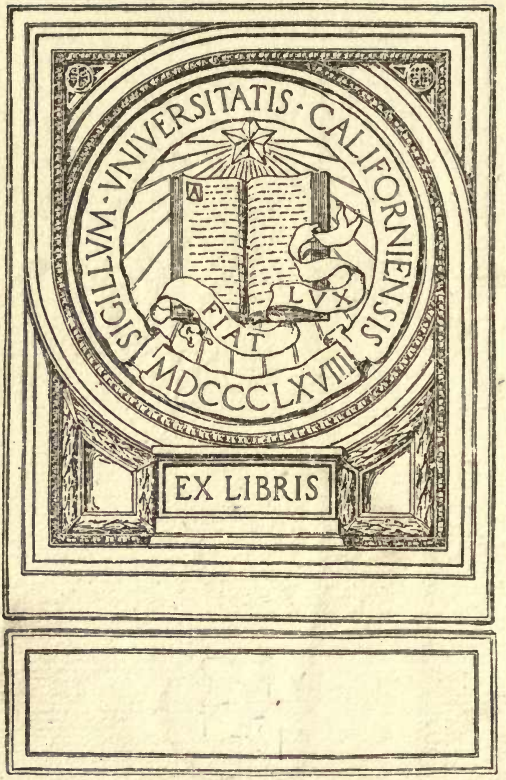

A SYSTEM OF

VOLUMETRIC ANALYSIS.

A SYSTEM

OF

VOLUMETRIC ANALYSIS.

By DR. EMIL FLEISCHER.

Translated, with Notes and Additions, from the Second German Edition,

By M. M. PATTISON MUIR, F.R.S.E.,

ASSISTANT LECTURER ON CHEMISTRY, THE OWENS COLLEGE, MANCHESTER.

WITH ILLUSTRATIONS.

𝔏𝔬𝔫𝔡𝔬𝔫:
MACMILLAN AND CO.
1877.

GLASGOW:
Printed at the University Press
BY ROBERT MACLEHOSE, 153 WEST NILE STREET.

TRANSLATOR'S PREFACE.

The aim of the book which is now presented to the English student is to systematise the processes of Volumetric Analysis.

In the English manual on Volumetric Analysis in common use the student is presented with a collection of the better processes for determining the majority of the bases and acids, and for the analysis of many chemical substances which are of technical importance. The work of Dr. Fleischer attempts to divide volumetric processes into a few great groups, to point out definitely the principles which underlie each group, to illustrate the application of these principles by well-chosen practical examples, and thus at once to convince the student of the paramount importance of Volumetric Analysis as an *art*, and to show him how this art may be applied, while at the same time to inculcate the necessity of studying this method of analysis as a branch of the *science* of Applied Chemistry.

A distinctive feature of the Work is the plan for the estimation of bases without previous separations.

In the translation I have endeavoured to present a fair rendering of the original; I have not, however, hesitated to condense the description given of any process where such condensation seemed to me to involve no sacrifice of clearness of expression.

I have generally very considerably shortened the introductory paragraphs to each section, and more than once I have done the same with the concluding remarks. A few notes have been added here and there, which it is hoped will be of service to the student in the laboratory.

One or two new processes have been introduced (see §§ 99, 101, 109, &c.), but I have not considered myself at liberty to multiply the processes to any great extent, as this would result in doing away with the distinctive feature of the Work, which is, not to present a complete collection of recipes for analysis, but rather to systematise the general methods of Volumetric Analysis. In accordance with the wish of the Author, the new processes are all placed in Part III. The greater part of the paragraph treating of water analysis has been added by me. Several of the tables in the appendix have also been added.

The author is a devoted admirer of the old system of notation; he has, however, allowed me to introduce those formulæ which are now all but universally employed by chemists. The old formulæ are placed in brackets after the new. Calculations are generally stated in terms both of the old and of the new notation. It may be that the old notation is still useful in some branches of inorganic chemistry; what the author has to say in its favour will be found (condensed) on p. 11. I cannot here enter into the arguments for and against the modern system; but it seems to me that to condemn a system of notation which has most powerfully aided in the recent wonderful advances of chemical science, and to return to another which has been shown to involve many contradictions, is unwise. Such arguments as those on page 11 concerning the meaning of a formula as representing something which really exists, have been met and, I think, answered again and again.

For all errors, and failures to make the various processes clear and intelligible, the blame is to be laid, not on the Author, but on the Translator.

M. M. PATTISON MUIR.

THE OWENS COLLEGE,
MANCHESTER, July, 1877.

AUTHOR'S PREFACE TO THE FIRST EDITION.

SINCE the appearance of my *Short Text-Book of Volumetric Analysis* (Leipzig, 1868), many new titration processes have appeared in the journals, and many old processes have been modified. From these (most of which I have myself tested) I was obliged to make a selection only for the purposes of the present work—partly because the aim of the work is not encyclopædic, and more especially because I wished to lay before the student only those processes which were undoubtedly trustworthy and at the same time simple.

I cannot regard the replacement of well-known and simple processes by complicated methods which are tedious to carry out and perhaps not very exact in their results, as an enrichment of Analytical Chemistry. In this, as in other branches of Chemistry, I should much prefer to see a striving after clearness and simplicity of method and of system such as was practised by the immortal Berzelius.

I have therefore endeavoured to replace difficult, by more easy methods, to simplify circuitous methods of separation, to do away with, or to modify uncertain final reactions—in a word, to render all uncertain and complicated processes more simple, so that they may become available even in the hands of comparatively unskilled analysts.

In Alkalimetry I employ $\frac{1}{2}$-normal caustic ammonia solution instead of the disagreeable caustic soda which is generally used. Instead of two acid liquids, normal sulphuric and normal nitric acids, I make use of but one—normal hydrochloric acid, which is as little volatile as nitric acid, does not exert an oxidising action like that acid, and is readily titrated. Many of the methods depending on oxidation are new, others are modified: such are the estimations of copper, bismuth, nickel, and cobalt, and some of the metallic sulphides.

I have subjected those methods of analysis which depend upon precipitation to a searching examination, and have rejected all in which the final point of the reaction is not, or cannot be made, plainly visible by a colorimetric change. Although this special branch of volumetric analysis is thus deprived of certain of its methods, yet I do not think that the system, as a whole, is a loser thereby, inasmuch as the precipitation processes which remain, as well as those which are modifications of the old processes, are so much the more certain and definite in their application.

I would draw especial attention to the volumetric methods of separation. In framing such methods considerations must be borne in mind different from those which guide one in forming methods of separation in gravimetric analysis. This field of enquiry, so promising in results of importance for the volumetric method, has scarcely as yet met with any cultivators.

The hope of developing volumetric methods of separation first led me to think of publishing the present Work, and I have naturally bestowed especial care on this part of my subject. I cannot expect that the methods described in the following pages should supersede the established gravimetric processes of separation; I have rather endeavoured so to arrange these established methods that they may be combined with, and so aid, the processes of volumetric separation. In the section entitled "Separation and Estimation of the Bases, without previous Group-Separations," I have endeavoured to point out in what way the methods of separation may be combined together, so as to render titration possible, without special separation of the groups by means of sulphuretted hydrogen and ammonium sulphide. All the changes introduced in this book are based upon accurate experiments, and the applicability of each method has been proved by special investigations.

I have paid no attention to the so-called modern formulæ, because these, even supposing that there is a "shadow of a reason" for their existence, as Mohr trenchantly remarks, are peculiarly unfitted for analytical chemistry and for mineralogy.

E. FLEISCHER.

DRESDEN, *January*, 1871.

AUTHOR'S PREFACE TO THE SECOND EDITION.

THE Second Edition of this book contains a considerable number of new processes and modifications of old processes, most of which are based upon investigations especially undertaken. I have been able to make use of only a few of the new processes which have appeared since the date of the publication of the first edition.

The longer I study the processes of Analytical Chemistry, and the application of those processes in manufactures, the more am I convinced of the necessity of framing general methods and of paying attention to special considerations only in those cases in which the general method cannot be advantageously applied. It is only thus that that inner completeness can be bestowed upon Analytical Chemistry which it so much requires in order to enable it to answer the questions propounded alike by Science and by Technology.

As Chemistry is continually being enriched by new methods for preparing the same substances, so is there a continual addition being made to the number of analytical processes of estimation. Many of these processes are doubtless of advantage in special cases, but their non-applicability as general methods is for the most part too evident. For instance, the new method of estimating silver by titration with potassium sulphocyanide, after addition of ferric sulphate, is not of general application. The red colour of ferric sulphocyanide, the production of which marks the final point of the reaction, is formed, it is true, in acid solutions, and the method is therefore applicable in such cases. But the presence of copper salts along with the silver—a not uncommon occurrence—renders this method of no avail, because these salts are precipitated by potassium sulphocyanide. This method, although an elegant one, was therefore forbidden to me, because the leading idea of this Work is to select a small number of processes, all of which are of general application, so that the student may gain a clear general survey of the titration methods, and also of the methods by which he may pursue quantitative analysis aided by these processes.

With this end in view I have again paid careful attention to the methods of separation, and, after a considerable amount of labour, I have been so fortunate as to devise a more simple, quicker, and more accurate method than that previously made use of. The new method is described in the chapter headed "General Method for Separation of Bases." The technical chemist will find this method of much service, inasmuch as by its aid he will be able easily to separate and quantitatively determine a given metal when mixed with many other substances. This method simplifies the work to be done, and is much easier of application than those processes now in use which were originally introduced as gravimetric, not as volumetric separations. I have added a few new original methods of titration: such are the processes for estimating sulphuric acid, tartaric and citric acids, &c.

In the third part of the Work, in which the methods already described are applied to the technical analysis of various substances, I have endeavoured to enlarge the knowledge of the student, but I have *not* aimed at making the book a catalogue of receipts whence special methods may be deduced for each analysis. I have rather endeavoured to show that the methods described in Parts I. and II. are sufficient, with slight modifications, for the analysis of technical products. I trust that I shall thus be doing a greater service to the student than by supplying him with a long list of processes, the carrying out of which, because requiring no thought on his part, would speedily reduce him to the condition of a slave to his text-book.

But all this can only be gained by striving after generalisation both in titration and in separation methods. And although this edition should meet the eye of a critic who may object to the omission of many special methods, yet the consciousness of more favourable judgments, as well as the knowledge that good results have actually been attained, will amply make amends for his fault-findings.

Especially should I rejoice to find other chemists, instead of adding new methods to the number of those which are already of little use, pursuing the path which I have opened up, by developing the processes for volumetric separations, and so aiding in the advancement of a branch of chemical analysis which supplies a long-felt need.

May this book aid the work to the best of its ability.

E. FLEISCHER.

DESSAU, *February*, 1876.

CONTENTS.

PART I.

THE VOLUMETRIC METHODS.

SECTION I.

VOLUMETRIC METHODS IN GENERAL. INSTRUMENTS FOR VOLUMETRIC WORK. STANDARD SOLUTIONS.

SECTION II.

ANALYSIS BY SATURATION (ALKALIMETRY AND ACIDIMETRY.)

A. Alkalimetry.

B. Acidimetry.

Section III.

ANALYSIS BY OXIDATION AND REDUCTION.

A. Oxidimetry.

B. Iodometry.

SECTION IV.

ANALYSIS BY PRECIPITATION.

PART II.

METHODS OF SEPARATION PRECEDING VOLUMETRIC ESTIMATIONS.

SECTION I.

SEPARATION OF THE BASES FROM ONE ANOTHER.

VOLUMETRIC ANALYSIS OF A FEW ORGANIC SUBSTANCES OF TECHNICAL IMPORTANCE, AND OF WATER.

ERRATA.

Page 66, 15th line from bottom, *for* 64, 32, *read* 6·4, 3·2.
70, 9th line from top, *for* 162, *read* 162·5.
72, 9th line from top, *after* "divided by 2," *insert* "and multiplied by 11·2."
120, 2nd line from bottom, *for* 40, *read* 20.
121, 5th line from top, *for* 14·525, *read* 12·5.

INTRODUCTION.

ANALYTICAL CHEMISTRY is concerned with the determination of the nature of the chemical substances contained in a given body (Qualitative Analysis), and of the quantities by weight in which these substances exist (Quantitative Analysis). The analysis of inorganic substances can alone be said to be thoroughly systematised. Although good methods for the analysis of organic bodies are not unknown, a systematic scheme of analysis for this class of chemical compounds does not as yet exist.

Quantitative Analysis, like qualitative, is based upon two fundamental principles, and from each of these springs a system of Analytical Chemistry.

In qualitative analysis attention may be paid to the behaviour of different substances towards reagents in aqueous solutions, or to the behaviour of substances when exposed to the action of reagents in the solid state at high temperatures: in other words, qualitative analysis divides itself into analysis *in the wet way*, and analysis *in the dry way* or *pyro-chemical* analysis.

The former of these methods had attained to so great perfection, that reactions belonging to the latter class came to be regarded as almost superfluous, until Bunsen showed, of late years, how accurate are the results obtainable by means of dry reactions. Since the publication of Bunsen's *Memoirs* it has become possible to construct an almost complete scheme of analysis in which dry reactions only are employed, and to arrive at conclusions more rapidly, and with perhaps greater accuracy, than by employing wet reactions. It is not impossible that analysis by means of dry reactions may, when these reactions are more fully developed, largely usurp the place now occupied by the other system of analytical chemistry. The two methods are of equal authority, and whether one or other is to be employed must depend upon the greater or less adaptability of each method to the circumstances of each analysis, and upon the accuracy of the results obtainable. A third fundamental principle upon which to base a system of qualitative analysis is inconceivable.

Quantitative analysis is also based upon two fundamental principles. The estimation of the quantities by weight in which the constituents of a chemical substance exist in that substance may be carried out by *physical* or by *chemical* methods. In the former methods use is made of the *balance*, in the latter of the *burette.*

Suppose, for example, it is required to determine the quantity of barium carbonate in a mixture of this salt with barium sulphate. Two methods present themselves. From one gram of the mixed salts the carbonate is dissolved by means of hydrochloric acid; the residue, consisting of barium sulphate, is dried and weighed. The quantity so obtained is deducted from the one gram originally taken; the residue represents barium carbonate. By the physical method the quantity of barium carbonate is thus obtained as the result of two weighings.

In order to determine the amount of this salt by the chemical method, the barium carbonate is dissolved in hydrochloric acid which is prepared of a strength such that 1 cb.c. contains twice the quantity of hydrochloric acid, in milligrams, expressed by the formula HCl. One cb.c. of this acid also exactly neutralises 2 cb.c. of a dilute ammonia solution. A measured quantity of this acid, more than sufficient for the complete solution of the barium carbonate, is employed; after the solution is effected, the liquid is boiled in order to expel carbon dioxide. A couple of drops of blue litmus tincture are added; the litmus becomes red, owing to the presence of the excess of acid. This excess of acid is determined by running in the dilute ammonia solution from a burette until the colour of the liquid just changes to blue. The number of cubic centimetres of ammonia employed is divided by 2, the result is deducted from the number of cubic centimetres of hydrochloric acid originally added, and the exact quantity of acid required for solution of the barium carbonate is thus obtained.

Inasmuch as 1 cb.c. of the hydrochloric acid contains 1 atom HCl, in milligrams, and inasmuch as 2 atoms HCl convert 1 atom barium carbonate into chloride, it follows that 2 cb.c. of the hydrochloric acid correspond to 1 atom of barium carbonate, in milligrams—that is, to 197 milligrams $BaCO_3$,—or, in old notation, 1 cb.c. hydrochloric acid converts 1 atom $BaOCO_2$ into BaCl, and therefore corresponds to 98·5 milligrams $BaOCO_2$. The amount of barium carbonate in the weight of mixed salts taken is thus easily calculated.

The barium carbonate has thus been determined, not by means of *ordinary* weights, but by means of *atomic* weights, and in place of the *balance*, a measuring instrument, the *burette*, has been employed.

The first-mentioned method of quantitative analysis is called the gravimetric, the second the volumetric method. The former method is of much earlier origin than the latter. The credit of placing volumetric analysis upon a scientific basis is due to Fr. Mohr. He it was who first introduced exact methods and delicate instruments into this branch of analytical chemistry. His work on volumetric analysis, as in other branches of science, is distinguished by peculiar accuracy, and readiness to turn to account every fact presented to him.

Volumetric analysis, or the titration method, as it is also called, is possessed of certain advantages as compared with gravimetric analysis. While the latter method requires that the substance to be determined shall be converted into a compound of known composition, and obtainable in the dry state, the former method is able to estimate the quantity of a substance when that substance is mixed with many others. It therefore either does away with, or at any rate simplifies, the frequent separations demanded in gravimetric analysis. Volumetric analysis consequently gains its results more quickly than the older method. In point of accuracy the processes of volumetric analysis often surpass those of the gravimetric system,[1] especially when small quantities are to be measured. In such cases the weight of the filter ash introduces errors. Lastly, the methods of volumetric analysis yield very good results even in comparatively unskilled hands. This is not the case with the gravimetric methods. Inasmuch as all bodies susceptible of estimation gravimetrically may also be estimated by titration (with the exception of a few of the rarer substances), it is surely time that the methods of volumetric analysis should become more used in scientific and technical investigations. The latter especially demand methods which shall give accurate results in a short space of time.

Gravimetric analysis is divided into two main sections —methods of estimation and methods of separation. The first methods teach how the substance to be estimated, after it has been separated from other substances, is to be brought into a form in which it may be weighed. The second methods teach how to effect the separations which must precede the estimation of the substance.

Volumetric analysis has hitherto trusted to the other branch of quantitative analysis for the separation of substances, and has contented itself with forming methods of estimation only. The more volumetric analysis advances, the more strongly is the need felt of methods of separation other than those supplied by gravimetric analysis, inasmuch as these methods generally introduce unnecessary complications. In gravimetric analysis the substance to be estimated must be separated completely from all other substances; in volumetric analysis such a complete separation is not generally required: it is sufficient that the substance be brought into a form in which it may be accurately titrated. This does not necessitate the removal of those bodies which are without influence

---

[1] This remark is of course only to be applied to accurate methods under both systems.

upon the process of titration. A volumetric separation is therefore a much easier process than a gravimetric separation.

In systematising the volumetric methods of separation —which systematising forms the peculiar feature of this work—I have availed myself of the rich literature of volumetric analysis. Inasmuch as I desired to reduce the titration methods to a complete system of analysis, independent of gravimetric methods, I have divided this work into three main parts—methods for volumetric estimation, methods for separation, and technical analyses. Many new methods are added to those in general use.

Volumetric methods must not only yield accurate results when the reactions are stated in chemical equations; the actual processes of measurement must be accurately carried out. Just as the exact determination of the weights, and the delicacy of the balance employed by the gravimetric analyst, are of the utmost importance, so is it essential that the volumetric analyst should provide himself with accurate measuring vessels (burettes and pipettes), and properly-graduated titration liquids, and that he should employ due quantities of these liquids in every analysis. It is evident that the measurements will be more accurate, and the results therefore more reliable, the greater the volume of liquid to be measured.

For this reason I have devoted a special chapter to a consideration of the methods of measurement and of titration, and I must beg the especial attention of the student to the contents of that chapter, inasmuch as the fundamental considerations which hold good in all processes of titration are there laid down.

The methods of separation of the metals are divided into two sections, "group-separations" and "estimations without group-separations." Both sections presuppose a knowledge of the methods of volumetric analysis contained in the chapters which precede them. The second part of the separation methods (estimation of bases without group-separations) takes for granted a knowledge, on the part of the student, of the chemical processes which have been described and illustrated in the foregoing chapter on group-separations. The advantages of this *general* method of separation will there become evident.

It is only from a knowledge of the most comprehensive methods of separation that it becomes possible to frame processes for the examination of substances occurring in manufactures. The advantage to the student of continually bearing in mind the *general* methods of volumetric analysis cannot be too strongly insisted upon. Only thus will he be able quickly to apply the proper method to a particular case, and to possess himself of true knowledge instead of learning by rote a number of receipts.

I trust that this work may aid the progress of the branch of chemistry to the consideration of which it is devoted, and that it may serve to impress on the minds of analytical chemists the paramount importance of volumetric analysis, so that in future there may be no more analysts trained in our laboratories, who, from a neglect of this branch of analysis, are unable to become sound technical chemists.

PART I.

THE VOLUMETRIC METHODS.

SECTION I.

VOLUMETRIC METHODS IN GENERAL. INSTRUMENTS FOR VOLUMETRIC WORK. STANDARD SOLUTIONS.

§ 1.

Volumetric Methods in general.

IN Volumetric Analysis, the quantities by weight of the various chemical compounds contained in the substance under examination are estimated by determining the number of volumes of a liquid of known composition required to bring about and completely finish a definite chemical process of saturation, oxidation, or precipitation. For this purpose standard solutions are required, that is to say, solutions containing a fixed weight of substance dissolved in a definite volume of liquid. The standard liquid is added, drop by drop, to a solution of the substance under examination until certain reactions occur which indicate that the necessary quantity of the liquid has been employed. The reaction which indicates the final point of the process is generally a

Change of colour, or the
Formation of a precipitate.

Sometimes the final reaction occurs in the solution itself, at other times it is necessary to remove a portion of the solution and test it with certain reagents.

The changes of colour are, of course, to be traced to very various causes. Nevertheless, in whole series of volumetric processes the final colour-change may be assigned to the same cause; for instance, the final point in a great many processes is determined by the change in colour undergone by litmus tincture, according as the reaction of the liquid is acid or alkaline. The names *Acidimetry,* and *Alkalimetry,* are given to the whole group of those processes which are dependent upon this change, because these processes are employed for determining the quantities of free acids and alkalies. In other processes the final point is determined by the production of blue iodide of starch; and to such processes, in which iodine, either free or combined, is employed as a standard liquid, the name of *Iodometry*[1] is given. A third series of processes are classed as *Oxidimetric* methods, because they essentially depend upon the giving up of oxygen, to the substances to be estimated, by potassium permanganate, the end of the reaction being determined by the change produced in the colour of the liquid itself when an excess of the standard solution has been added. The last group of methods comprises those in which the substance to be estimated is *precipitated* from a solution by means of the standard liquid. In these processes the final point is seldom determined by a change of colour produced within the liquid itself; the more general method consists in bringing a drop of the liquid into contact with some other liquid, or indicator, upon a white slab, and noticing the change of colour which thereupon ensues. Such processes (called by Mohr spot-analyses) are very useful, and—when filtration is not necessary—are as trustworthy as those in which the change of colour occurs in the bulk of the solution itself. Other precipitation methods in which the final point is determined without the aid of a colour-change, are liable to mislead. For this reason I have included in the present work (which is not intended to be an encyclopædia of volumetric methods) only those processes the termination of which can be accurately determined by means of a colour-change. The methods described are, however, sufficient for the

---

[1] I have ventured to use this word as equivalent to the German "Iodometrie."—*Tr.*

analysis of all ordinary substances, and do not necessitate the preparation of any great number of standard solutions.

In this book I have made use of the old formulæ in preference to those which are erroneously styled "modern."

These modern formulæ are founded on the most daring hypotheses. I believe that the distressing complexity which they have produced, and the phraseology which has accompanied them, far outweigh any slight advantage which they have bestowed upon science. If a formula be regarded as a number representing something which *really exists*, then, so far at least as inorganic chemistry is concerned, the modern method must be abandoned. Experiment tells us that the substances CaO and SO_3 combine to form a new substance $CaOSO_3$, that MnO and SO_3 form $MnOSO_3$; but we do not know that substances having the composition expressed by the formulæ $CaSO_4$ and $MnSO_4$ really exist, because SO_4 is a substance whose existence is only hypothetical. But if formulæ are to express really existing substances, such hypothetical speculations are out of place.[1]

§ 2.

Instruments for Volumetric Work.

a. BURETTES.—The most important instrument employed in volumetric analysis is the Burette (Fig. 1), which consists of a glass tube graduated in fifths or tenths of a cubic centimetre. Burettes having a capacity of 20 and 50 cb.c., and graduated in one-tenths cb.c., are the most useful for general work. The lower extremity is drawn to a narrow opening, and a small glass tube, also drawn to a point, is attached to this extremity by means of a little piece of caoutchouc tubing, which is encircled by a brass pinchcock (Fig. 2), by opening or closing which the flow of liquid may be regulated.[2]

---

[1] See Translator's Preface.

[2] Burettes are now furnished with glass stopcocks, which are in every way preferable to the more old-fashioned tube and pinchcock arrangement. Dr. Fleischer thinks that this form of burette

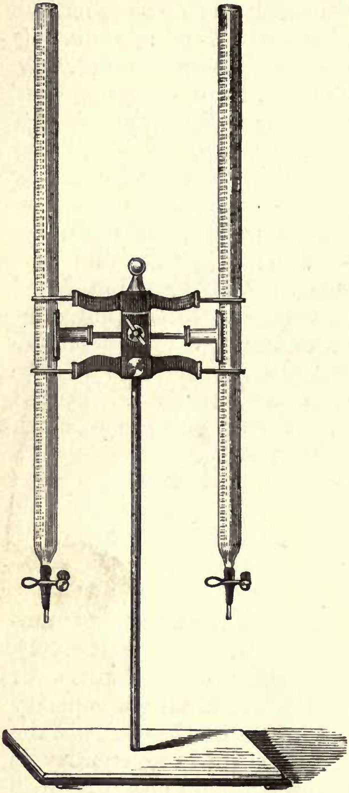

Fig. 1.

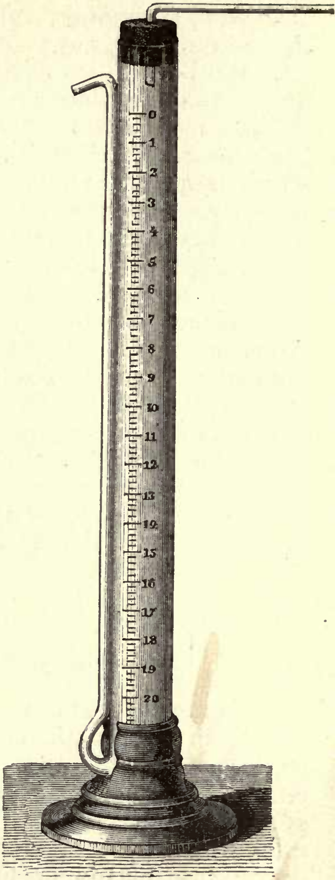

Fig. 3.

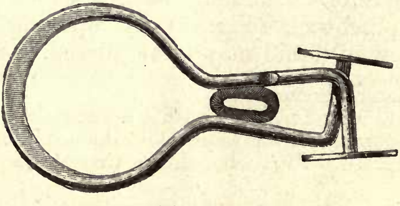

Fig. 2.

The burette is mounted upon a stand; the form of stand shown in the figure is one of the best. The burette is filled with the standard liquid, and by opening the stopcock the level of the liquid is adjusted at the zero mark on the instrument. Care must be taken to remove any air bubbles which may have found their way into the liquid in the burette. In technical laboratories and places where liquids are allowed to remain in burettes for considerable periods of time, the upper orifice of the instrument should be covered (most simply by means of a test tube) to prevent dust from falling into the liquid.

Another form of burette, introduced by Gay Lussac, is shown in Fig. 3. This instrument is furnished with two tubes, one of which—viz., the exit tube for the liquid—is much narrower than the other. In using this burette the level of the liquid is adjusted to the zero mark. Any air bubbles are removed by sucking at the opening of the wider tube; by inclining the burette the liquid is caused to flow steadily out of the orifice of the narrower tube. A steady flow of liquid may be insured by pressing the finger sharply against the mouth of the wider tube from time to time, or by closing this tube with a cork, carrying a bent glass tube, through which air may be blown when required. This burette is mounted upon a wooden foot.[1]

Fig. 2 *a*.

---

is possessed of little advantage over that described in the text; this opinion is not shared in by those who have worked much with both forms. Fig. 2 *a* shows the glass stopcock held in its place by means of a caoutchouc ring; this arrangement is very satisfactory.—*Tr.*

[1] Since the introduction of burettes furnished with glass stopcocks, Gay Lussac's instrument has been little used: it was chiefly employed for containing liquids (permanganate, iodine, &c.) which exert an action upon caoutchouc. In reading off burettes the instrument called Erdmann's float is very useful. This instrument consists of an elongated glass bulb containing a little mercury; it is made of such a diameter as

It is above all things essential in reading off burettes that the instrument should be firmly clamped in one position, and that a few minutes should be allowed to elapse after closing the stopcock before the reading is taken, so that the level of the liquid may become constant.

If the liquid in the burette be so dark-coloured as to be opaque, the light must be allowed to fall upon the instrument, and a piece of white paper must be held behind the liquid. The upper level of the meniscus is read off. In the case of colourless, or but slightly coloured liquids, a piece of paper is held a few millimetres higher than the level of the liquid in the burette, and the lower level of the meniscus is read off. In each case the eye ought to be maintained at the level of the liquid in the burette.

b. Pipettes.—A pipette is an instrument for measuring off quantities of liquid. Fig. 4 represents a pipette graduated from 1 to 5 cb.c. in hundredths of cb.c. and used for delivering varying quantities of liquid. Such pipettes are graduated to *contain* a certain volume, or to *deliver* a certain volume of liquid. Figs. 5 and 6 represent pipettes which are graduated for one volume of liquid only, and which therefore differ from that just described. These pipettes are furnished with a mark which indicates the quantity of liquid *de-*

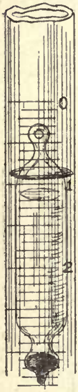

Fig. 3 *a.*

shall allow it to slide easily inside of the burette without touching either side. A line is scratched encircling the bulb near its centre. The quantity of mercury is adjusted so that the bulb floats wholly immersed in the liquid in the burette. The level of this liquid is adjusted so that the mark on the float is exactly coincident with the zero mark on the burette. See Fig. 3 *a.* Dr. Fleischer only recommends the use of Erdmann's float when wide burettes are employed. To me it appears difficult always to hit upon the exact reading without some such aid as this, even when narrow burettes are used, because a slight alteration in the position of the eye may make a considerable difference in the readings. There is, however, no doubt that the readiness with which drops of liquid stick to the sides of the burette above the float is a drawback to the use of this instrument in narrow burettes.—*Tr.*

livered by the instrument. For pipettes intended to contain small quantities of liquid (2 to 5 cb.c.), the form represented in fig. 5 is to be preferred; larger pipettes may be made of the form shown in fig. 6. In using pipettes the liquid is sucked up, generally by the mouth, and the upper orifice is closed by means of the finger, as shown in the figure; by allowing air to enter at this orifice the liquid is caused to flow out at the lower opening of the pipette. The liquid should be allowed to flow against the side of the vessel containing the

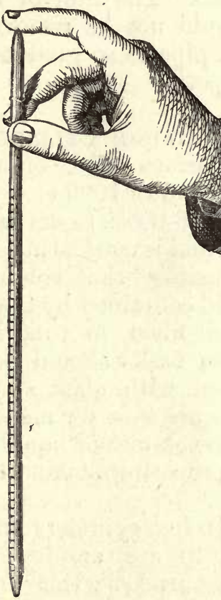
Fig. 4.


Fig. 5.


Fig. 6.

solution under examination, and not directly into that solution, in order that loss by spirting may be avoided. In graduating pipettes to deliver a certain volume, the liquid is allowed to flow freely from the pipette, and the drop which adheres to the instrument is removed by touching the surface of the liquid in the vessel underneath. From the volume of liquid so determined the pipette is graduated. The film of liquid which remains in the pipette should not be removed by blowing into the instrument. A pipette so graduated is called a "free flow and touch" pipette.[1]

c. MEASURING FLASKS AND MIXING CYLINDERS.—Measuring flasks (fig. 7) are of various sizes, containing from 100 to 1000 cb.c. The neck of these flasks is narrow, and is marked at a point indicating the volume of liquid contained by the flask when filled to that mark. These flasks should be furnished with glass stoppers. They are used for measuring large volumes of liquids, and for preparing standard solutions.[2]

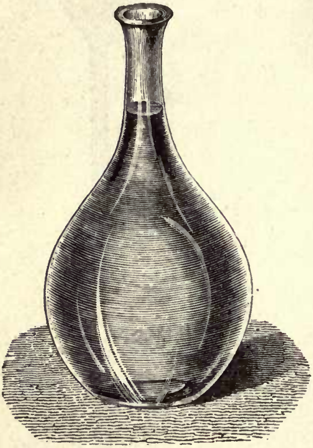

Fig. 7.

Mixing cylinders (figs. 8 and 9) are employed for like purposes; their indications are not (from the form of the vessels) so trustworthy as those of measuring flasks. If these cylinders are employed for measuring liquids, the larger sizes (250 to 500 cb.c.) should show differences of 5 cb.c., and the smaller (50 to 200 cb.c.) differences of 1 cb.c.

---

[1] See note at end of paragraph 3.

[2] It is very useful to graduate these flasks both to *contain* and to *deliver* definite volumes.—*Tr.*

§ 3.

Avoidance of Errors in Measuring Liquids and in Titrating.

Nature alone presents us with measures of mathematical exactitude. The most carefully constructed standards are not absolutely exact. Even were we possessed of standards of absolute accuracy, our measurements carried out with the aid of these standards would not be altogether exact; because over and above the 'personal error' of the observer, there are a number of errors due to

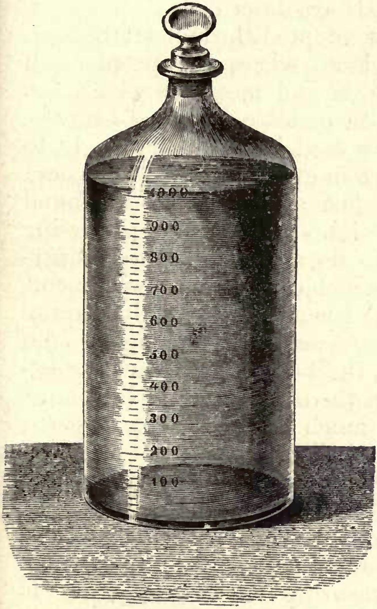

Fig. 8.

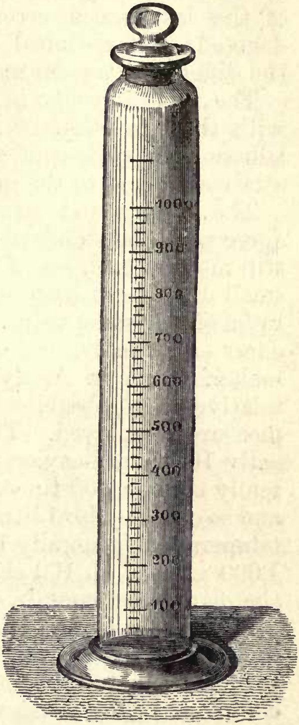

Fig. 9.

physical and psychological causes, which creep into every measurement. In certain cases, the magnitude of the 'experimental errors' may be calculated by the mathematical method of least squares. In Analytical Chemistry attention is chiefly paid to the errors inherent in the process of analysis itself (chemical errors), or to those dependent upon the method by which the process is carried out (physical errors). It is to a consideration of the last-named errors that this paragraph is to be devoted: the chemical errors will be considered when the different titration methods are described.

The metric system is now adopted throughout Europe, with the exception of England, where the people still adhere to a system of weights and measures which has attained almost to the greatest possible degree of badness.

The weights and measures used in chemistry ought to agree with the standards, yet in every set of weights, and still more in each set of measuring flasks, there are found small differences between weights or measures professing to be of the same value. To do away with these differences ought to be one of the objects of the instrument-maker. But in Analytical Chemistry we only require relative, not absolute, exactness in the weights and measures employed. Thus, the 1 gram piece must be exactly 10 times heavier than the 0·1 gram; the litre must really contain 100 times as much as the 10 cb.c. pipette, and so on. So also 1 litre of distilled water at the standard temperature (generally 14° R.$=$17°·5 C.) must really weigh 1,000 grams: an 100 cb.c. flask filled with this water to the mark must contain exactly 100 grams of water, &c.

We generally find small differences in the capacities of burettes, pipettes, and measuring flasks. In order to correct for these differences, the quantity of water actually contained in the given vessel must be weighed, and from its weight the volume of the water must be found. In a similar manner the value of each cubic centimetre division in the burette should be determined.[1] But there still remain sources of error. Let us adopt a fixed limit of error.

---

[1] See note at end of this paragraph.

In a good analytical method the error should not exceed $\frac{1}{5}$th to $\frac{1}{3}$rd of a per cent. In technical analyses the error often amounts to $\frac{1}{2}$ per cent in good methods.

In a good titration method, which is founded on a definite chemical reaction, the *chemical* error is small, and scarcely amounts to $\frac{1}{10}$th per cent. The errors of the process are to be traced to inaccuracies in the standard solutions, errors in the instruments, and errors in determining the final point of the reaction. The *chemical* error may then amount to $\frac{1}{10}$th per cent, and we may set down the error due to the instruments and liquids as also $\frac{1}{10}$th per cent, making in all $\frac{1}{5}$th per cent. We must then use instruments the error of which does not exceed $\frac{1}{10}$th per cent. It is scarcely possible to attain this degree of accuracy with all measuring instruments. A litre flask may readily be accurate to $\frac{1}{1000}$th, that is, to 1 cb.c., or even to 0·5 cb.c.: the quantities of water delivered from a 20 cb.c. pipette will, however, hardly differ by less than 0·02 grams; and the weights of single cubic centimetres of water delivered from burettes will generally differ by more than one milligram. Large volumes of liquids can therefore be measured with greater exactness than small volumes. The error in measuring volumes of liquids less than 20 cb.c. will amount to $\frac{1}{5}$th to $\frac{1}{10}$th per cent. In the case of larger volumes the error may fall below $\frac{1}{10}$th per cent.

But, in determining the final point of the reaction, a more serious source of error than that due to inaccuracies in measuring vessels is liable to creep in. It is possible to read off the indications of a burette to $\frac{1}{20}$th cb.c., but we may suppose that the readings differ among themselves by $\frac{1}{10}$th of a cb.c. One drop from a burette corresponds to about $\frac{1}{20}$th cb.c.; in some reactions the addition of one drop, more or less, serves to complete the reaction: let us suppose that in an exact titration the error due to the excess or deficit of reagent added amounts to two drops, *i.e.*, to $\frac{1}{10}$th cb.c. If 10 cb.c. of liquid be employed in a reaction, the error in the analysis, on the above supposition, may amount to 1 per cent. The possibility of such an error is sufficient to cause us to call in question the exactitude even of the best titration methods. But it is evident that the magnitude of this error decreases, the greater is the volume of liquid employed. If 20 cb.c. be used, an error of $\frac{1}{10}$th of a cb.c. either way corresponds to 0·5 per cent. In order to reduce the error to 0·2 per cent, at least 50 cb.c. of liquid must be made use of.

It has been proposed to carry out the titration by means of two liquids, a less dilute, by means of which the greater part of the reaction is accomplished, and a more dilute, which serves for determining the final point. Although this method is often used, yet I cannot see what great advantages it possesses over the other in which but one liquid is employed; and chiefly because it is necessary, in many reactions, to add a certain small excess of liquid, which excess corresponds to so many more volumes of standard the more dilute that standard is. We arrive more easily at a greater degree of precision by arranging the amount of substance used, so that at least 50 cb.c. of the standard liquid shall be employed in titration. If less than this volume be used, it is better to make a new analysis, and to use such an amount of the substance as shall insure that 50 cb.c. at least be required. If, however, it is not possible to use such a quantity of the substance under examination, a dilute standard solution is specially prepared, by the use of at least 50 cb.c. of which the titration is carried out. If it be necessary to employ a larger quantity of standard liquid than that which the burette contains, it is not advisable to refill the burette several times, but rather to run in a measured quantity of liquid from a pipette, and to finish the titration by the use of the burette.

Although we have thus arrived at the conclusion that the greater the volume of standard liquid employed the greater will be the accuracy of the determination, and that the minimum quantity of liquid should be 50 cb.c., it is nevertheless not to be supposed that in every analysis no smaller volume than this can be made use of. According to the value which is placed on an exact determination, so will a greater or less quantity of the substance be weighed out for analysis.

For instance, in the estimation of the alkali in a sample of soda, containing 1 per cent of common salt, an error in the determination of the latter substance even amounting to 1 per cent is of little consequence; but in the estimation of the alkali care must of course be taken that the volume of test liquid employed amounts to at least 50 cb.c., so that the error of determination may not exceed 0·20 per cent.

I have now to show how the error in the determination of the final point of the reaction neutralizes and eliminates small errors in the measuring instruments. Suppose that we are working with absolutely correct standard liquids. The error of measurement in the burette amounts to 0·2 per cent: 50 cb.c. therefore really correspond to 50·1 cb.c., and in every titration there is therefore an excess of 0·1 cb.c. employed. Suppose that in a titration of sulphuric acid 50 cb.c. have been used, and suppose that each cb.c. corresponds to 20 m.gm. SO_3, we should therefore have found $50 \times 20 = 1{,}000$ m.gm. SO_3. We have, however, actually used 50·1 cb.c., which corresponds to 1,002 m.gm. SO_3; but inasmuch as the excess used in determining the final point amounts to 0·1 cb.c., the two errors neutralize one another, and the result—viz., 1,000 m.gm. SO_3—is correct.

Let us now suppose that 50 cb.c. on the burette really corresponds to 49·9 cb.c., we should have the following result—

With 0·1 cb.c. excess there
  has been used . . 50 cb.c. = 1,000 m.gm. SO^3
Really used, . . . 49·9 „ = 998 „ „
True amount corresponds to 49·9 „ = 998 „ „

Instead of 998 m.gm. we have found 1,000 m.gm., and have made an error of 0·2 per cent. But inasmuch as there is really an error of 0·2 per cent in the measurement, which error has not been taken into account, it is evident that the error in determining the final point of the reaction has eliminated the error in measurement. Errors of 0·2 per cent in the burettes do not therefore really introduce errors in the titration when we work with standard liquids which are *exactly correct.* In order that these liquids may be correct the error in the measuring instruments must not exceed $\frac{1}{10}$th per cent. We must also be careful to use our liquids at the standard temperature of 14°·5 R., or at least within the limits 10° to 20° R. = 12°·5 to 25° C.

NOTE *on determining the Capacity of Measuring Instruments.*

In determining the capacity of measuring instruments, especially of the larger instruments, it becomes important to carry out the determinations at a fixed temperature. Some analysts recommend that each instrument should contain really that number of volumes of water which it indicates: for example, that a litre flask should really hold 1,000 cb.c. of water. If this method be adopted, the water must, of course, be measured at its point of maximum density, viz., at 4° C. Other analysts (and with these Dr. Fleischer appears to agree) recommend that the instrument should contain that volume of water which is indicated upon it, but measured at a temperature which more nearly approaches the ordinary atmospheric temperature than 4°. Whichever plan be adopted, the whole set of measuring instruments must be graduated on the same system.

In graduating measuring instruments the following table will be found useful—

The weight of 1,000 *cb.c. of water at* t° C. *when determined by means of brass weights in air at* t° C., *and under a pressure of* 760 *m.m. of mercury is equal to* 1,000 − x *grams.*[1]

t°	*x*	*t°*	*x*	*t°*	*x*	*t°*	*x*	*t°*	*x*	*t°*	*x*
0	1·25 F.	5	1·13	10	1·34	15	1·89	20	2·74	25	3·88
1	1·20	6	1·14	11	1·43	16	2·04	21	2·95	26	4·13
2	1·15	7	1·16	12	1·52	17	2·20	22	3·17	27	4·39
3	1·13	8	1·21	13	1·63	18	2·37	23	3·39	28	4·67
4	1·12	9	1·27	14	1·76	19	2·55	24	3·63	29	4·94

[1] Watt's *Dictionary*, vol. I., p. 256

In graduating measuring vessels the temperature of the water employed must be noted, and a correction made if necessary. Let us suppose that it is required to graduate a one-fourth litre flask to contain 250 cb.c. of water at 4° C., and that the temperature of the water is actually 17°, 1,000 cb.c. of water at this temperature weighs—according to the table—1,000 − 2·20 grams, therefore 250 cb.c. weighs $250-\frac{2{\cdot}20}{4}=249{\cdot}45$ grams. The flask is tared on the balance, 249·45 grams are placed in the other pan, and distilled water is poured into the flask until equilibrium is restored. If, however, the flask is to contain 250 cb.c. of water at 16°—which is often chosen as a mean temperature—and if the temperature is actually 17°, the very small correction which is theoretically required may safely be disregarded. In practice it is therefore preferable to graduate our measuring vessels so that they shall contain the indicated volume of water at a temperature of 16° to 18° C.

In graduating pipettes the instrument is filled with water to the mark; the water is then allowed to flow into a dry and weighed beaker; when the last drop has run out the point of the burette is caused to touch the surface of the water, and the beaker and its contents are again weighed. The actual capacity to the mark is thus determined. If the weight of water be too small or too large, the burette is again filled beyond, or scarcely to, the mark; the level of the water is indicated by a line drawn on a piece of paper gummed on to the stem, the water is run out and again weighed, and so on till the correct graduation is obtained.

A more ready, and, in all respects, as accurate a method of graduating pipettes has been described by Thorpe in his *Quantitative Chemical Analysis*, pp. 119-121. In this method the pipette is filled with water, which is then allowed to flow out, and the point of the instrument is touched against the surface of the water; a piece of caoutchouc tube carrying a thermometer tube drawn to a fine point, and furnished with a pinchcock, is placed over the upper orifice of the pipette, and the whole is suspended from one end of the beam of a balance, and accurately tared. The thermometer tube is withdrawn, a piece of ordinary tubing is put in its place, and the pipette is filled, past the mark, with water, the pinchcock is closed, and the thermometer tubing replaced. Weights representing the amount of water which the burette *should* contain are now placed in the other pan of the balance. By slightly opening the pinchcock water is allowed to flow very slowly from the burette. The instant that equilibrium is restored, the pinchcock is closed, and the level of the water is marked on the stem of the burette.—*Tr.*

§ 4.

Preparation of Standard and Normal Solutions in general.

Standard, and normal solutions, are solutions containing a determinate weight of substance dissolved in a definite volume of liquid. These solutions are generally prepared by dissolving the amount, in grams, expressed by the formula of the substance in one litre of liquid. Thus, one litre of normal hydrochloric acid contains 36·5 grams of the acid (HCl.)

It is oftentimes necessary to employ more dilute solutions. When this is the case deci- and centi-normal liquids are prepared by diluting normal solutions with 9, or 99, times their volume of water, so that the litre contains $\frac{1}{10}$th or $\frac{1}{100}$th of the amount, in grams, expressed by the formula of the substance. In the use of normal solutions prepared as described, very little calculation is required. Thus, 1 cb.c. of normal hydrochloric acid containing 36·5 m.gm. HCl neutralizes an equivalent of caustic soda in m.gms.—*i.e.*, 40 m.gm.; 2 cb.c. neutralize 80 m.gm. NaHO, and so on. (In old notation 1 cb.c. normal acid neutralizes 32 m.gm. NaHO.) In order to obtain the quantity of caustic soda in a given solution the number of cubic centimetres of normal hydrochloric acid required for neutralization must be multiplied by the combining number of caustic soda. Besides normal solutions others are required, the strength of which is determined by titration against a known weight of the substance for the estimation of which they are to be employed. Thus, in estimating silver, a solution of sodium chloride is needed, each cubic centimetre of which is capable of precipitating 5 or 10 m.gm. of metallic silver. So again a potassium permanganate solution is required for estimating iron, 1 cb.c. of which is equivalent to 10 m.gm. of iron. These solutions are also frequently diluted to $\frac{1}{10}$th or $\frac{1}{100}$th of their original strength.

The strength of standard solutions, however prepared, must be most carefully determined; and the determination should be repeated from time to time, as the strength of all solutions does not remain constant.

In preparing standard and normal solutions the following general points ought to be attended to:—

If a normal solution is to be prepared by dissolving a solid substance, the greatest care must be taken that the solid be perfectly pure and in a form represented by a definite chemical formula, so that the reaction, on which the use of the liquid is based, may be accurately calculated. For instance, in preparing normal sodium carbonate solution, chemically pure bicarbonate must be strongly heated until the water is entirely driven off and until the salt is converted into normal carbonate. In other instances the salt is weighed after crystallisation. Thus, the hydrated barium chloride $BaCl_2 2H_2O$ (BaCl2HO) is chosen. In many cases it is necessary to subject the salt to an exact quantitative analysis.

The required quantity of the salt is dissolved in a litre flask, in a little distilled water at the ordinary temperature, 14° to 15° R.=17°·5 to 18°·7 C. After complete solution, the litre flask is made up nearly to the mark with distilled water, with constant shaking. Any air bubbles are allowed to escape, and distilled water is added until the level of the liquid exactly coincides with the mark on the neck of the flask.

It is not advisable to prepare smaller quantities of standard liquids than 500 cb.c., because the errors both of weighing and of mixing are greater when small quantities of liquid are prepared. In preparing standard solutions of liquid substances, the specific gravity of the chemically pure liquid is to be determined either by means of the specific gravity bottle, or by filling a tared $\frac{1}{4}$ litre flask with the liquid and weighing it. The former method is more reliable. The hydrometer can only be employed for determining specific gravities of liquids, which are to be used in the preparation of normal solutions, when the indications of the instrument are trustworthy to the third decimal place. From the specific gravity, the quantity of the chemical compound in the liquid is determined by aid of the tables at the end of this book; the proper quantity of liquid is measured off into a litre flask, which is then filled to the mark with distilled water.

A better method, however, for preparing normal solutions of liquid substances, consists in determining by analysis the quantity of the definite chemical compound contained in a given volume of the liquid in question, and from this calculating the quantity of liquid which must be employed. Normal liquids should be titrated against a solution containing a determinate weight of some substance, the action of which upon the liquid is definitely known, or against another normal solution which is known to be of the proper strength, and the general action of which is opposed to that of the standard liquid under examination. In titrating the normal liquid, care must be taken that at least 50 cb.c. of the solution used for controlling the strength of the standard be employed in order that trustworthy results may be obtained. Glass-stoppered bottles should be used for strong normal liquids: these bottles should be kept in a dark place, free from dust.

Special directions for the preparation of the individual normal solutions will be given when describing the different titration methods.

§ 5.

Filtration.

Although a description of the ordinary processes of evaporation, weighing, igniting, &c., is quite beyond the limits of the present work, I am yet desirous of describing the process of filtration somewhat in detail. This process, which is so often tedious, is considerably shortened by the employment of the simple apparatus which I shall describe. In gravimetric analysis it is generally necessary to *thoroughly* wash all precipitates, because these are afterwards to be weighed and treated as chemically pure substances. Such complete washing of precipitates is not, for the most part, required in volumetric processes, inasmuch as the correct titration of a substance is but seldom dependent upon its chemical purity. The following two principles may be laid down concerning filtration, in so far as volumetric analysis is concerned:—

1. Complete washing of a precipitate is only necessary in those cases where the liquid from which the precipitate has been separated, contains substances which are capable of exerting an influence upon the titration of the precipitate.

2. If it be required to estimate one or more substances dissolved in a liquid from which a precipitate has been thrown down, the liquid must be diluted to a certain volume after the precipitation is completed, filtered through a dry filter, and a measured volume of the filtrate must be used for titration, the results obtained being calculated to the total volume.

In reference to (1), I may remark that there is generally no difficulty in determining whether substances are present in solution which are capable of exerting an influence upon the process of titration of the precipitate. Special attention will be directed to this point in the description of individual processes.

In reference to (2) it is evident that the titration of several substances simultaneously present in a solution becomes possible only when each is capable of being acted upon *only by one,* and not by many, definite test liquids. It is also to be noted that the volume of liquid obtained by dilution must be at least 200 times as heavy as the dry precipitate. Calculated on the quantity of the substance originally weighed out, 200 cb.c. of liquid must be obtained, as a minimum, for each gram of substance.

By following these fundamental rules much time and trouble will be saved in processes of filtration and of washing. I take for granted a knowledge on the part of the student of the methods of filtration, whereby loss by spirting, &c., is avoided. I may remark, in passing, that I do not approve of bringing the filter along with its contents into the vessel in which titration is to be carried out, but prefer, whenever possible, to remove the precipitate entirely from the filter. Ribbed filters are therefore not to be recommended in cases where the precipitate is subsequently to be titrated.

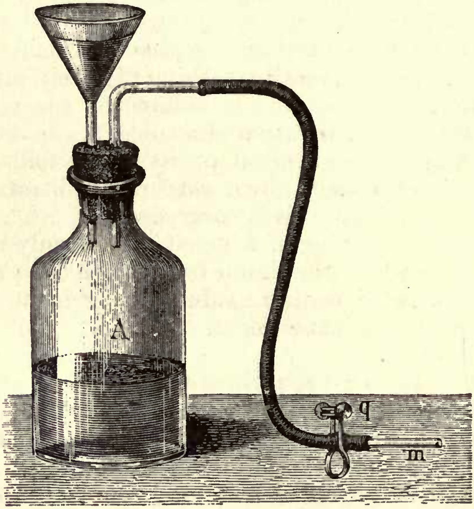

Fig. 10.

Many methods for securing rapid filtration have been proposed; among these the use of Bunsen's filter-pump holds a pre-eminent position. This method, notwithstanding its many advantages, has certain drawbacks. Finely divided precipitates are very liable to pass through the pores of the filter, especially when filtration is conducted under considerably diminished pressure. If the platinum cone get a little out of shape, the filter paper is exceedingly liable to be torn during the filtration: lastly, the apparatus is not transportable. These drawbacks are obviated in my apparatus, which is of very simple construction. The apparatus will be understood by reference to fig. 10. The flask has a capacity of $\frac{3}{4}$ to 1 litre; the neck of the flask is 5 or 6 c.m. in width; the diameter of the funnel is 6 to 7 c.m.: the width of the tube of this funnel must *not, however, exceed* 6 m.m. The glass tube *m* is about 1 dc.m. in length, and 4 to 5 m.m. in width: it communicates by means of caoutchouc tubing with the tube, bent at right angles, which passes through a hole in the cork of the flask. The pinchcock *q* shuts off communication with the outer air; when this communication is to be opened, the pinchcock is moved on to the tube *m*. All joints must be thoroughly air-tight, and the filter must accurately fit into the funnel. To attain the latter purpose two filters are cut, one corresponding in size to the funnel, the other possessing a radius of only 1 to $1\frac{1}{2}$ c.m. (but not less). Both filters are folded into half circles, and the larger is placed within the smaller, so that the centres of each coincide, as shown in fig. 11. The filters are then further folded in the ordinary manner, and a filter is thus obtained double at the narrow end,

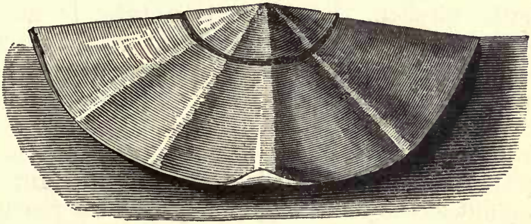

Fig. 11.

but single throughout its greater extent. The filter is placed in the funnel (the point being depressed into the funnel tube as much as possible), and thoroughly wetted. By applying suction at *m* the filter is pressed tightly against the funnel, so that the passage of air between funnel and filter during filtration is, as far as possible, prevented.[1]

The method of using the apparatus is simple. *q* is placed on *m*, and a few drops of liquid are allowed to pass through the filter; suction, several times repeated, is applied at *m* (the caoutchouc tube being closed by *q* between each application). If any air passes through between the filter and funnel, the filter is carefully pressed against the funnel, again wetted if necessary, and suction is once more applied at *m*. When the air in A has been sufficiently rarefied, the caoutchouc tube is closed by means of the pinchcock. On account of the rarefaction of the large volume of air in A, the apparatus works uninterruptedly, until the liquid has all passed through the filter.

A fresh quantity of liquid is now placed on the filter, and suction is again applied at *m*. On account of the double point of the filter, even finely-divided precipitates yield perfectly clear filtrates. The rapidity of filtration is four or five times as great as by the ordinary method. When filtration is complete, and the precipitate has been washed, the cork of A is removed, the funnel is placed over a beaker, and the precipitate is washed through the perforated filter into the beaker, or the precipitate and filter are removed (this is easily done by blowing in at *m*), the filter is spread upon a glass plate, and the precipitate is washed into a basin.

If it be desired to dry, ignite, and weigh the precipitate, the filter is carefully removed from the funnel, placed in another funnel, and dried in the hot chamber.

No great effort is required in order to produce the necessary degree of rarefaction in A: four or five good

---

[1] Dr. Fleischer tells me that if the upper (single) part of the filter be ribbed, the process of filtration is materially hastened.—*Tr.*

inspirations are sufficient to cause the total liquid contents of the funnel to pass quickly through the filter.

The filter paper employed must be of a strength such that a *single* layer of it is sufficient to resist the increased pressure to which it is subjected (the rarefaction in A is generally equal to about 1 metre of water). Such paper is not, however, to be altogether relied upon; it does not adhere well to the sides of the funnel. I have therefore recommended the use of a filter which is double at the point. The use of too fine paper introduces a risk of tearing the filter. I find that one sq. dc.m. of the paper used by me weighs, when dry, 0·824 grams. The presence of acetic acid or of ammonia, even in hot liquids, if these be not very concentrated, causes no inconvenience; in such cases it is, of course, easy to intercalate a tube containing ferrous sulphate, or soda.

SECTION II.

ANALYSIS BY SATURATION.

(Alkalimetry and Acidimetry.)

VOLUMETRIC analysis, by means of saturation, includes those processes in which a base is neutralized by means of acids, or an acid by means of bases—the quantity of base or of acid used serving as a datum whence the amount of the substance to be estimated may be calculated. The processes of analysis by saturation may, therefore, be divided into two classes: *Alkalimetry* (estimation of bases) and *Acidimetry* (estimation of acids).

§ 6.

Standard Solutions.

Two solutions are required—an acid, for alkalimetric processes, and an alkali for acidimetric.

As acid solutions, it has been customary to employ either oxalic or sulphuric acid; these are both non-volatile. No objection could be taken to the employment of these acids, did they form easily soluble salts with the metals of the alkaline earths (which earths it is so frequently required to estimate volumetrically), and had not experiment shown that nitric and hydrochloric acids form quite as permanent and more easily used titration liquids. My own experiments have proved that the strength of a normal hydrochloric acid solution is unaltered after half a year's keeping; nor have I been able to obtain any acid reaction with litmus paper placed in the steam given off by a solution of $\frac{1}{10}$ or even $\frac{1}{5}$ normal acid kept in ebullition for 10 minutes. The ease with which pure hydrochloric acid may be obtained, and the fact that this acid forms readily soluble salts with the metals of the alkalies and of the alkaline earths, recommend this acid in an especial manner as a standard for titration processes. Hydrochloric acid has the further fact in its favour that it does not exert an oxidising action as nitric acid does. Moreover, the quantity of true hydrochloric acid in any solution may be estimated not only by acidimetric processes, but also, as a control, by means of silver. I invariably make use of hydrochloric in preference to all other acids in my alkalimetric processes. The hydrochloric acid which is to be employed for preparing standard liquids should give no blue colour when tested with potassium iodide and starch after neutralisation with sodium bicarbonate, (the production of a blue colour being indicative of the presence of free chlorine). Nor should the blue colour which is produced by adding one drop of iodine tincture to starch paste be destroyed by the addition of a small quantity of the acid (proving the absence of sulphurous acid). After partial neutralisation with ammonia, the acid should not be rendered turbid to more than a very slight extent by the addition of barium chloride; the presence of traces of sulphuric acid may be overlooked.

The quantity of chlorine in diluted hydrochloric acid may be estimated by means of silver nitrate, and from the numbers so obtained the strength of the acid may be deduced. But, inasmuch as hydrochloric acid very frequently contains metallic chlorides (shown by the formation of a residue when a portion of the sample is evaporated on platinum foil), this method cannot be trusted to give the absolute quantity of pure acid. It is better to titrate the acid against a solid substance. Chemically pure calcium carbonate is very suitable for this purpose. This salt is prepared by adding a little ammonia and a few drops of ammonium sulphide to a solution of calcium chloride, boiling, filtering from any precipitate which may form, and adding an excess of ammonium carbonate to the *boiling* filtrate. The precipitated calcium carbonate must be washed with hot water so long as the washings are rendered turbid by the addition of silver nitrate after acidulation with nitric acid. The dried precipitate must be heated in a platinum crucible until the sides of the vessel just begin to glow. If the heating be then stopped, there is no necessity for moistening with ammonium carbonate solution and heating again, as is sometimes done. The ammonium carbonate is liable to contain traces of chloride.

Before detailing the process for *determining the strength* of the standard acid, I shall describe the preparation of the liquid which I always employ in place of the troublesome, although generally used, standard caustic potash.

It is difficult to prepare pure caustic potash; when prepared, this substance is very readily converted into carbonate by the action of the air. Hence it is exceedingly difficult to preserve standard solutions of potash unaltered. In addition to these drawbacks, caustic potash, because of the method of its manufacture, very frequently contains calcium hydrate, a circumstance which militates powerfully against its use in the analysis of calcium salts. Finally, caustic potash acts on glass, and a standard solution kept in glass bottles, therefore, alters in strength. On the other hand, there is no difficulty in obtaining chemically pure caustic ammonia; this liquid does not readily undergo transformation into carbonate; its action on litmus is as marked as that of caustic potash. Half-normal caustic ammonia which I kept for three months in glass-stopped bottles was shown to be free from carbonate at the expiry of this time. Caustic ammonia is volatile, nevertheless I find that the alteration in the strength of a half-normal solution amounts, after four months' keeping in a glass-stoppered bottle, to so small a figure as to be almost without influence upon the processes of titration carried out with the solution. I have not been able to find any alteration in the strength of such a solution after it has been kept for one month. A slight change in strength, when the real amount of ammonia may be easily estimated at any time, is, however, more than compensated for by the facts that ammonia is not readily transformed into carbonate, that it may be easily obtained pure, and that it is a more agreeable liquid to work with than caustic potash. For these reasons I have been in the habit of employing half-normal caustic ammonia solution in acidimetric analyses, and have had every reason to be satisfied with the results obtained.

The normal hydrochloric acid solution must contain 36·5 m.gm. of acid ($HCl=36·5$); and the half-normal ammonia must contain 17·5 m.gm. of ammonia, calculated as NH_4HO ($NH_4HO=35$), or 8·5 m.gm. calculated as NH_3 ($NH_3=17$) per cubic centimetre. 200 cb.c. of chemically pure hydrochloric acid are mixed in a litre flask with 800 cb.c. of distilled water; similarly, 120 cb.c. of pure caustic ammonia solution are diluted with 880 cb.c. of distilled water. To 20 cb.c. of the acid placed in a beaker glass, a few drops of litmus tincture are added, and the ammonia solution is run in drop by drop from a burette, until the red colour of the liquid in the beaker changes to a permanent blue. This process is repeated, and from the mean result, the value of 1 cb.c. of ammonia solution in terms of the acid is calculated.

1 gram. of chemically pure calcium carbonate is weighed out, 20 cb.c. of the hydrochloric acid are added, a drop of litmus is brought into the solution, and the whole of the carbonic acid is removed by boiling. After the clear liquid has become quite cold, the excess of acid is determined by means of the prepared ammonia solution. The number expressing the cubic centimetres of free acid in the liquid is deducted from 20 (the number of cb.c. of acid originally added), and the number of cb.c. of acid required for the conversion of 1 gram of calcium carbonate into chloride is thus obtained. Inasmuch as the reaction between hydrochloric acid and calcium carbonate is expressed by the equation—

$$2\,HCl + CaCO_3 = CaCl_2 + CO_2 + H_2O,$$

it follows that 100 m.gm. of calcium carbonate are neutralised by 36·5 × 2 m.gm. of hydrochloric acid: 1 cb.c. of normal acid will therefore neutralise $\frac{100}{2}$ m.gm. of calcium carbonate, or 20 cb.c. will exactly neutralise 1 gram of calcium carbonate.

In order to calculate, from the results of such an experiment as that just described, the quantity of water which must be added to the prepared hydrochloric acid, in order to make an exactly normal liquid, the following formula is employed—$\phi = \frac{20\ V}{v}$, where ϕ represents the volume to which the prepared acid must be diluted, V the actual volume of that acid, and v the number of cb.c. of the acid required to neutralise 1 gram of calcium carbonate. For example, if 16 cb.c. of prepared acid have been required, and if the total volume of acid amounts to 960 cb.c., then this volume must be increased to $\frac{960 \times 20}{16} = 1{,}200$ cb.c. in order to obtain normal acid—*i.e.*, 240 cb.c. of distilled water must be added.

(If the old notation be employed, the normal acid must still contain 36·5 m.gm. HCl per cb.c.; but each cb.c. of ammonia, if the solution is to be half normal, must contain 13 m.gms. NH_4O. 20 cb.c. of normal acid will then correspond to 1 gram of calcium carbonate, because $CaOCO_2 = 50$ and $CaOCO_2 + HCl = CaCl + CO_2 + HO$.[1])

The results of one titration cannot be relied upon as a datum whence to calculate the quantity of water which must be added to the prepared acid in order to render it normal. Another experiment must be carried out, using 3 or 4 grams of calcium carbonate, and, of course, a larger quantity of acid. After the acid has been diluted it is well to repeat the titration. As the ammonia solution is to be half normal, 2 cb.c. (=35 m.gm. NH_4HO) of it must

---

[1] In the foregoing experiments it would be preferable not to attempt to weigh exactly 1 gram of calcium carbonate, but to weigh *accurately about* 1 gram, and, from the results of the titration, to calculate how many cb.c. of acid are required for the neutralisation of 1 gram.—*i.e.*, to calculate the value of v in the formula given.—*Tr.*

neutralise 1 cb.c. of normal acid. The relation between the acid and the ammonia must be several times determined, using larger and larger volumes of ammonia for titration.

The standard liquids are to be preserved in well-stoppered glass bottles, placed in a cool position, and accurately labelled. The date of preparation should be marked on the labels. If necessary, more dilute solutions may be prepared—half-normal acid and quarter-normal alkali—simply by adding the proper quantity of water to those already made. The standards, the preparation of which has been described, will however be found sufficient for all ordinary work. The analyses conducted by means of these liquids are generally completed by titrating back with the half-normal ammonia, and, inasmuch as 2 cb.c. of this solution neutralise 1 cb.c. of the normal acid, any error due to the too hasty addition of the liquid is greatly diminished, and the excess of acid which has been added is much more accurately determined, than if liquids exactly equal, volume for volume, were employed.

A third solution, sometimes made use of in saturation analyses, is normal potassium carbonate. This solution serves for the estimation of combined acids, inasmuch as many soluble and insoluble salts are decomposed by boiling with this salt, with the production of insoluble oxides or carbonates, and the setting free of the acid. For instance, normal potassium carbonate solution is employed in the determination of the sulphuric acid in gypsum, the hydrochloric acid in iron and zinc chlorides, &c. The use of this solution will be described under the heading of Special Methods.

A normal solution of potassium carbonate is prepared by dissolving 138·2 grams of potassium carbonate, prepared from the tartrate, in 1,000 cb.c. of distilled water. In order to determine whether the liquid so prepared is really normal, 20 cb.c. are saturated with 60 cb.c. of normal hydrochloric acid, the carbon dioxide is removed by boiling, and the excess of acid is titrated (after cooling) by half-normal ammonia. By making use of the results so obtained the liquid may be readily rendered normal, if it be not so already.

The use of sodium carbonate in place of the potassium salt is not to be recommended.

Many substances have been proposed as indicators in place of litmus tincture in the processes now under consideration. Most of these substances I have tried: cabbage infusion, georgia tincture, extract of the seeds of *Solanum guinense*, the colouring matter of the leaves of *Coleus Verschaffelti*, cochineal, logwood extract, iron sulphocyanide, Prussian blue, ammonium phlorizeate, turmeric, alizarin, and cyanin, &c., but I have always found that these substances are either not sufficiently sensitive, or that in the presence of traces of iron or aluminium salts their indications are not to be depended upon, or altogether fail. Cyanin is altered by carbonic acid. Rosolic acid has no special advantages over litmus and cochineal; its use is, however, strongly to be recommended in the titration of alkaline sulphides, because it is unacted upon by sulphuretted hydrogen which bleaches most of the other colouring matters. I cannot, therefore, recommend any indicator for general use in preference to litmus tincture, and, when perfectly pure, alcoholic tincture of cochineal.[2] The best method of preparing litmus tincture consists in digesting commercial litmus with strong spirit of wine, decanting the liquid and extracting the residue with hot water. The aqueous extract is then acidified with sulphuric acid, and saturated with caustic baryta solution. The excess of baryta is removed by means of a stream of carbon dioxide; the liquid is heated to boiling and filtered.

More simply, the tincture may be divided into two portions, of which one is rendered slightly acid, and the other slightly alkaline (by dilute potash solution); the two portions are then mixed.

The tincture should be kept in bottles fitted with corks, having grooves cut in them to admit air. Like other

---

[1] In old notation 69·1 grams $KOCO_2$ are employed per litre of water: to 20 cb.c., 30 cb.c. of normal acid are added.

[2] For certain analysis Eosin is an exceedingly delicate indicator. See process for analysis of soap in Part III.—*Tr.*

vegetable decoctions, litmus rapidly becomes mouldy. The addition of a very few drops of a solution of salicylic acid in 30 to 40 parts of alcohol effectually prevents decomposition for a very considerable time without exercising any appreciable chemical action upon the litmus. I cannot too highly recommend salicylic acid as a preservative for chemical reagents which are liable to undergo putrefactive decomposition.

Cochineal tincture, on account of its being much less affected by carbonic acid than litmus, is preferable to the latter as an indicator in the titration of alkaline carbonates, especially when the process is carried out in hot solutions. Turmeric paper is also used as an indicator, especially in the titration of coloured liquids. To prepare it, filter paper is soaked in an alcoholic solution of the colouring matter; the paper is dried in a position where it is preserved from the action of the air—most easily in pasteboard boxes. If a drop of a liquid which contains a trace of free caustic alkali be brought into contact with this paper a peculiar reddish brown colour is developed.

§ 7.

Upon Determining the Final Point of the Reaction in Saturation Analyses.

In all saturation analyses the determination of the exact point at which the change of colour marking the termination of the reaction takes place becomes a matter of the utmost importance. Certain rules must be observed in determining this point.

Such a quantity of litmus should be added as suffices to render the liquid distinctly red when acid, and visibly blue when alkaline. If the final point is to be known by the sudden change from red to blue, every trace of carbonic acid must be removed from the liquid: this is best effected by boiling for three or five minutes after placing a very small piece of glass rod in the liquid. In using the standard ammonia solution care must be taken that the liquids to which it is added be perfectly cold: ammonium salts, especially the sulphate, have the power of feebly reddening litmus in warm solutions.

Cochineal tincture (prepared by digesting the material in dilute alcohol) should be employed in warm liquids, because any escaping carbonic acid is, in such liquids, without action on the colouring matter.

Cochineal cannot be used as an indicator in the presence of traces of iron or aluminium salts: it is much less suitable for the titration of acids than for that of alkaline carbonates. By paying regard to these precautions the final point in titrations with caustic ammonia may be most accurately determined.

A.—Alkalimetry.

§ 8.

Estimation of Caustic Alkalies and Alkaline Carbonates; of Alkaline Earths and of Lead Oxide.

Solutions of the caustic alkalies and of the alkaline earths may be titrated directly by the use of normal acid, after the addition of litmus tincture. The more free the bases are from carbonic acid, the more easily are they titrated. This method of direct titration is therefore especially applicable to the estimation of caustic ammonia, caustic baryta, and strontia, and freshly prepared caustic potash and soda. The process described for estimating the carbonates of the alkalies is more applicable than that just mentioned, in the cases of caustic lime and magnesia.

The reaction of the carbonates of the alkalies is alkaline, but this alkalinity ceases when double carbonates, or free carbonic acid, are formed by the addition of the standard acid. Pure sodium, potassium, or ammonium bicarbonate, does not produce any blue colour with red litmus paper. In estimating alkaline carbonates, the titration must therefore either be carried out in boiling solutions, whereby the production of salts having acid reactions is prevented, or an excess of standard acid must be added, and after the carbonic acid has been completely expelled by boiling, and the liquid has become cold, the excess of acid must be determined by means of half-normal ammonia solution. The latter method is preferable. The difference between the number of cb.c. of normal acid added, and half the sum of the number of cb.c. of half-normal ammonia employed, represents the number of cb.c. of normal acid required to saturate the amount of alkaline carbonate present. By using cochineal tincture in place of litmus, and by carrying out the process in a warm liquid, the quantity of alkaline carbonate may be directly determined by titrating with normal acid, until the colour changes to yellowish-red. The more preferable method is, however, that described above, the half-normal ammonia being run in until the colour becomes blue-violet. In this titration the absence of alumina and iron must be ensured.

The carbonates of the earths, and the difficultly soluble alkaline earths themselves, are estimated in a similar manner. The substance is suspended in water heated to 60° or 70°, 20 cb.c. of normal acid are added by means of a pipette, and the heating is continued. The carbonic acid soon makes its escape from the warm liquid. If everything be not now dissolved, a further quantity of acid (10 cb.c.) is added. If on the addition of litmus the colour of the liquid does not at once become red, more acid is added. This addition of acid is continued until bubbles of gas cease to be evolved, and until the solution remains red after long-continued heating. After a sufficient measured quantity of acid has been added, the liquid is boiled for a few minutes, allowed to cool, and the excess of acid is determined by means of half-normal ammonia. Care must be taken that there is such a quantity of water present, as shall serve to dilute the excess of acid to 3 or 4 times its original volume. Thus if 10 cb.c. of acid have been added in excess, the liquid must measure at least 40 cb.c., else there is danger of traces of hydrochloric acid being lost during boiling. If the liquid be boiled in a beaker, the vessel must be covered with a watch glass to avoid loss by spirting. If a flask be used it should be held by means of a retort clamp. Porcelain basins are most useful in these alkalimetric titrations, both because of the ease with which carbonic acid escapes, and also because of the readiness with which the change of colour marking the close of the reaction may be determined.

Lead oxide may be estimated by a method exactly similar to that just described for the alkaline carbonates. If the lead has been precipitated as sulphate, this salt may be collected, washed, and warmed for a few minutes with a measured volume of normal potassium carbonate solution. After filtering, the liquid is titrated, and the quantity of potassium carbonate so obtained (which represents the excess of that salt added over and above the quantity required for the decomposition of the lead sulphate) is deducted from the amount originally added. The residue represents the quantity of K_2CO_3 required to decompose the lead sulphate, and from this the amount of lead may be calculated. In place of this method, the following may be employed. The lead sulphate is decomposed by means of an unmeasured volume of potassium carbonate solution, the washed residue is dissolved in an excess of normal hydrochloric or, better, of normal nitric acid, the lead is precipitated as sulphate by the addition of sodium sulphate, and the excess of acid is estimated in the filtrate.

In the foregoing estimation it is to be borne in mind that 1 cb.c. of normal hydrochloric acid neutralises that amount of one of the caustic alkalies in m.gms, which is expressed by the formula; but half that amount of either alkaline carbonate, alkaline earth, earthy carbonate, or lead oxide expressed by the formula of these substances. (In the old notation 1 cb.c. normal acid neutralises one atom of *all* these bodies.)

§ 9.

Mixtures of Carbonates and Caustic Alkalies.

For analysing a mixture of these salts, the following process may be adopted. A weighed quantity of the substance is dissolved in water, and the solution is boiled with barium chloride. When the precipitate has somewhat settled, it is removed by filtration, and, after washing with hot water, the filtrate is titrated by means of normal hydrochloric acid. The quantity of *free* caustic alkali is thus obtained.

The washed precipitate is now to be dissolved in a beaker in a measured quantity (excess) of normal hydrochloric acid, and the excess of acid is to be determined by half-normal ammonia. The quantity of barium carbonate is thus obtained, and from this the quality of alkaline carbonate originally present is readily calculated.[1]

Two points are to be especially noticed in carrying out this process. Only *one* alkali as carbonate and as caustic can be estimated in a given solution. The filtration should be carried out as quickly as possible, and in a covered filter, in order that the free alkali may not absorb carbonic acid from the atmosphere.

The filtering apparatus already described will be found very serviceable here. The absorption of the barium-containing liquid by the filter paper is a circumstance which renders the process just described somewhat untrustworthy. A better process for achieving the same aim will be described under *Acidimetry.* I have, however, detailed the present process in order to show how a compound may be *indirectly* estimated by volumetric processes.

In the present case it is the barium carbonate which is actually determined, and from the results of this determination the amount of alkaline carbonate is deduced.

---

[1] 1 cb.c. normal hydrochloric = 98·5 m.gm. barium carbonate = $\frac{BaCO_3}{2}$, = 69·1 m.gm. potassium carbonate = $\frac{K_2CO_3}{2}$, or 51 m.gm. sodium carbonate = $\frac{Na_2CO_3}{2}$.—*Tr.*

We shall hereafter frequently have occasion to employ indirect methods of analysis. These methods frequently enable us to do away with tedious separation processes which would otherwise be necessary.

§ 10.

Alkaline Earths in Soluble Salts.

Baryta, strontia, lime, or magnesia may be estimated in soluble salts as follows: A weighed quantity is dissolved in water, or, if already in solution, a measured quantity of the solution is taken; the liquid is boiled with ammonium carbonate (magnesia salts with caustic potash) in excess, the precipitate is filtered off, washed, and dissolved in a porcelain basin in a measured excess of normal hydrochloric acid. The excess of acid is determined by means of half-normal ammonia solution.

1 cb.c. normal acid = BaO, SrO, CaO, or $MgO \div 2$.
In old notation,
1 cb.c. normal acid = BaO, SrO, CaO, or MgO.

§ 11.

Estimation of Ammonia, Nitric Acid, and Nitrogen.

Ammonia may be driven out of any liquid by boiling, after addition of excess of caustic alkali, and may be estimated by absorption in a measured volume of normal acid. This method is the simplest, and often the only available method for the estimation of ammonia. The frothing of the liquid during ebullition is, however, a drawback to the process, as a loss is apt to ensue, inasmuch as the flask containing the boiling liquid must not be of too large a size. Especially disagreeable results are liable to ensue from the frothing and bumping of the liquids in cases where a precipitate is present, as, for instance, in the estimation of ammonia in the double sulphate of ammonium and iron. Those drawbacks are, however, easily obviated by adding to the liquid an equal volume of strong alcohol, and heating only to incipient boiling. So long as alcohol is present the liquid boils quietly; whenever frothing begins the flame should be extinguished, and the apparatus allowed to remain for half an hour at rest before the titration is carried out. The whole of the ammonia will by this time have passed over. Perfect certainty on this point may be gained by setting the flask containing the liquid in a water bath, and heating the water for some time. Fig. 12 represents the disposition of the apparatus. A contains the liquid in which ammonia is to be estimated. It is furnished with an exit tube only; if the potash is added in the solid form, there is no danger of any loss of ammonia taking place before the cork is fitted into the flask. B and C both contain measured quantities of normal hydrochloric acid. If A and B be connected by caoutchouc tubing, the alcohol which comes over with the ammonia will dissolve particles of this substance, which will render the acid somewhat turbid, but this does not affect the

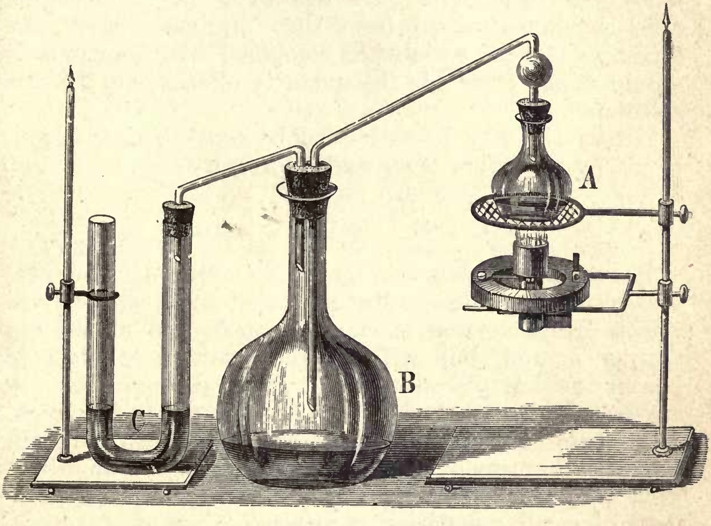

Fig. 12.

titration. The apparatus having been made air-tight, the liquid under examination is placed in A along with its own volume of alcohol, a considerable quantity of caustic potash, in sticks, is added, and the liquid is boiled until bumping begins; a dish containing boiling water is then placed underneath A, and this water is kept hot for a quarter, or half an hour. The contents of B and C are poured into a beaker, the vessels are washed with distilled water, and the excess of acid is determined by means of half-normal ammonia. By deducting the acid which remains unneutralised from that originally used, the quantity of acid which has combined with ammonia is obtained, and from this the quantity of ammonia itself is calculated.

Nitric acid may be estimated by conversion into ammonia by the action of nascent hydrogen—

$$HNO_3 + H_8 = NH_3 + 3H_2O.$$
$$(NO_5 + H_8 = NH_4O + 4HO).$$

The apparatus shown in fig. 12 is employed. The solution containing the nitrate is placed in A along with a considerable excess of caustic potash and aluminium powder or foil, but without the addition of alcohol.[1] Normal acid is placed in B and C, and the contents of A are boiled until the whole of the ammonia is driven off. A mixture of 1 part of iron with 2 of zinc (free from arsenic and antimony) may be used instead of aluminium. This process is less serviceable for the estimation of large than of small quantities of nitrates (1 gram potassium nitrate is regarded as a large quantity) because, in the former cases, long-continued boiling is required. For the estimation of such small quantities of nitrates as we find in waters the process is admirably adapted. In these analyses it is better to use $\frac{1}{10}$th-normal hydrochloric acid and to titrate with $\frac{1}{20}$th-normal ammonia.

The analysis of ammonium nitrate may be accomplished by boiling with potash, whereby ammonia is evolved, and

---

[1] For 1 part of solid potassium nitrate, supposing this to be the nitrate under examination, 5 parts by weight of aluminium, and 15 parts of solid potash are required.

then adding zinc or aluminium, and again boiling, whereby the nitric acid is reduced to ammonia, which is again evolved.

The nitrogen in many organic bodies may be converted into ammonia by heating with soda lime. For this purpose a little asbestos is placed at the closed end of a piece of combustion tubing, after this a few crystals of oxalic acid are laid in the tube, then an intimate mixture of a weighed quantity of the organic body with four times its weight of soda lime, followed by a further quantity of soda lime. The contents of the tube are shaken so as to afford an easy exit for the gases. The open end of the tube is connected with a bulb apparatus containing a known quantity of normal acid; the tube is placed in a combustion furnace, and heat is applied, beginning at the end with which the bulb apparatus is connected. The ammonia which is evolved is measured as already described.

All organic bodies do not yield their nitrogen as ammonia by this treatment. Indigo, brucine and many other alkaloids, for instance, yield only a portion of their nitrogen in the form of ammonia, when heated with soda lime.

In such cases the nitrogen is best estimated after evolution in the form of gas: the processes by which this measurement is effected do not, however, strictly belong to the titration methods of analysis.

The following simple method serves to estimate *ammonia in presence of the alkalies or alkaline earths,* but not in presence of the earths proper or of metallic oxides; arsenic and phosphoric acids are supposed to be absent.

If the solution be not already acid it is rendered so by addition of hydrochloric acid; litmus is added, and half normal ammonia or caustic potash of known strength is run in until the colour changes to blue. If half-normal ammonia is used, the number of cb.c. of solution employed must be noted. Such a measured volume of caustic potash of known strength is then added as is sufficient to decompose the whole of the ammonium salts present. The presence of a little carbonate in the potash solution does not affect the results. The liquid is now boiled in a porcelain basin, every precaution being taken to avoid spirting, until the issuing vapours cease to colour red litmus paper blue. The potash remaining in the liquid is now determined and deducted from the quantity originally added: the amount required for the decomposition of the ammonium salts is thus obtained ($KHO = NH_3$). If the solution has been rendered neutral before the decomposition of the ammonium salts by means of ammonia, the amount added for this purpose must be deducted from the total ammonia found.

§ 12.

Alkalimetric Estimation of Potash and Soda in Soluble Salts which are devoid of Alkaline Reaction.

The alkali salt of a volatile acid may be converted into sulphate by evaporation to dryness with sulphuric acid. By boiling the sulphate with caustic baryta, passing carbonic acid into the liquid, and filtering, the whole of the alkali may be obtained in the form of carbonate, which may then be estimated by the method already described.

This method of procedure is applicable in the presence of earths and alkaline earths, or, indeed, of most of the metallic salts, inasmuch as these substances are insoluble in potassium carbonate. In order to prevent the formation of too large a precipitate, care should be taken that the alkali salt forms the main constituent of the liquid to be evaporated with sulphuric acid. The use of a great excess of caustic baryta should also be avoided. If an alkali salt contain a non-volatile acid, this must be removed, unless it be readily transformed into a volatile substance by the action of sulphuric acid. The greater number of the non-volatile acids may be removed by the addition of lead acetate to neutral or slightly acid solutions. Among the acids whose removal may be thus effected may be named: *Chromic, phosphoric, tungstic,* *molybdic, arsenic,* and *tartaric acids,* &c. It is evident that this method, and, indeed, alkalimetric methods in general, suffices for estimating only a single base. At the close of this paragraph a method will, however, be described which serves for the estimation of both soda and potash when present together.

Another method for estimating potash and soda is that given by Stolba, and consists in precipitating these substances by means of hydrofluosilicic acid and an equal volume of strong alcohol, from a solution made slightly acid with hydrochloric, or, better, with acetic acid. The precipitate, after being washed with 60 per cent alcohol, is dissolved, according to Stolba's directions, in a measured quantity of hot normal potash solution, and the excess of alkali is determined by means of normal acid.

On account of the difficulty of determining the exact point at which the colour changes to reddish blue in this reaction, I prefer to decompose the precipitate by boiling with milk of lime for ten minutes, to conduct carbonic acid into the liquid until the excess of lime is entirely converted into carbonate, to filter, and wash while hot, with water. The filtrate, which should give no precipitate with carbonic acid, now contains the whole of the potash or soda as carbonate, which is estimated by titration with normal hydrochloric acid, cochineal tincture being employed as indicator.

If this process be applied to sulphates of the alkalies, the sulphuric acid must be removed by means of calcium acetate and alcohol before precipitation of the alkali by means of hydrofluosilicic acid.

Silico-fluoride of calcium may be made use of instead of the acid itself in the foregoing process. I prepare this salt as follows: 1 part of crystallised barium hydrate is dissolved in 5 to 7 parts of water, and to this solution, while boiling, finely powdered cryolite is added in quantity sufficient to convert almost the whole of the barium into fluoride. For 5 parts of baryta about 1 part of cryolite is employed. The liquid is boiled for fifteen minutes, filtered while hot, and washed until the filtrate ceases to become turbid when boiled with sal-ammoniac. The precipitated barium fluoride is mixed with a quantity of artificially prepared silicic acid, or of quartz-powder, produced by throwing strongly heated quartz into water, equal to the weight of cryolite used, and with 5 to 7 times this quantity of dilute hydrochloric acid; barium silico-fluoride is hereby produced. After some hours the greater part of the free acid is carefully neutralised by means of barium or calcium carbonate; calcium acetate is added in excess, and after an hour the barium silico-fluoride is filtered off. The precipitate is washed with dilute alcohol, and boiled for five minutes with water containing finely divided gypsum in suspension. The barium is thus entirely precipitated in the form of sulphate. A considerable volume of strong alcohol is now added to the liquid, which is then filtered. The filtrate is a solution of pure calcium silico-fluoride, very well adapted for precipitating potash and soda. Calcium silico-fluoride may also be prepared by saturating hydrofluosilicic acid with barium chloride, or, better, with barium acetate, adding an equal volume of alcohol, and treating the precipitated barium silico-fluoride as already described.

As the precipitates of potassium and sodium silico-fluoride form slowly, the liquids in which these salts are produced must be allowed to stand for several hours. Inasmuch also as the presence of free nitric, or hydrochloric acid prevents the formation of these salts, the solution should either be treated with calcium acetate before precipitation, or calcium silico-fluoride should be used, instead of hydrofluosilicic acid, as a precipitant.

Potassium may also be precipitated by means of tartaric acid; but in this case all bases other than the alkalies must be removed. This can readily be done by the use of ammonium carbonate.

In a solution containing only potash and soda (not ammonia), potash may be estimated by Mohr's method. This method succeeds best when the amount of potash present is not very small. Acid sodium tartrate is added in quantity sufficient to precipitate the potassium, and the liquid is evaporated to dryness. The residue is thoroughly shaken with 150 to 200 cb.c. of a cold saturated solution of cream of tartar; after some time the liquid is filtered, and the precipitate, after washing with the tartar solution, is dissolved in a large quantity of hot water, and titrated by means of normal potash. The amount of potash used in titration is equal to that originally present in the solution.

In the following process I have been able to perfect a method in which tartaric acid serves as a reagent, both for precipitating potash, and also for separating it from soda. This method gives accurate results, and is easily executed.

The solution must contain no other bases except the alkalies, and must be free from all acids with the exception of hydrochloric, nitric, or acetic.[1] The solution having been rendered slightly alkaline with ammonia is evaporated to the bulk of 20 to 30 cb.c., 10 or 15 cb.c. of ordinary liquid ammonium acetate are added (as this substance is usually acid, it should be previously rendered neutral with ammonia), followed by the addition of such a quantity of perfectly pure tartaric acid, crystallised from alcohol, as suffices to transform the whole of the potassium into tartrate, and a part, *but not the whole*, of the ammonium acetate into tartrate. For 10 cb.c. of ammonium acetate, of sp. gravity 1·035, not more than 5 grams of tartaric acid must be employed. If the quantity of potassium be approximately known, then it is better to add a little more tartaric acid than is sufficient to convert the whole of this into tartrate.

The tartaric acid is added in the form of fine powder; the liquid is repeatedly stirred with a glass rod, care being taken not to rub the sides of the glass vessel, and after five minutes or so, an equal volume of 95 per cent alcohol is added, and the liquid is again repeatedly stirred. When the precipitate has completely settled it is collected on a filter, and washed with a mixture of two parts alcohol and one part water, until the washings cease to be rendered turbid by the addition of hydrofluosilicic acid,

---

[1] The alkaline earths may be removed by means of carbonate or phosphate of ammonium. Sulphuric, chromic, phosphoric, arsenic, &c., acids may be removed by means of barium chloride, the excess of which salt is then precipitated by ammonium carbonate.

or by silver nitrate if chlorine was originally present. The precipitate contains the whole of the potassium as tartrate, and also most of the remaining tartaric acid which was added, as ammonium tartrate: *it is entirely free from sodium.*

In the event of sodium acetate being present, sal-ammoniac must be added (in order to convert the sodium into chloride) before the addition of tartaric acid; otherwise sodium tartrate might be formed. The precipitate of potassium tartrate and ammonium tartrate is brought into a porcelain basin, dissolved in 100 to 150 cb.c. of hot water, and titrated with normal caustic potash solution. The number of cb.c. required having been noted, an equal, or somewhat greater number of cb.c. is added, and the solution is boiled until the whole of the ammonia is driven off. When this is accomplished, and the liquid is reduced to half of its original bulk, or less, the excess of potash is estimated by titration with normal hydrochloric acid. The amount of potash thus found is deducted from that which was added in excess after titrating the precipitate of potassium and ammonium tartrates; the difference represents the quantity of ammonia which has been volatilised: by deducting this difference from the quantity of potash required in the first titration, the amount of potash in the substance is obtained.

Supposing that 26·7 cb.c. of potash were required for the first titration, and that 30 cb.c. were then added, and that after evaporation 9·3 cb.c. of normal hydrochloric acid were required for titrating back, it is evident that the precipitate contained that quantity of ammonia which is saturated by $30-9{\cdot}3=20{\cdot}7$ cb.c. of normal hydrochloric acid. By deducting this from the potash used in the first titration, we have $26{\cdot}7-20{\cdot}7=6{\cdot}0$ cb.c. as representing the quantity of potash in the precipitate, or $6\times56{\cdot}1$ m.gm. KHO, or $6\times\frac{94{\cdot}2}{2}$ m.gm. K_2O (old notation, $6\times47{\cdot}1$ m.gm. KO). If exactly the same quantity of potash be added before driving off the ammonia as was required in the first titration, it is evident that the quantity of normal hydrochloric acid employed in titrating back corresponds directly to the quantity of potash (KHO) in the precipitate, for the two titration processes may be thus represented—

$$2KH.H_4C_4O_6 + 2NH_4.H_4C_4O_6 + 4KHO = 3K_2.H_4C_4O_6 + (NH_4)_2H_4C_4O_6 + 4H_2O,$$

and

$$3K_2.H_4C_4O_6 + (NH_4)_2H_4C_4O_6 + 2KHO = 4K_2.H_4C_4O_6 + 2NH_3 + 2H_2O.$$

Or, in old notation,

$$KO2C_4H_2O_5 + NH_4O.2C_4H_2O_5 + 2KO = 3KO.C_4H_2O_5 + NH_4O.C_4H_2O_5,$$

and

$$3KO.C_4H_2O_5 + NH_4O.C_4H_2O_5 + KO = 4KO.C_4H_2O_5 + NH_4O.$$

The smallest quantities of potash may be separated from soda and estimated with great accuracy by this method. The precipitate might perhaps be ignited and the quantity of potassium carbonate thus obtained directly estimated. But the risks of loss in the process of ignition do not recommend this modification of the original process.

The soda remaining in solution may be precipitated by means of hydrofluosilicic acid or by calcium silico-fluoride and estimated as already described. Or the liquid may be evaporated to dryness with hydrochloric acid in a platinum dish and the residue weighed as sodium chloride. Inasmuch as the accuracy of the method chiefly depends upon exact titration it is better perhaps to employ half normal potash, or a dilute potash solution which has been titrated against normal hydrochloric acid. If too much potash be added, the excess may be determined by means of normal acid. This is the only volumetric method which allows of the direct estimation of potash in presence of soda. The same object may be accurately accomplished by indirect methods, as we shall see hereafter.

B. Acidimetry.

It is worthy of notice that acidimetric processes are not applicable for the estimation of the whole of the free acids. *Hydrochloric, hydrobromic, hydriodic, nitric, sulphuric,* *oxalic, tartaric, citric, acetic,* and *formic acids* can, it is true, be estimated, when in the free state, by titration with half-normal ammonia, but this method is not applicable in the cases of the *acids of phosphorus, of sulphur* (other than *sulphuric*) and of *arsenic.* Neither can *carbonic, boric, hydrocyanic, hydrosulphuric,* nor even *hydrofluoric acid,* be estimated by direct titration with ammonia, potash, or soda, because these acids do not form salts with the alkalies, which are without action upon litmus. It may thus be laid down as a general rule that only those acids whose combinations with the alkalies are neutral, without action on litmus, soluble, and not coloured, can be estimated by direct titration by means of alkaline liquids. Certain acids can, however, be estimated indirectly by alkalimetric methods. *Hydrofluosilicic acid,* for instance, may be estimated by precipitation with potassium chloride from a dilute alcoholic solution, and decomposition of the precipitate by lime, the potash being then determined. *Hydrofluoric* acid again may be transformed into potassium silico-fluoride, by addition of acidified soluble glass solution, and the potash estimated by a process similar to the foregoing, by means of lime. *Boric* and *carbonic* acids may be estimated after transformation into salts of the alkaline earths, by solution in normal hydrochloric acid and titration with half-normal ammonia: the amount of alkaline earth so found being deducted from the amount of borate or carbonate of the earth used, and the difference being reported as boric or carbonic acid. As the estimations of those acids which are determined by direct titration with half-normal ammonia present no special difficulties, we shall chiefly occupy ourselves with a consideration of such acids as can only be estimated by more or less indirect methods.

§ 13.

Estimation of Carbonic Acid.

All the carbonates may be decomposed by means of hydrochloric or sulphuric acid, and the carbonic acid estimated by conducting it into caustic baryta solution and determining the quantity of barium carbonate formed. The process is carried out by me as follows: The substance under examination is placed in a long-necked flask furnished with a caoutchouc stopper carrying a funnel tube leading to the bottom of the flask, for the delivery of the acid—this tube may be closed at will by a stopcock —and an exit tube which passes into a small flask. This flask is connected with another of the same size, to which are attached two U tubes. Each of the small flasks contains about 100 cb.c. of clear baryta solution (1:25); a quantity of the same solution is placed in each of the U tubes. The second U tube serves to absorb carbonic acid from the outer air. A few fragments of granulated zinc are placed along with the carbonate to be examined in the evolution flask. The apparatus having been properly adjusted, small quantities of hydrochloric acid are allowed successively to flow into the first flask which is at the same time gently warmed. When the evolution of carbonic acid has nearly ceased, a larger quantity of acid is run in so as to insure the evolution of a tolerably brisk current of hydrogen, and the contents of the flask are boiled for ten minutes or so. After cooling, the contents of the two small flasks and of the first U tube are washed into a beaker glass, and about five grams of ammonium oxalate, dissolved in a little water slightly acidulated with oxalic acid, are added. The excess of baryta is thus transformed into oxalate, but the barium carbonate remains altogether unacted upon. The precipitate of mixed carbonate and oxalate of barium is well washed with hot water, dissolved in a measured volume of standard hydrochloric acid, and after the carbonic acid has been removed by boiling, the barium is precipitated by means of potassium sulphate. A measured portion of the clear liquid is filtered off, and the free hydrochloric acid therein is estimated by half-normal ammonia. From the amount of barium carbonate found the carbonic acid is calculated.

This process directly estimates the quantity of carbonic acid in the substance examined, and is possessed of the further advantage that any hydrochloric acid carried over mechanically is without influence upon the result, inasmuch as it is only the precipitated barium carbonate which is determined.[1] The evolution of hydrogen simultaneously with the carbonic acid is not absolutely necessary, but is to be recommended in most cases; this part of the process must, however, be omitted if metals reduceable by zinc (copper, silver, &c.), or if lower oxides of sulphur (S_2O_3 and SO_2) be present. Lower sulphur acids, if present, must be oxidised before the carbonic acid is liberated: this may be effected by adding a considerable quantity of ferric chloride to the hydrochloric acid, and allowing the carbonic acid to be evolved very slowly without warming. If it be desired to estimate carbonic acid in a mixture of a carbonate and sulphide, the evolution of sulphuretted hydrogen may be prevented by the addition of ferric chloride.

The following process presents a simple gravimetric method for estimating carbonic acid in such carbonates as are decomposed by dilute acids *in the cold*. About twenty grams of dilute hydrochloric acid (concentrated acid with half its own volume of water) are accurately weighed into a 100 cb.c weighed beaker. A determinate portion of the carbonate in a small tube—amounting to at least five grams—is carefully placed in the beaker, which is set in a sloping position. After the evolution of gas has ceased, an accurately determined quantity—about five grams—of tartaric acid is added, and when this has entirely dissolved and the beaker has been allowed to remain at rest for quarter of an hour or so, the whole is again weighed. The loss of weight represents carbonic acid. Sulphuric acid of 40 per cent may be used instead of hydrochloric, except in analyses of the alkaline earth carbonates or of lead carbonate. The error in this process, if carefully carried out, does not exceed three-fourths of a per cent.

---

[1] It is to be remembered that one cb.c. of normal hydrochloric acid $= \frac{CO_2}{2} = 22$ m.gm. CO_2.—*Tr.*

§ 14.

Estimation of Sulphuric Acid.

The direct titration of this acid by means of half-normal ammonia calls for no especial remarks. The two following indirect methods, serve for the estimation of the free or combined acid in the presence of many other compounds.

The first method consists in acidifying the solution with hydrochloric acid, and precipitating the sulphuric acid by means of a solution of strontium chloride, which must be perfectly free from barium or calcium salts. Absolute alcohol, in quantity equal to half of the total volume of liquid, is then added. The precipitate is collected, washed with tolerably strong alcohol, and removed from the filter to a beaker glass. An excess of potassium (not sodium) carbonate is added, and the whole is boiled for some time, whereby the strontium sulphate is converted into carbonate, which is then filtered off, washed and dissolved in a measured quantity of normal hydrochloric acid, the excess of which is titrated by means of half-normal ammonia. The half of the number of cb.c. of ammonia used, deducted from the total number of cb.c. of acid employed for solution, represents the quantity of normal hydrochloric to be calculated to sulphuric acid.

$$\text{1 cb.c. normal HCl} = \frac{96}{2} \text{ m.gm. } SO_4$$

$$= \frac{98}{2} \text{ m.gm. } H_2SO_4$$

In old notation,

$$\text{1 cb.c. normal HCl} = 40 \text{ m.gm. } SO_3.$$

The second method is more simple; it is carried out as follows:—

After acidification with hydrochloric acid, the whole of the sulphuric acid is precipitated in the boiling liquid by a measured volume (excess) of barium chloride solution of known strength. The liquid is then rendered alkaline by addition of ammonia, and the excess of barium is precipitated by means of ammonium carbonate. The quantity of barium carbonate contained in the washed precipitate is determined according to § 10, and is calculated to barium chloride.

$$\underset{197}{BaCO_3} = \underset{208}{BaCl_2}\text{; old notation, }\underset{98{\cdot}5}{BaOCO_2} = \underset{104}{BaCl}.$$

By deducting the amount of barium chloride thus found from the total quantity used, a residue is obtained, which represents the quantity of this salt required to precipitate the whole of the sulphuric acid.

$$\underset{208}{BaCl_2} = \underset{98}{H_2SO_4}\text{; old notation, }\underset{104}{BaCl} = \underset{40}{SO_3}.$$

This method can only be applied for the estimation of sulphuric acid combined with alkalies, other bases being supposed absent. A much more general method will be described further on.

§ 15.

Estimation of Acetic Acid.

On account of the solubility of the acetates, the acid contained in them is readily transformed into an alkaline salt, by the addition of caustic potash, or potassium carbonate. On account of its volatility, acetic acid may also be readily removed from combination by means of another acid, and, after distillation, may be directly titrated by ammonia. Care must be taken that, besides acetic acid, the liquid contains only less volatile or non-volatile inorganic or organic acids. Distillation is then performed after addition of phosphoric acid, which does not cause volatilisation of nitric or hydrochloric acid, and the acetic acid is estimated in the distillate. Should small quantities of hydrochloric acid have been carried over, it is only necessary to estimate the chlorine in an aliquot part of the distillate by the method to be described hereafter, and, after calculating this to hydrochloric acid, to deduct the amount from the total acid found. This process is accurate if too rapid ebullition be avoided, and if the receiver be kept well cooled. A condensing apparatus should be employed in the distillation.

The distillation may be omitted in analysing pure acetates, the metal of which is completely precipitated by sulphuric acid. The quantity of acetic acid in acetate of barium, strontium, or lead for instance, may be determined by adding a measured volume of normal sulphuric acid, diluting to a fixed bulk—say 250 cb.c.—filtering two equal portions, and determining the total acid in one, and the sulphuric acid in the other, by the method detailed in the preceding paragraph. The quantity of acetic acid may be calculated from these data:—

2 cb.c. half-normal ammonia—

$$= \frac{98}{2} = 49 \text{ m.gm. } H_2SO_4.$$

$$= 60 \text{ m.gm. } C_2H_3O.OH.$$

In old notation,

2 cb.c. half-normal ammonia—

$$= 40 \text{ m.gm. } SO_3.$$

$$= 51 \text{ m.gm. } C_4H_3O_3.$$

This process is not applicable for the estimation of acetates containing other bases or acids.

This may be a fitting place to say a few words concerning the removal of the commoner volatile acids.

Sulphuretted hydrogen, sulphurous, and *hyposulphurous (thiosulphuric) acids* may be got rid of by the use of potassium permanganate or chromate. By the addition of zinc chloride, after excess of potassium carbonate, and filtering, free *chlorine, bromine* and *iodine,* and *hypochlorous acid* are rendered harmless. *Hydrocyanic acid* is removed by adding ferrous sulphate, followed by excess of potash, acidifying and filtering. The presence of *ferrocyanides, boric* and *carbonic acids* may be disregarded.

Certain *metallic oxides,* more especially the oxides of *iron, aluminium, uranium, lead,* and *tin,* form precipitates with phosphoric acid in acetic acid solutions; the presence of these salts is therefore to be avoided. *Iron salts* may be removed by the addition of potassium carbonate in excess. Lastly, the presence of *oxysalts of ammonium* influences more or less the correctness of the results. This source of error may be removed by the addition of a quantity of calcium chloride, sufficient to convert the ammonium into calcium salts. Permanganate of potassium serves to destroy *formic acid; benzoic* and *succinic acids* may be precipitated from slightly alkaline or neutral solutions by means of ferric chloride.

Generally, then, a method may be found by the use of which the estimation of acetic acid is rendered possible. Cases, in which the presence of volatile acids which cannot be removed nor destroyed by oxidizing agents, renders the method inapplicable, are comparatively rare. Most of the organic acids are precipitable by barium or lead salts in aqueous or alcoholic liquids. The salts of acetic acid on the other hand are all soluble in water, and generally also in alcohol.

§ 16.

Estimation of Tartaric and Citric Acids.

These acids, when in the free state, are readily estimated (like oxalic acid) by titration with ammonia.

2 c.b.c. half-normal ammonia

$$= \frac{150}{2} = 75 \text{ m.gm. } H_2.H_4C_4O_6.$$

$$= \frac{192}{3} = 64 \text{ m.gm. } H_3.H_5C_6O_7.$$

In old notation,

2 cb.c. half-normal ammonia

$$= 75 \text{ m.gm. } H_2C_4O_5.HO.$$

$$= 70 \text{ m.gm. } H_2C_4O_4 + \tfrac{4}{3}HO.$$

Tartaric acid may be precipitated from neutral alkali salts as potassium tartrate by the addition of potassium acetate (after acidification with acetic acid) and $1\frac{1}{2}$ volumes of alcohol: the precipitate may be titrated as described in § 12. This reaction of tartaric acid serves to distinguish it from most of the other acids, and especially from citric acid, which in many respects it so closely resembles. A process will be described hereafter for the estimation of these acids under somewhat complicated conditions.

§ 17.

General Estimation Methods for Combined Acids.

There are two reagents, the use of which enables us to estimate all acids which can be determined acidimetrically when in combination with metals other than those of the alkalies. The first of these reagents is *sulphuretted hydrogen.* This gas precipitates many metals as sulphides. After filtering, and boiling off excess of sulphuretted hydrogen, the acid which was formerly in combination may be estimated directly by half-normal ammonia. In mixtures of metallic salts precipitable by this reagent, the total acid may be estimated by the same process. This method fails, however, when salts are present which have an acid reaction, but which are not precipitated by sulphuretted hydrogen. Thus, in a solution containing copper sulphate and iron oxide, the acid could not be estimated directly by this process. The presence of the oxides of those metals which are precipitable by ammonium sulphide, or of those compounds of the earths with mineral acids which exhibit an acid reaction, generally renders the method unavailable.

Potassium carbonate is of much more general use than sulphuretted hydrogen as a reagent for the estimation of combined acids, inasmuch as not only the alkaline and the true earths, but very many of the metallic oxides likewise, are precipitated from their solutions by this reagent, the acid which was in combination with the precipitated metal at the same time entering into combination with the potassium.

The quantity of acid in any salt of a mineral acid, with the exception of the salts of tin, mercury, and antimony, and the other salts soluble in ammonium sulphide, may be determined with greater or less exactness by the use of potassium carbonate. The method of procedure is very simple. A measured volume of normal potassium carbonate solution, containing at least twice as much of the salt as is needed for the required reaction, is boiled in a beaker glass, the salt under examination is added little by little with constant shaking, the whole is transferred to a measuring vessel, which is filled to the mark (200 or 300 cb.c.) with water. After shaking and settling, an aliquot part of the clear liquid ($\frac{1}{2}$ to $\frac{3}{4}$) is poured through a dry filter into a suitable vessel, and the quantity of potassium carbonate therein is determined. This is calculated to the whole volume of liquid, and deducted from the potassium carbonate used. The residue represents the amount of this salt corresponding to the combined acid.[1]

The acids in certain insoluble or difficultly-soluble salts may be determined in the same way. The quantity of sulphuric acid in gypsum, for instance, may be readily estimated by this method; so also may the oxalic acid in insoluble lead oxalate be transformed into potassium oxalate by five or ten minutes boiling with potassium carbonate.

In the decomposition of certain substances, such as salts of iron, aluminium, and zinc, portions of the potassium carbonate are retained in the precipitate. These may be removed by allowing the precipitates produced after the decomposition to settle, decanting the clear liquid into the measuring vessel, boiling the precipitate with distilled water, to which a little potassium sulphate may be added, and then bringing the whole into the measuring flask. Care must be taken that the liquid amounts to at least 200 times the weight of the dry precipitate.

The presence of alkalies is without influence on these processes. If ammonium salts be present, the precipitation by potassium carbonate must take place at ordinary temperatures, in order that the volatilisation of ammonium carbonate may be avoided. In these cases, I have found

---

[1] 1 cb.c. normal potassium carbonate
= 1 equivalent, in m.gms., of a dibasic acid.
= $\frac{1}{2}$ equivalent, in m.gms., of a monobasic acid.—*Tr.*

it preferable to digest the precipitate with the potassium carbonate for several hours at the ordinary temperature in a closed vessel, to pour off the clear liquid into the measuring vessel, and to wash the precipitate with potassium sulphate solution. This method of procedure is especially to be recommended when dealing with iron and aluminium salts. Such a quantity of potassium carbonate must be employed as shall insure the transformation of the whole, or almost the whole, of the ammonium salts present into carbonate. The use of a flask, fitted with a caoutchouc or glass stopper, allows of the process being quickened by bringing the flask into boiling water for a quarter of an hour, and then cooling the liquid before transferring it to the measuring flask. If salts of metals whose oxides are more or less soluble in ammonium salts be present, the process can only be depended upon in the absence of ammonium salts. This caution is also to be observed in applying the process to magnesium salts. Magnesium carbonate, moreover, tends to retain alkaline carbonates, and is not insoluble in water. Hence, the process is not to be recommended for salts of this metal. This process is especially applicable for the ready determination of hydrochloric, sulphuric, nitric, acetic, and oxalic acids in presence of metallic oxides. It is also exceedingly useful for controlling the results of estimations of these acids performed by other methods.

Other acids, which are estimated with more difficulty than those mentioned, may be indirectly determined by this method ; as the following example shows :—

It is required to estimate nitric acid which has been found present in a sample of ferric chloride.

The chloride is decomposed by a measured volume of normal potassium carbonate solution. Two equal aliquot portions of the filtrate are treated as follows. One portion is decomposed by means of potassium chromate and calcium acetate, and the amount of chlorine is determined by a method to be hereafter described, and calculated to hydrochloric acid. To the other portion litmus tincture is added, then a measured excess of hydrochloric acid, and after boiling to expel carbonic acid, the acid which remains free is estimated by titration with half-normal ammonia. By deducting the quantity of hydrochloric acid so found from the total quantity determined in the first portion, a residue of hydrochloric acid is obtained which is equivalent to the quantity of nitric acid in the portion operated upon. This residue must be multiplied by $\frac{63}{36{\cdot}5}$ $\left(\text{old notation } \frac{54}{36{\cdot}5}\right)$ in order to obtain the corresponding quantity of nitric acid. Had the chloride contained sulphuric acid this might have been precipitated by barium chloride; and although the final results as regards hydrochloric acid would have been vitiated, yet the estimation of nitric acid would not have been interfered with.

SECTION III.

ANALYSIS BY OXIDATION AND REDUCTION.

IN analysis by means of oxidation and reduction the substance to be estimated is either oxidised or reduced, and its quantity is estimated by determining the amount of the oxidising or reducing agent required. The process supposes the absence of all foreign oxidising or reducing substances, as well as of all substances, except that which is to be estimated, which are capable, under the conditions of the process, of undergoing oxidation or reduction. The most commonly employed oxidisers are potassium permanganate and a solution of iodine in potassium iodide; the most common reducing agents are oxalic acid and sodium thiosulphate. The methods may be broadly classed as methods of *Oxydimetry* and of *Iodometry*; in the first or oxydimetric methods, the quantity of oxygen given up by potassium permanganate is determined; in the second or iodometric methods, the quantity of iodine which can combine with, or which is liberated by, the substance to be estimated, is determined, and from this the quantity of the substance itself is calculated.

A.—Oxydimetry.

§ 18.

Preparation of Permanganate Solution.

There is no difficulty in obtaining potassium permanganate in a nearly pure state. Permanganate solution is very frequently employed in the estimation of iron salts and of oxalic acid; its strength is best determined by titration against these substances. As, however, two equivalents of iron are converted from the state of protoxide into that of peroxide by the same quantity of oxygen as suffices to completely oxidize one equivalent of oxalic acid,[1] it is well to make the permanganate of a strength such that 1 cb.c. corresponds to $\frac{2}{10}$ equivalent of iron, *i.e.*, to 11·2 m.gm. of iron (in old notation to 5·6 m.gm. iron). We shall then have a solution of which

1 cb.c. = 11·2 m.gm. iron
= 12·6 m.gm. crystallised oxalic acid.

In old notation,

1 c.bc. = 5·6 m.gm. iron
= 3·6 m.gm. oxalic acid, C_2O_3.

If it be desired, however, to employ the permanganate very frequently for iron estimations—as in the laboratory of an iron-work—it is better to make it so that 1 cb.c. is equal to 10 m.gm. of iron. So also in an oxalic acid manufactory, the permanganate may be made of that strength which is found most suitable for the special purpose for which it is employed.

In order to prepare the solution of permanganate, about 64 grams of the crystals (3·2 if the old notation be employed) are dissolved in 1,000 cb.c. of cold distilled water; after solution is complete the liquid is allowed to remain at rest for some hours, and is then decanted from any precipitated matter. This method is to be preferred to that of dissolving the salt in a little hot water and making up with cold. The solution must be preserved in glass-stoppered bottles in a dark place.

The best substance to employ in the titration of the prepared permanganate is thin bright iron wire. Oxalic acid, it is true, is more easily used, and a solution of this substance may be prepared and employed repeatedly. I make use of oxalic acid for controlling the titration only when the crystals leave no residue after heating on platinum foil, and after a solution of the acid in dis-

[1] $2FeO + O = Fe_2O_3$
$C_2H_2O_4.2H_2O + O = 2CO_2 + 3H_2O$.

tilled water has been most carefully titrated against half-normal ammonia liquid. Other substances, such as potassium ferrocyanide, ferrous oxalate, or ferrous ammonium sulphate are sometimes used. These, with the exception of the last named, cannot be easily prepared in a state of purity.

In dissolving clean iron wire in dilute sulphuric acid traces of ferric salt are always formed, probably by the action of those oxides of nitrogen which are never entirely absent even from so-called pure sulphuric acid. The best method of removing the ferric salt I find to be, to carry out the solution in a test tube about fifteen c.m. long and one or one and a half c.m. in diameter, and after the iron is completely dissolved to add a little piece of zinc, and close the mouth of the tube with a cork carrying a piece of glass tubing drawn to a fine orifice. The reducing action of the hydrogen formed during the solution of the zinc effectually reconverts the ferric into ferrous salt. This method I find to be much preferable to that of leading carbon dioxide into the liquid while the iron is being dissolved; an iron solution thus prepared always gives a red tint with potassium sulphocyanide.[1]

I find it best to dissolve 100 m.gms. of thin iron wire in about five cb.c. of strong sulphuric acid diluted with twice its volume of water. The iron wire is previously polished with emery paper and carefully rubbed with clean leather. The solution may be aided by heating, but care must be taken that no little pieces of wire are allowed to remain on the sides of the tube. The reduction by means of zinc may also be allowed to proceed in a warm liquid. So soon as evolution of gas has ceased, the tube is to be filled with distilled water, and after standing a few minutes the liquid is to be decanted into a flask: water is again to be added, followed by decantation. This is repeated several times—

---

[1] In testing for ferric salts by means of potassium sulphocyanide it should be remembered that the reaction is masked by the presence of many non-volatile organic acids. Almost every specimen of potassium sulphocyanide gives a red tint on addition of pure sulphuric or hydrochloric acid: this tint is removed by adding a small piece of zinc. A solution of potassium sulphocyanide thus prepared can alone be safely employed as a test for small traces of ferric salts.

any small pieces of undissolved zinc being allowed to remain in the test tube. If a few fragments of zinc should be decanted along with the liquid into the flask, their presence will not interfere with the subsequent titration process, inasmuch as zinc exercises no disturbing action on either permanganate or iron solution when the liquid is very dilute and not strongly acid. The liquid in the flask should amount to at least 60 cb.c.; before running in permanganate a few drops of sulphuric acid should be added. The permanganate is added from a burette—either a Gay Lussac's or a glass stoppered, preferably the latter—until a permanent pink colour is produced. This colour quickly fades, the solution becoming simultaneously turbid from precipitated manganese dioxide. From the results of this trial the permanganate is diluted until 1 cb.c. corresponds to 11·2 m.gm. of iron: after dilution the liquid must be again titrated.

Ferrous ammonium sulphate may be made use of instead of iron wire as a substance against which to titrate the permanganate. This salt is readily prepared in the pure state, and can be kept for a long time without undergoing change. It contains exactly one-seventh of its own weight of iron. A solution of ferrous ammonium sulphate generally gives a faint red colour with potassium sulphocyanide: I have, however, convinced myself by experiment that the error which may arise from the trace of ferric salt is exceedingly minute, indeed that it is probably less than that into which we fall by considering thin iron wire to be pure metallic iron.

3·92 grams of the double sulphate (1·96 grams if old notation be employed) are dissolved in about 60 cb.c. of water acidulated with sulphuric acid. If the permanganate be of proper strength exactly 50 cb.c. will be required to produce a permanent pink colour with the above solution of ferrous ammonium sulphate. This solution will remain of constant strength for several months if kept in a dark place.[1]

---

[1] One cubic centimetre of a solution of potassium permanganate when equal to two-tenths of an atom of iron is also equal to one-tenth atom of oxalic acid, one-tenth atom of lime, of manganese dioxide, &c.

Certain substances exert a reducing action upon potassium permanganate in acid solutions: of these the most commonly occurring are ferrous, cuprous and mercurous salts, stannous chloride, antimonious and arsenious oxides, metallic suboxides (of bismuth, molybdenum, silver, &c.), most of the metallic sulphides and iodides, especially those which are soluble in hydrochloric acid. Among the acids, hydrochloric and hydrosulphuric, arsenious, nitrous, phosphorous, and the sulphur acids, with the exception of sulphuric, are the most common. The greater number of those organic compounds which are met with in quantitative analysis also exert a reducing action on permanganate: from the number, acetic acid and the ammonium salts of non-reduceable acids, must be excepted.

Hydrogen dioxide may be estimated by means of permanganate, which salt it reduces with evolution of the same quantity of oxygen as it withdraws from the permanganate.

§ 19.

Iron Estimation.

In order to determine ferrous salts they are dissolved in water, or in dilute sulphuric acid, and permanganate is run into the cold, dilute, but acid liquid until a permanent pink colour is produced.

Supposing 50 cb.c. of two-tenths normal permanganate have been employed, this will be equal to $50 \times 0{\cdot}0112 = 0{\cdot}56$ grams iron, or $\frac{9}{7} \times 0{\cdot}66 = 0{\cdot}72$ grams ferrous oxide, (56 of iron = 72 of ferrous oxide: the same factor $\frac{9}{7}$ expresses the relation if old notation be employed).

The amount of iron in a ferric salt is determined by dissolving in dilute sulphuric acid, adding a couple of grams of finely granulated zinc, covering the vessel containing the liquid with a glass plate, and warming. So soon as the liquid has become perfectly colourless and a drop of it gives only a very faint colour with potassium sulphocyanide, the solution is decanted from undissolved zinc into a flask, the vessel being well washed with water, and the washings added to the contents of the flask, into which permanganate is then run until a faint permanent pink colour is produced.

1 cb.c. $\frac{2}{10}$ normal permanganate
= 160 m.gm. ferric oxide (Fe_2O_3).
= 325 m.gm. ferric chloride (Fe_2Cl_6).

Or in old notation,
= 80 m.gm. ferric oxide (Fe_2O_3).
= 162 m.gm. ferric chloride (Fe_2Cl_3).

In a solution containing both ferrous and ferric salts the former are estimated, as has been described, in a measured quantity of the liquid. The ferric salt in another portion of the liquid is reduced by means of zinc, and the total iron is then determined. By deducting the quantity of iron existing as ferrous salt, a residue is obtained which is then calculated to ferric salt.

If a = total iron, and b = iron existing as ferrous salt, then
$b \times \frac{9}{7}$ = ferrous oxide,
or $b \times 2{\cdot}268$ = ferrous chloride,
and $a - b \times \frac{10}{7}$ = ferric oxide,
or $a - b \times 2{\cdot}893$ = ferric chloride.

Lenssen and Löwenthal have shown that oxidation of ferrous chloride takes place in solutions containing hydrochloric acid without evolution of chlorine only under certain conditions of concentration. If 1 cb.c. of liquid contains more than 1 m.gm. of iron, chlorine is evolved, and secondary reactions ensue which vitiate the results. Fresenius recommends to dilute the liquid containing ferrous chloride and hydrochloric acid to 250 cb.c.: to withdraw 50 cb.c., and, after adding a large quantity of water containing sulphuric acid, to titrate with permanganate, then to add again 50 cb.c. of the liquid and again titrate, and so on three or four times. When the same quantity of permanganate is used in two titrations, the process may be stopped and the quantity of iron calculated.

The estimation of iron by means of permanganate may be carried out in presence of all bases which do not exercise a reducing action upon this liquid. Inasmuch as of the commonly occurring metallic salts, stannous chloride, cuprous chloride, antimonious and arsenious oxides alone exert such an action, this process for the estimation of iron is one which admits of exceedingly wide application. Even from organic compounds iron may be precipitated by means of ammonium sulphide, and after washing, dissolving in sulphuric acid, and removing sulphuretted hydrogen by boiling, may be estimated by means of permanganate. Previous precipitation of iron as sulphide or oxide is also necessary in presence of oxidising or reducing acids, more especially of nitric, hydriodic, or oxalic acid.

§ 20.

Oxalic Acid Estimation.

Oxalic acid and oxalates may be readily determined by means of permanganate. The liquid must be acidulated with hydrochloric or sulphuric acid (my own experiments show that it is immaterial which is used) and warmed to about 50° C. The fact that oxalates may be dissolved in hydrochloric acid and directly titrated with permanganate makes this process very generally applicable: the hydrochloric acid apparently takes no part in the oxidation of the oxalic acid.

1 cb.c. $\frac{2}{10}$-normal permanganate
= 12·6 mg.m. oxalic acid $H_2C_2O_42H_2O$.

In old notation,

1 cb.c. $\frac{2}{10}$-normal permanganate
= 3·6 mg.m. C_2O_3, or
= 6·3 mg.m. C_2O_33HO.

§ 21.

Estimation of Calcium Salts, Acetates, and Oxalates.

Soluble calcium salts are readily transformed into oxalates by precipitation with ammonium oxalate: in this form they may be estimated. The solution is made alkaline with ammonia or acid with acetic acid, and an excess of ammonium oxalate is added. After warming, the precipitate is filtered off, washed with hot water, and dissolved in dilute hydrochloric acid.

1 equivalent of lime is equal to 1 equivalent of oxalic acid. As 1 equivalent calcium oxalate (CaC_2O_4) requires for oxidation as much oxygen as 2 equivalents ferrous oxide (FeO), and as the equivalent of lime ($CaO=56$) is the same as that of iron, it follows that the number of cb.c. of $\frac{2}{10}$-normal permanganate used divided by 2 gives the amount of lime in m.gms. (This holds good also for old notation.)

Even difficultly soluble calcium salts, such as the sulphate, phosphate, tartrate, and citrate, may be converted into oxalates by treatment with oxalic acid or ammonium oxalate; the great stability of calcium oxalate renders this process for the estimation of calcium salts of wide application. This process will be further developed in Part II.

If the solution of a calcium salt contain no other substance capable of reducing permanganate, the calcium may be precipitated by adding a measured quantity of titrated oxalic acid, along with sodium acetate, to the warm liquid: after making up to 250 cb.c., the excess of oxalic acid is estimated in a measured quantity of the filtrate which has been acidulated with hydrochloric acid.

Fresenius has recommended this method for estimating acetic acid in tolerably pure samples of calcium acetate. The lime is precipitated by means of a measured quantity of oxalic acid, the strength of which has been determined acidimetrically: the whole is diluted to 250 cb.c.; two portions of 100 cb.c. each are passed through dry filters, in one the total quantity of acid is determined, in the other the quantity of oxalic acid is determined by means of permanganate. From these results the quantity of acetic acid is calculated by a method which will be apparent after consulting § 15. The process is less suited for coloured samples of calcium acetate.

It will be readily understood that the oxalic acid in soluble oxalates (those of the alkalies, for instance), and also in insoluble oxalates (those of strontium, barium, &c.) may be determined by means of permanganate.

The potash in salt of sorrel may be determined by ignition, provided acids other than oxalic are absent, solution of the residue in water, filtration from any insoluble calcium carbonate, and titration of the potassium carbonate by alkalimetric methods.

§ 22.

Copper Estimation.

Copper may be precipitated from almost any solution in the form of cuprous oxide. For this purpose tartaric acid is added, followed by excess of caustic potash or soda: if a clear deep blue liquid is not thus obtained more tartaric acid must be used. A considerable quantity of grape sugar is now added, and the liquid is boiled until the precipitate becomes bright red in colour. The precipitate is filtered and washed with hot water until the washings are perfectly clear and colourless. The precipitate is then transferred to a solution of ferric sulphate (prepared by dissolving ferric oxide in sulphuric acid) which is free from hydrochloric and nitric acids, and warmed.

The cuprous oxide is dissolved in accordance with the reaction.

$$Cu_2O + Fe_2 3SO_4 + H_2SO_4 = 2CuSO_4 + 2FeSO_4 + H_2O.$$

Old notation,

$$Cu_2O + Fe_2O_3 3SO_3 + SO_3 = 2CuOSO_3 + 2FeOSO_3.$$

For every two equivalents of copper (=126·4) two equivalents of ferrous sulphate are produced. By determining the quantity of ferrous salt in solution by means of permanganate, the quantity of copper originally present may be readily calculated.

1 cb.c. $\frac{2}{10}$-normal permanganate = 12·64 m.gm. copper.

Old notation,

1 c.bc. $\frac{2}{10}$-normal permanganate = 6·32 m.gm. copper.

Other methods of reducing the copper to the form of a cuprous salt may be adopted. Some of these, being applicable for acid solutions containing other metals besides copper, are more expeditious than that which has been described.

Copper may be precipitated from a solution containing hydrochloric acid in the form of insoluble cuprous iodide, by the addition of stannous chloride and potassium iodide. The cuprous iodide may be transformed into the corresponding oxide by boiling with caustic potash, or it may be dissolved in ferric sulphate solution, and the ferrous sulphate estimated by permanganate after boiling off the free iodine.

$$Cu_2I_2 + 2Fe_23SO_4 = 2CuSO_4 + 4FeSO_4 + I_2.$$

Old notation,

$$Cu_2I + 2Fe_2O_33SO_3 = 2CuOSO_3 + 4FeOSO_3 + I.$$

Inasmuch as two equivalents of ferrous salt are formed for each equivalent of copper, it follows that

1 cb.c. $\frac{2}{10}$-normal permanganate = 6·32 m.gm. copper.

Old notation,

1 cb.c. $\frac{2}{10}$-normal permanganate = 3·16 m.gm. copper.

Further observations on this method, which is of general application, will be found under the heading of *Iodometry*. Copper may also be precipitated, and separated from any other metals, by reducing its hydrochloric acid solutions by means of sulphurous acid or sodium sulphite, and precipitating with potassium sulphocyanide. By boiling the precipitated cuprous sulphocyanide with caustic potash, and washing until the washings cease to be reddened on addition of ferric chloride, pure cuprous oxide is obtained, which may then be dissolved in ferric sulphate solution.

The ferric sulphate solution used in the foregoing and in several other volumetric processes is most readily prepared by saturating pure ferrous sulphate with a quantity of nitric acid sufficient for its complete oxidation, adding sulphuric acid, and evaporating until the whole of the nitric, and the greater part of the free sulphuric acid is expelled. The salt may also be purchased; before use it should be moistened with a little strong sulphuric acid, and dissolved in 20 or 30 times its own weight of water.

§ 23.

Manganese Estimation.

The volumetric valuation of manganese ores is carried out by an indirect method: the quantity of oxygen capable of acting upon a ferrous salt, contained in the sample, is determined. For technical purposes, this method is of very wide application. A weighed quantity of the finely powdered sample is mixed with dilute sulphuric acid and a known amount of ferrous sulphate, and the whole is gently warmed. The following action thereupon takes place.

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_23SO_4 + 2H_2O.$$

Old notation,

$$MnO_2 + 2FeOSO_3 + 2SO_3 = MnOSO_3 + Fe_2O_33SO_3.$$

By determining the amount of residual ferrous salt by means of permanganate, and deducting this from the total quantity of ferrous salt used, the amount of this salt which has undergone oxidation is found, and from this the available oxygen in the sample of manganese is deduced. Thus, supposing that a quantity of ferrous sulphate containing 2·78 grams of iron as ferrous salt has been employed, that after the action 0·63 grams of iron remain as ferrous salt, then $2·78 - 0·63 = 2·15$ grams of iron have undergone oxidation. But as 112 of iron correspond to 16 of oxygen (see foregoing equation) it follows that to obtain the amount of available oxygen in the manganese, we must multiply the quantity of iron which has undergone oxidation by $\frac{1}{7}$: in the present case, the quantity of available oxygen is found to be $2·15 \times \frac{1}{7} = 0·307$ grams. (The same fraction $\frac{1}{7}$ is used when working with old notation.)

The quantity of pure manganese dioxide may be calculated by remembering that each 16 of oxygen correspond to 87 of MnO_2 or to 55 of Mn (old notation, 8 oxygen $= 43{\cdot}5$ $MnO_2 = 27{\cdot}5$ Mn).

The natural ores of manganese, however, generally contain lower oxides than MnO_2: in the Third Part of this book the analyses of these ores will be more minutely described; meanwhile I wish to show how the manganese compounds in general may be transformed into the pure dioxide, and estimated as such.

The soluble manganese salts all give precipitates of manganese dioxide—containing the whole of the manganese originally present—when treated with oxidizing agents in slightly acid solutions. For instance, a solution of a manganous salt in hydrochloric or sulphuric acid, when treated with excess of sodium acetate dissolved in acetic acid, followed by addition of sodium hypochlorite to the boiling liquid, yields the whole of its manganese in the form of precipitated dioxide. This precipitate may then be filtered off, washed, and titrated, as has been already described. Inasmuch as no oxide of manganese other than MnO_2 is present, it is only necessary to multiply the quantity of iron which has been converted into ferric salt by $\frac{71}{112} = 0{\cdot}63393$ in order to obtain the amount of MnO in the sample (in old notation same factor is employed).

A titrated solution of oxalic acid may be employed instead of ferrous sulphate for the purpose of reducing the manganese peroxide; the amount of undecomposed oxalic acid is determined by means of permanganate.

126 parts crystallised oxalic acid = 55 parts manganese.
= 71 parts manganous oxide.

Old notation,

36 parts C_2O_3, or 63 parts $C_2O_3 3HO$ = 27·5 parts Mn.
= 35·5 parts MnO.

The presence of ferric salts does not interfere with manganese estimations by either method.

§ 24.

Separation and Estimation of Cobalt and Nickel.

The method for separating and estimating cobalt and nickel which I have devised is based upon the fact that these metals may be completely precipitated as sesquioxides, but that the two sesquioxides behave differently towards ammonia.

An acid solution of the two metals is decomposed by means of an excess of sodium hypochlorite and caustic soda, a further quantity of hypochlorite is added, and the liquid is boiled until the precipitate becomes perfectly black. After standing a few moments the precipitate is filtered off.

A complete precipitation of cobalt and nickel may thus be effected. The liquid must be strongly alkaline. The use of caustic soda is to be preferred to that of carbonate. Bromine may be employed in place of sodium hypochlorite. The precipitated sesquioxides (R_2O_3) must be completely free from protoxides; if the precipitate be granular and very dark brown or black, and if the liquid smell strongly of chlorine, the absence of protoxides is ensured.

The sesquioxides of cobalt and nickel closely resemble one another in their general properties; the nickel salt is, however, the more easily reduced of the two. Nickel sesquioxide is very readily reduced to protoxide by ammonia even without warming. Cobalt sesquioxide, on the other hand, is unacted upon by either cold or boiling ammonia. Warm ammonia reacts upon nickel sesquioxide with the production of nitrogen and nickelous oxide (NiO), which is partially dissolved in the excess of ammonia. If the mixed sesquioxides of cobalt and nickel be heated to boiling with dilute ammonia, the residue, on filtration, contains the whole of the cobalt as Co_2O_3, mixed with more or less NiO, but not a trace of Ni_2O_3. The separation by means of ammonia is only partial, the reduction of the nickel salt is complete. The cobalt contained in the residue may be determined by treatment with a measured quantity of ferrous sulphate and titration with permanganate.

$$2FeSO_4 + Co_2O_3 + 3H_2SO_4 = Fe_23SO_4 + 2CoSO_4 + 3H_2O.$$

Old notation,

$$2FeOSO_3 + Co_2O_3 + 3SO_3 = Fe_2O_33SO_3 + 2CoOSO_3.$$

112 parts of iron oxidised to ferric salt
= 117·6 parts of cobalt originally present.

Old notation,

56 parts of iron oxidised to ferric salt
= 58·8 parts of cobalt originally present.

By precipitating the two sesquioxides in a fresh portion of the original liquid, treating the precipitate with ferrous sulphate, *without* previous boiling with ammonia, and titrating with permanganate, the quantity of nickel may be determined.

This method gives good results. Care must be taken in the precipitation of the sesquioxides, and also in the treatment with ammonia. I make use of perfectly pure ammonia of 0·96 spec. grav. diluted with three volumes of water; the precipitate is heated to boiling with 30 to 50 cb.c. of this liquid, which is then at once filtered off; the residue is then washed with hot water.

A large excess of ferrous sulphate should be avoided. The addition of sulphuric acid should be made after that of the iron salt.

This method is applicable in the presence of many metallic oxides, especially those of zinc, iron, chromium, cadmium, tin, aluminium, and the alkaline earth metals. The other metals either form higher oxides by treatment with sodium hypochlorite in alkaline solutions, or they more or less hinder the oxidation of cobalt and nickel; they must, therefore, be removed.

Manganese may be separated from nickel, but not from cobalt, by precipitation with sodium hypochlorite in an acetic acid solution. Methods of separation from cobalt will be described in Part II.

Cobalt and nickel may also be directly estimated by saturating the solution which contains the two metals with caustic potash, and adding potassium cyanide until the precipitated oxides are again dissolved. Bromine is then added, the liquid being kept *cold*, whereby the whole of the nickel is precipitated as Ni_2O_3 without a trace of cobalt. The nickel in the precipitate is estimated by the ferrous sulphate and permanganate method. By precipitating both sesquioxides in another portion of the original liquid, and decomposing the Ni_2O_3 by means of ammonia (*without* treatment with potassium cyanide), a residue is obtained in which cobalt may be directly determined. This method is exact, and is exceedingly well adapted for correct estimations of nickel.

§ 25.

Estimation of Chlorine Water, and of Bleaching Powder.

Free chlorine, or the hypochlorites—which evolve chlorine when treated with hydrochloric acid—may be determined by allowing them to react upon a known quantity of ferrous sulphate or chloride, and estimating the residual ferrous salt by titration with permanganate.

One equivalent of ferrous chloride is converted into ferric chloride by two equivalents of chlorine—

$$Fe_2Cl_4 + Cl_2 = Fe_2Cl_6.$$

Old notation,

$$2FeCl + Cl = Fe_2Cl_3.$$

In order to determine the quantity of chlorine in chlorine water, the amount of iron converted into ferric chloride must be multiplied by $\frac{71}{112} = 0{\cdot}633$ (old notation, same factor).

If it be desired to determine the quantity of hypochlorous acid in bleaching powder, the following reaction may be taken advantage of:—

$$Ca(ClO)_2 + 4HCl + 2Fe_2Cl_4 = CaCl_2 + 2H_2O + 2Fe_2Cl_6.$$

Old notation,

$$CaOClO + 2HCl + 4FeCl = CaCl + 2HO + 2Fe_2Cl_3.$$

Four equivalents of iron converted into ferric salt correspond to two equivalents of hypochlorous acid

(HClO); therefore, to calculate the quantity of this acid in the bleaching powder it is necessary to multiply the amount of iron converted into ferric salt by $\frac{105}{448}$ = 0·2344. (In old notation the factor becomes $\frac{43 \cdot 5}{112}$ = 0·388: ClO = hypochlorous acid).

Inasmuch, however, as bleaching powder is usually valued by the amount of chlorine which is disengaged on acidification, the calculation given for free chlorine is more frequently made use of.

The oxydimetric method just described is applicable to the estimation of chlorates as well as hypochlorites in acid solutions. Inasmuch, however, as chlorates do not bleach, this method cannot be applied for the estimation of the bleaching value of hypochlorites containing chlorates: in such a case a process must be employed which is applicable in alkaline solutions, and which is not interfered with by the presence of chlorates. Such a process will be described in Part III.

It is well to bear in mind that ferrous ammonium sulphate cannot be made use of in the foregoing processes, because of the action exerted on chlorine by ammonia.

§ 26.

Estimation of Chromic Acid and Chromates.

The equation expressing the action of chromic acid upon ferrous sulphate in presence of sulphuric acid is as follows:—

$aK_2Cr_2O_6$

$$2H_2CrO_4 + 6FeSO_4 + 6H_2SO_4 = Cr_23SO_4 + 3Fe_23SO_4 + 8H_2O.$$

Old notation,

$$2CrO_3 + 6FeOSO_3 + 6SO_3 = Cr_2O_33SO_3 + 3Fe_2O_33SO_3.$$

From this equation we learn that 3 equivalents of ferrous salt correspond to 1 equivalent of chromic acid. Chromic acid, free or combined, may be estimated by a process which is exactly similar to those already described. The greater the quantity of sulphuric acid used, the more easy is it to determine the final point of the reaction, inasmuch as the green colour of the chromium sulphate is rendered less marked.

In order to calculate the quantity of chromic acid, it is only necessary to multiply the amount of iron converted into ferric salt by 0·7024; to calculate chromium oxide, Cr_2O_3, the factor is 0·453; and to calculate metallic chromium, 0·3107. (In old notation these factors are 0·496, 0·453, and 0·3107 respectively.)

All chromium compounds may be converted into chromic acid by reducing to chromium oxide, and then boiling, in alkaline solution, with a little bromine; they may then be determined by the foregoing method.[1]

§ 27.

Estimation of Barium, Lead, and Bismuth.

These three metals may be completely precipitated by means of potassium chromate, or, better, potassium dichromate. In precipitating lead salts the solution may be neutral, or, preferably, acidified with acetic acid. The latter condition is readily attained by adding sodium acetate to a solution of the lead salt in nitric acid. The precipitate obtained in the case of lead salts has the formula $PbCrO_4$ ($PbOCrO_3$). By decomposing this precipitate by means of strongly-acidified ferrous sulphate, or, better, ferrous chloride solution, of known strength, determining the amount of iron converted into ferric salt, and multiplying this by 1·232, the quantity of lead may be found (old notation, same factor).

In estimating bismuth the acid solution is neutralised with sodium carbonate until it becomes slightly turbid; a couple of drops of nitric acid are added, followed by addition of potassium dichromate. The precipitated chromate, $Bi_2O_32CrO_3$ (BiO_32CrO_3), after being washed, is treated with ferrous chloride, &c. The quan-

---

[1] Chromic acid is best precipitated from acid liquids by means of lead acetate, from alkaline liquids by means of barium chloride. In the precipitated chromates the chromic acid may be readily estimated.

tity of iron converted into ferric salt, multiplied by 1·232, gives metallic bismuth (old notation, same factor).

Barium chromate is quite insoluble in water containing ammonia: ammonium salts do not interfere with the formation of the chromate. To the solution containing barium, ammonia, free from carbonate, is added. A solution of potassium dichromate, free from sulphate, and made alkaline with ammonia, is then added; the precipitated barium chromate is washed until the washings no longer render lead acetate solution turbid, treated with ferrous sulphate, and the ferric salt so produced is estimated by means of permanganate. It is not necessary to filter off the barium sulphate which is formed before titrating. Barium chromate has the formula $BaCrO_4$: the quantity of iron changed to ferric salt, multiplied by 0·8155, gives the amount of barium (old notation, factor = 0·6116; Ba = 68·5).

Barium may be separated from strontium and calcium by precipitation as chromate, salts of the latter metals giving no precipitate with potassium dichromate in presence of sal-ammoniac and at ordinary temperatures.

§ 28.

Estimation of Ferro- and Ferri-Cyanides.

Soluble ferrocyanides are converted into ferricyanides by the action of permanganate of potassium.

A quantity of the ferrocyanide is dissolved in water, so that 100 cb.c. of the liquid contain about 0·1 gram of the salt; the liquid is strongly acidified with hydrochloric acid, and titrated with permanganate.

As it is difficult to determine the final point of the reaction in the ordinary way, it is advisable to bring a drop of the liquid from time to time on to a porcelain slab along with a drop of ferric chloride: so soon as no blue colour is produced, the process is finished. It is also advisable to titrate the permanganate used against a solution of pure potassium ferrocyanide of known strength, and from the result to calculate the amount of ferrocyanide in the sample.

Ferricyanides must be reduced to ferrocyanides before they can be estimated by this method. The reduction is best brought about by boiling the solution after addition of excess of caustic potash and ferrous sulphate; the precipitate which forms is filtered off, and the ferrocyanide is estimated in the filtrate, after acidification. By multiplying the amount of ferrocyanide found by 0·893, the amount of ferricyanide is deduced (old notation, same factor).

If ferro- and ferri-cyanides are simultaneously present, the former is estimated in a portion of the liquid, while in another portion the ferri- is reduced to ferro-cyanide, and the total salt then estimated.

If the solution contain sulphocyanide, the ferrocyanide is precipitated by means of ferric chloride, filtered off, well washed and boiled with caustic potash. After filtering off the ferric oxide produced, the ferrocyanide is estimated in the filtrate.

If ferricyanide, ferrocyanide, and sulphocyanide are simultaneously present, the ferrocyanide is to be determined as has just been described. Another portion is to be boiled with caustic potash and mercuric oxide, whereby the whole of the iron is precipitated as oxide. This precipitate is to be dissolved in hydrochloric acid, the mercury removed by precipitation as sulphide, and, after boiling off all sulphuretted hydrogen, any ferric salt is to be reduced to ferrous salt, and the iron estimated by means of permanganate. By deducting the quantity of iron found as ferrocyanide, a residue is obtained representing the amount existing as ferricyanide.

§ 29.

Tin Estimation.

Tin may be determined by taking advantage of the fact that stannous chloride reduces ferric to ferrous chloride.

$$SnCl_2 + Fe_2Cl_6 = Fe_2Cl_4 + SnCl_4.$$

Old notation,

$$SnCl + Fe_2Cl_3 = 2FeCl + SnCl_2.$$

The quantity of ferrous salt produced is determined by means of permanganate.

1 cb.c. $\frac{2}{10}$ths-normal permanganate = 11·8 m.gm. tin.

In old notation,

1 cb.c. $\frac{2}{10}$ths-normal permanganate = 5·9 m.gm. tin.

Or, Tin = metallic iron × 1·05357 (same factor in old notation).

Stannic salts are reduced to stannous by means of zinc, free from iron, in hydrochloric acid solution, in a stream of carbon dioxide. So soon as all zinc and tin are dissolved, ferric chloride is added, and titration proceeded with.

In mixtures of stannous and stannic salts a method similar to that described in § 19 for iron salts is adopted.

§ 30.

Estimation of Zinc, Cadmium, Tin, and Sulphides of the Alkali Metals.

Certain metallic sulphides, obtained by precipitating with sulphuretted hydrogen or ammonium sulphide, are capable of undergoing decomposition in presence of ferric sulphate or chloride, whereby an amount of iron, equivalent to the amount of sulphur in the sulphide, is reduced to the state of ferrous salt, the metal at the same time going into solution, and sulphur being deposited. Inasmuch as many metals are separated in the form of sulphides, this method becomes of very wide application, and is much to be preferred to the older method of precipitation by means of a titrated solution of sodium sulphide.

The method is especially applicable in the cases of zinc, cadmium, tin, manganese, and iron; inasmuch, however, as extremely good and ready methods are known for the estimation of the two last-named metals, I recommend the present method only for the estimation of the other three metals and of the alkaline sulphides.

Zinc is precipitated as sulphide by passing sulphuretted hydrogen through an acetic acid solution; the sulphide is brought into a solution of ferric sulphate, and the quantity of ferrous salt formed is estimated by permanganate, after the zinc is entirely dissolved and the whole of the sulphur is precipitated.

$$Fe_23SO_4 + ZnS = ZnSO_4 + 2FeSO_4 + S.$$
$$(Fe_2O_33SO_3 + ZnS = ZnOSO_3 + 2FeOSO_3 + S).$$

112 parts of iron converted into ferrous salt = 65·1 parts of zinc.

In old notation,

56 parts of iron converted into ferrous salt = 32·55 parts of zinc.

Cadmium may be estimated in a similar manner, making use of ferric chloride instead of sulphate.

112 of iron = 112 of cadmium.

Follenius[1] has shown that when cadmium is precipitated as sulphide from acid liquids the precipitate invariably contains small quantities (2 to 4 per cent of the total amount) of cadmium salts other than the sulphide; this precipitation of mixed salts does not take place when the cadmium sulphide is thrown down from alkaline solutions; it is then, however, very difficult to filter. The precipitation of cadmium sulphide is best accomplished from hot solutions containing sulphuric acid of 1·19 sp. gravity, to the extent of 30 per cent by volume. From solutions containing hydrochloric acid cadmium is completely precipitated as sulphide only when not more than 5 per cent of an acid of 1·11 sp. gravity is present, if the liquid be hot, and not more than 14 per cent if the liquid be cold.

Tin must be precipitated in the form of stannic sulphide, SnS_2. Before precipitation stannous must be converted into stannic salts either by means of free chlorine or potassium chlorate; excess of chlorine may be converted into hydrochloric acid by adding oxalic acid. The precipitated stannic sulphide is boiled along with ferric chloride and hydrochloric acid. In titrating the

---

[1] *Zeits. für Anal. Chem.* xiii., parts 3 and 4.

ferrous chloride formed, the precautions detailed in § 19 must be attended to.

The equation

$$2Fe_2Cl_6 + SnS_2 = SnCl_4 + 2S + 2Fe_2Cl_4$$
$$(2Fe_2Cl_3 + SnS_2 = SnCl_2 + 2S + 4FeCl)$$

shows that Sn = Fe × 0·527.

Sulphides of the alkalies may be directly determined by causing them to act upon ferric sulphate in acid solution; but inasmuch as these sulphides generally contain lower oxides of sulphur which are more or less oxidised by ferric salts, it is preferable to precipitate the sulphur from the sulphide under examination by means of zinc sulphate, or, better, by means of cadmium sulphate, and to dissolve the precipitate of zinc or cadmium sulphide in ferric chloride, &c. If, however, alkaline polysulphides are under examination, the precipitated zinc or cadmium sulphide will be mixed with free sulphur. We shall revert to the examination of these polysulphides in Part III.

The solution of ferric sulphate or chloride employed in the foregoing estimations must be tolerably concentrated (about 1:10), and it must also be rendered acid. Neither nitric acid nor free chlorine can be present.

§ 31.

Oxydimetric Estimation of a few of the Rarer Substances.

(*Nitrous, Titanic, and Molybdic Acids, and Hydrogen Peroxide.*)

Nitrous acid may be estimated in very dilute acidified solutions by direct titration with permanganate.[1]

$$5HNO_2 + 2HMnO_4 = 2Mn2NO_3 + HNO_3 + 3H_2O.$$

It appears from this equation that that amount of permanganate which is capable of oxidising two equivalents

---

[1] In the presence of other substances which decolorise permanganate, nitrous acid may be determined after distillation with sulphuric acid. This method is serviceable in the analysis of drinking waters.

of iron is only capable of oxidising one equivalent of nitrous acid; hence,

1 cb.c. $\frac{2}{10}$-normal permanganate = 4·7 m.gm. HNO_2.

In old notation,

1 cb.c. $\frac{2}{10}$-normal permanganate = 1·9 m.gm. NO_3.

Titanic and molybdic acids may be reduced by means of zinc in solutions containing sulphuric acid, whereby coloured hydrates are produced. By treating the coloured liquids with permanganate they are decolorised, and finally the colour of the permanganate itself becomes apparent. This method is, however, liable to the objection that it is extremely difficult to tell when the reduction by means of zinc is complete. If the solution be free from other heavy metals, the two metals may be precipitated with lead acetate, and the amount of lead determined in the precipitate after ignition and weighing. By deducting this from the total weight the quantity of molybdic or titanic acid is found. Ammonium molybdate may be directly ignited along with lead oxide and the acid calculated from the increase in weight.

Hydrogen peroxide may be determined by means of permanganate after acidification with sulphuric acid; the titration must be carried out at ordinary temperatures.

$$5H_2O_2 + 2HMnO_4 + 2H_2SO_4 = 2MnSO_4 + 8H_2O + 10O.$$
$$(5HO_2 + Mn_2O_7 + 2SO_3 = 2MnOSO_3 + 5HO + 10O).$$

1 cb.c. $\frac{2}{10}$-normal permanganate = 3·4 m.gm. H_2O_2.

In old notation,

1 cb.c. $\frac{2}{10}$-normal permanganate = 1·7 m.gm. HO_2.

B.—Iodometry.

The iodometric methods depend on the power which free iodine possesses of oxidising many substances. Iodine is not however so energetic an oxidiser as free chlorine or potassium permanganate. A solution of ferrous sulphate for instance is not oxidised by iodine: on the contrary, ferric chloride is reduced to ferrous chloride by means of potassium iodide, iodine being simultaneously separated. These reactions only however hold good for the iron salts of the stronger mineral acids: ferrous acetate is oxidised at once by means of iodine.

Inasmuch as free iodine may be estimated with great exactness, and inasmuch also as many substances either combine with iodine, or separate iodine from its compounds, the iodometric methods are of very wide application. The advantages of these methods become the more apparent when we remember that many substances which can be easily and accurately determined by means of iodine can only otherwise be estimated by complicated and often not very exact gravimetric processes. This is especially true of sulphuretted hydrogen, and of sulphurous and thiosulphuric acids.

When free iodine is brought into contact with sodium thiosulphate, sodium iodide and sodium tetrathionate are produced—

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$
$$(2NaOS_2O_2 + I = NaOS_4O_5 + NaI.)$$

So also iodine oxidises sulphurous to sulphuric acid—

$$H_2SO_3 + H_2O + I_2 = H_2SO_4 + 2HI.$$
$$(SO_2 + 2HO + I = HOSO_3 + HI.)$$

Concentrated solutions of sulphurous acid are, however, but little acted upon by iodine: the reaction takes place only when the aqueous solution contains not more than 0·04 to 0·05 per cent of sulphur dioxide (SO_2) (Bunsen). Mohr has however shown that sulphurous acid may be estimated in concentrated solutions by means of iodine by adding excess of sodium carbonate.

I find that the use of borax is preferable to that of sodium carbonate inasmuch as effervescence is hereby avoided.

Free iodine decomposes sulphuretted hydrogen with formation of hydriodic acid and sulphur—

$$H_2S + I_2 = 2HI + S.$$
$$(HS + I = HI + S.)$$

In this case the process is improved by adding a little sodium acetate solution before titration, in order to convert the hydriodic acid into sodium iodide.

Those substances which oxidise ferrous salts in acid solutions (MnO_2, CrO_3, HOCl, &c.), also separate iodine from potassium iodide and may therefore be estimated by iodometric methods. Titration with permanganate is however so easily carried out, and the results are generally so accurate that oxydimetric methods are as a rule to be preferred to iodometric. In the following methods I shall therefore only describe those which cannot be advantageously replaced by processes involving the use of permanganate.

§ 32.

Preparation and Standardising of the Solutions required for Iodometry.

The following solutions are required—

1. *A Solution of Iodine of known strength—preferably deci-normal:* prepared by dissolving 12·7 grams of pure dry iodine[1] along with 20 to 30 grams of potassium iodide in 1,000 cb.c. of distilled water. The potassium iodide must be free from iodate: a few grains when tested with a little starch paste and a drop of hydrochloric acid should give no blue colour.

2. *A Deci-normal Solution of Sodium Thiosulphate:* prepared by dissolving 24·8 grams of the pure dry salt in 1,000 cb.c. of water containing about 2 grams of ammonium carbonate.[2]

3. *A Solution of Starch:* prepared by triturating starch with about 100 times its own weight of distilled water, and boiling. The solution must remain clear and free from lumps when cold. The addition of a couple of

---

[1] Obtained by subliming iodine along with a little potassium iodide and drying for a few hours over sulphuric acid in an exsiccator.

[2] A very dilute solution of sulphur dioxide containing not more than 0·04 per cent may be used instead; but the liquid must be titrated daily.

drops of an alcoholic solution of salicylic acid preserves the starch from decomposition.

If the iodine solution is to serve as a standard liquid it is necessary that it be prepared with great accuracy.

10 cb.c. of the thiosulphate solution are placed in a beaker along with a few drops of starch solution, and the iodine is run in from a glass-stoppered burette graduated in 10ths cb.c., until a permanent blue colour is produced. From the results of this trial (which had better be twice repeated) the two liquids are adjusted so that 1 cb.c. of deci-normal iodine exactly corresponds to 1 cb.c. of deci-normal thiosulphate solution. The formation of blue iodide of starch, by the action of free iodine upon starch, is a reaction of the greatest delicacy; it is brought about either in acid liquids or in liquids containing carbonates of the alkalies. The less concentrated the acid and the lower the temperature, the more delicate is the reaction. Those substances which combine with free iodine, more especially thiosulphates and sulphites, decolorise iodide of starch; but the blue colour again becomes apparent so soon as there is the slightest trace of free iodine in the liquid. A large excess of iodine produces a blue-violet colour with starch, but by neutralising the greater part of the iodine with sodium thiosulphate, a pure blue colour is again produced. It is evident that the accuracy of the foregoing methods of standardising the normal liquids are entirely dependent upon the purity of the iodine employed. Iodine is, however, hygroscopic, somewhat volatile at ordinary temperatures, and generally contains chlorine or bromine.

Sodium thiosulphate can however be readily obtained in a state of almost perfect purity; this salt moreover is not efflorescent and is non-volatile. The presence of traces of sulphites (recognised by the production of a turbidity on addition of barium chloride and iodine solution) has no appreciable influence upon the use of the salt in iodometric methods. Nevertheless there is no difficulty in obtaining a salt absolutely free from sulphites. Crystallized sodium thiosulphate has the formula $Na_2S_2O_35H_2O = 248$; by dissolving 24·8 grams in one litre of water a solution is obtained, 1 cb.c. of which corresponds to 1 cb.c. of deci-normal iodine solution = 12·7 m.gm. iodine. (In old notation $NaOS_2O_25HO$ = 124: 24·8 grams in 1000 cb.c. of water give a $\frac{2}{10}$-normal liquid, 1 cb.c. of which = 12·7 m.gm. iodine.) The addition of about 5 grams of ammonium carbonate to each litre of thiosulphate solution materially increases the stability of the liquid. The solution should be kept in bottles made of dark glass, or in ordinary bottles covered so as to exclude the light. The salt may be weighed out from a stoppered tube.[1]

It is well to test both iodine and thiosulphate from month to month. 1·240 grams of freshly crystallised thiosulphate, dissolved in 50 or 100 cb.c. of water, should require exactly 50 cb.c. of iodine, if the latter be accurately deci-normal. Having obtained the exact strength of the iodine the stock thiosulphate solution is titrated against a known volume of iodine, and in this way any alteration in strength is detected and estimated.

Any form of burette may be employed for thiosulphate, only a glass-stoppered or Gay Lussac burette (preferably the former) for iodine solution.

It is sometimes advisable to employ centi-normal solutions of iodine and thiosulphate in the estimation of sulphuretted hydrogen and sulphurous acid, in mineral waters for instance. Such solutions are at once prepared by diluting the deci-normal liquids with nine times their own volume of water.

§ 33.

Iodometric Processes in General.

In iodometric titration processes it is required to estimate the amount of iodine either set free by, or

---

[1] In subliming iodine two crucibles may be used, one inverted upon and exactly fitting over the other, or two large test tubes one just fitting inside of the other: the iodine is sublimed from the lower into the upper. The apparatus should be heated on a sand bath. The sublimed iodine is loosened from the sides of the upper vessel which is then placed over strong sulphuric acid for some hours, after which the dry iodine is quickly transferred to a stoppered weighing tube.—*Tr.*

taken into combination with the substance to be determined.

For this purpose starch is added to the liquid containing free iodine and thiosulphate is run in until the blue colour is completely discharged. From the quantity of thiosulphate consumed the amount of free iodine is directly known, and from this the amount of the substance to be determined is calculated. Sometimes thiosulphate is added in excess, and the excess determined by standard iodine, which is run in until a permanent blue colour is obtained. The production of a colour is generally to be preferred as a means for determining the termination of a reaction, to the decolorisation of a coloured liquid.

Inasmuch as caustic alkalies and normal carbonates of the alkalies combine with free iodine, the bicarbonates must be employed when it is required to carry out iodometric methods in alkaline solutions.

§ 34.

Estimation of Sulphur Dioxide (Sulphurous Acid) and Sulphuretted Hydrogen.

The reactions upon which the processes for the estimation of these two substances are based are these :—

$$(1)\quad SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI.$$
$$(SO_2 + 2HO + I = HOSO_3 + HI.)$$
$$(2)\quad H_2S + I_2 = 2HI + S.$$
$$(HS + I = HI + S).$$

The solution must not contain more than 0·04 to 0·05 per cent of SO_2 or of H_2S: otherwise the equations formulated above do not represent the only actions which occur.

(In the first case the sulphur dioxide is not completely changed into sulphuric acid : in the second sulphuric acid is produced.)

The liquid containing sulphur dioxide, or sulphuretted hydrogen, after dilution with distilled water which has been previously boiled and allowed to cool in a closed vessel, is placed in a beaker or preferably in a flask; starch is added and iodine is run in until a permanent blue colour is produced.

Iodine used × 0·25196 = SO_2
Do. × 0·13385 = H_2S
Do. × 0.12598 = S
Same factors in old notation.

1 cb.c. iodine = $\frac{1}{20}$th atom of SO_2, H_2S, or S.

In old notation,

1 cb.c. iodine = $\frac{1}{10}$th atom of SO_2, HS, or S.

100 cb.c. of sulphur dioxide solution must not use more than 12·5 cb.c. of deci-normal iodine, nor 100 cb.c. of sulphuretted hydrogen solution more than 30 cb.c. of iodine, else the solutions are too concentrated.

Instead, however, of diluting the solutions, I find it preferable to add excess of borax to the sulphur dioxide liquid, and excess of sodium acetate to the sulphuretted hydrogen, and to titrate at once with iodine. The results are quite as accurate as by the other method.

Centi-normal iodine must be employed for the estimation of very small quantities of sulphur dioxide or sulphuretted hydrogen.

Traces of heavy metals may be determined by means of the processes just described. (See end of this Section.)

§ 35.

Antimony Estimation.

Antimony trioxide in alkaline solutions is converted into pentoxide by the action of iodine.

$$Sb_2O_3 + 2I_2 + 4NaHO = Sb_2O_5 + 4NaI + 2H_2O.$$
$$(SbO_3 + 2I + 2NaO = SbO_5 + 2NaI.)$$

1 cb.c. deci-normal iodine = 7·315 m.gm. Sb_2O_3 = 6·115 m.gm. Sb.
(Same for old notation.)

To 10 cb.c. of a tolerably concentrated solution containing antimony trioxide tartaric acid is added, the liquid is neutralised by means of sodium carbonate, and at least 20 cb.c. of a cold saturated solution of sodium bicarbonate are added; iodine is then run in until a distinct blue colour is obtained.

This process is applicable to all estimations of antimony, inasmuch as, after precipitation with sulphuretted hydrogen, solution in hydrochloric acid, removal of sulphuretted hydrogen by boiling, and addition of tartaric acid and alkaline carbonate, the antimony is obtained as Sb_2O_3. The process is much to be preferred to the oxydimetric one, which is often employed. Care must be taken that sodium bicarbonate be added in considerable excess, as the process of oxidation then takes place more rapidly.

§ 36.

Estimation of Arsenic and Tin.

Arsenious oxide in alkaline solutions is oxidised to arsenic oxide by means of free iodine.

$$As_2O_3 + 2I_2 + 4NaHO = As_2O_5 + 4NaI + 2H_2O.$$
$$(AsO_3 + 2I + 2NaO = AsO_5 + 2NaI.)$$

Iodine used × 0·38977 = As_2O_3 (same factor in old notation).

1 cb.c. iodine = 4·9575 m.gm. As_2O_3 = 3·7575 m.gm. As.

In old notation,

1 cb.c. iodine = 4·9575 m.gm. AsO_3 = 3·7575 m.gm. As.

If the liquid containing arsenious oxide be alkaline, it is acidified, and sodium bicarbonate is then added in excess before titrating with iodine.

Arsenic oxide may be estimated after reduction to arsenious. The reduction may be effected by conducting sulphur dioxide into the liquid, or by boiling the acidified liquid with a sulphite. Before titration the liquid must be boiled until every trace of sulphur dioxide is removed, which is known by the fumes giving no blue colour with a paper soaked in ferric chloride and potassium ferricyanide.

If arsenious and arsenic oxide exist simultaneously in solution, the former may be directly estimated in one portion of the liquid, while the total arsenious oxide, after reduction of the arsenic oxide, may be estimated in another portion.

Arsenic may be readily and accurately separated from other heavy metals by taking advantage of the fact that its sulphide is soluble in ammonium carbonate. By precipitating the sulphur from the ammoniacal solution by means of silver nitrate, and filtering, an alkaline solution of arsenious oxide is obtained, in which the arsenic may be determined as already described. Arsenic oxide, if present, may be removed by means of magnesia mixture, or it may be determined in a second portion of the liquid.

Mohr has shown that the iodometric estimation of arsenic may be more successfully performed in a solution containing bicarbonate of potassium than in one containing bicarbonate of sodium, but that ammonium carbonate is preferable to either.

Tin in the form of stannous salts may also be estimated by dissolving in bicarbonate of sodium in presence of tartaric acid, adding starch and titrating with iodine. Stannic salts must be altogether absent.

$$\text{Iodine used} \times 0{\cdot}4646 = \text{tin (Sn)}.$$

Stannic salts may be estimated, after reduction to stannous salts, according to § 29. This method is to be preferred to the oxydimetric method when small quantities of tin are to be estimated.

§ 37.

Estimation of Copper and Iodine.

A method for estimating copper, put forward by De Haen, has been known for some years. It consists in adding excess of potassium iodide to the slightly-acidified solution containing copper, and determining, by means of thiosulphate, the amount of iodine liberated. This process is, however, inexact, because, before the decomposition has reached completion, part of the iodine combines with copper to form insoluble cuprous iodide. It is, therefore, difficult to hit exactly the final point, inasmuch as the liquid becomes blue after it has been decolorised by means of thiosulphate.

Copper may be precipitated in the form of cuprous iodide from acid solutions, but the completeness of the precipitation depends greatly on the substance employed as a reducing agent. Sometimes ferrous sulphate is employed, but the ferric salt formed exerts a solvent action on the cuprous iodide. Sulphur dioxide is preferable; nevertheless it also dissolves a portion of the cuprous iodide. By using stannous chloride, the copper salt is entirely reduced, the iodide being also perfectly insoluble in stannic chloride. The precipitation is rendered still more complete by the addition of sal-ammoniac. The solution of stannous chloride should be tolerably concentrated; it may be mixed with sal-ammoniac, along with a few strips of metallic tin, whereby oxidation is prevented.

After the addition of a considerable quantity of stannous chloride, potassium iodide mixed with ammonium chloride is added until the whole of the copper is thrown down. After standing for fifteen minutes or so the precipitate is collected on a filter, washed with ammonium chloride solution, and brought into a solution of ferric sulphate or chloride.

$$Cu_2I_2 + 2Fe_23SO_4 = 2CuSO_4 + 4FeSO_4 + I_2.$$
$$(Cu_2I + 2Fe_2O_33SO_3 = 2CuOSO_3 + 4FeOSO_3 + I.)$$

The iodine may be boiled off, and the amount of ferrous salt determined by means of permanganate (see § 22); or the iodine may be conducted into a solution of potassium iodide, and determined by means of thiosulphate.

1 cb.c. thiosulphate = 6·32 m.gms. copper
(same in old notation).

The precipitation of cuprous iodide must be effected in *cold* solutions, as the salt is somewhat soluble in warm liquids containing hydrochloric acid.

Copper may be determined by means of this process in the presence of many other metals. Mercury, silver, bismuth, lead, and antimony more or less interfere with the reaction. Silver may be removed by means of hydrochloric acid; mercury by means of stannous chloride; lead by sulphuric acid; and bismuth and antimony, sufficiently, by neutralising the warm liquid containing hydrochloric acid by means of ammonia.

Combined iodine may be precipitated and estimated by means of cupric sulphate, in presence of sal-ammoniac and stannous chloride.

This method for estimating iodine can be carried out in presence of chlorine and bromine; its application will be described hereafter.

§ 38.

Estimation of Iron and Iodine.

Although the oxydimetric method for estimating iron is exceedingly good and accurate, nevertheless it has the disadvantage of being somewhat interfered with by the presence of hydrochloric acid. This disadvantage does not apply to the iodometric method. Ferric salts are reduced to ferrous salts by means of potassium iodide: thus, for ferric chloride the reaction may be formulated.

$$Fe_2Cl_6 + 6KI = Fe_2I_4 + 6KCl + I_2.$$
$$(Fe_2Cl_3 + 3KI = 2FeI + 3KCl + I.)$$

127 parts of iodine liberated correspond to 56 parts of iron (same in old notation).

In order to carry out the process the ferric salt (free from nitric acid and free chlorine) is brought into the bulb *a*, Fig. 13. A considerable quantity of potassium iodide (free from iodate) is added, along with hydrochloric acid. The bulb is then connected by means of non-vulcanised (black) caoutchouc tubing with the tube *b*, dipping beneath the surface of a solution of potassium iodide contained in the reversed retort *c*. The bulb *a* is heated so long as the vapours passing into *c* are coloured.[1]

---

[1] The bulbs on *b* and *c* prevent the liquid in *c* from rushing backwards into *a*.

The contents of the retort are removed to a beaker, and the amount of free iodine is estimated by means of thiosulphate: the amount of this salt used multiplied by 0·441 gives the quantity of iron (same factor for old notation).

Combined iodine may be separated and estimated by this process, even in presence of chlorine and bromine. Insoluble iodides must be first fused with soda and potassium oxalate in order to convert them into alkaline iodides.

The process of distillation may be obviated by boiling off the liberated iodine, and determining the amount of ferrous salt by means of permanganate.

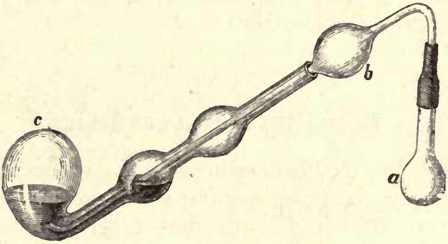

Fig. 13.

Mohr has lately simplified the iodometric estimation of iron. He brings the ferric chloride solution along with potassium iodide into a flask, which is then closed with a glass stopper, and heated in a water-bath for half an hour; after cooling, the amount of liberated iodine is determined with thiosulphate.

Kremers and Landolt have shown that ferric salts, after being converted into acetate by means of sodium acetate, may be reduced by means of sodium thiosulphate; by determining the excess of thiosulphate by means of iodine the quantity of iron may be calculated.

The authors supposed that thiosulphate of sodium was less readily acted upon by hydrochloric or sulphuric acid when acetic acid was present, hence the reason for adding sodium acetate. My own investigations have however shown that it is more to the dilution of the liquid than to the presence of acetic acid that the non-decomposition of the thiosulphate is to be traced. Further, I have shown that ferric acetate is not so readily, and generally not so completely, reduced by means of thiosulphate as ferric chloride is. Finally, the presence of acetic acid renders it more difficult to determine whether ferric salt is present, by means of the sulphocyanide of potassium test, inasmuch as acetic acid and acetates interfere with the production of ferric sulphocyanide.

In seeking to perfect a modification of the method which should allow of the process being carried out in solutions containing hydrochloric acid, I found that the decomposition of sodium thiosulphate by hydrochloric acid is greatly dependent upon temperature and degree of dilution of the liquid. Pure hydrochloric acid of 30 per cent strength, when diluted with 10 times its own volume of water, exerts no decomposing action upon thiosulphuric acid at ordinary temperatures: at any rate, after half an hour, no turbidity or deposition of sulphur is noticeable in the liquid. The same thing is true of a mixture of 1 cb.c. deci-normal thiosulphate solution with 1 cb.c. of the above-mentioned hydrochloric acid; but by warming this liquid to 40° C., deposition of sulphur soon becomes apparent. In the reduction of ferric chloride by means of sodium thiosulphate, the liquid must not therefore contain more than $\frac{1}{10}$th of its own volume of hydrochloric acid of 30 per cent, and the decomposition must proceed at the ordinary temperature.

These conditions may be conveniently fulfilled by adopting the following process:—

To the dilute solution of ferric chloride sodium carbonate is added until a slight precipitate of ferric hydrate is produced, hydrochloric acid is then carefully added until all turbidity disappears. Thiosulphate is then added in small successive quantities. The liquid should be colourless when the reduction is completed; if it assumes a yellowish colour, a few drops of hydrochloric acid must be added. In order to determine whether the reduction is complete, a very little potassium sulphocyanide is added: if a red colour is produced, a little more thiosulphate is added. The sulphocyanide exerts no reducing action on ferric salts *at* *ordinary temperatures,* nor does it influence the subsequent titration with iodine. When the reduction is complete, a few drops of starch solution are added, and the excess of thiosulphate is determined by means of iodine. By deducting this from the total quantity of thiosulphate used, a residue is obtained from which the amount of iron may be calculated. From the following equation—

$$2Fe_2Cl_6 + 4Na_2S_2O_3 = 2FeS_4O_6 + Fe_2Cl_4 + 8NaCl.$$
$$(Fe_2Cl_3 + 2NaOS_2O_2 = FeOS_4O_5 + FeCl + 2NaCl).$$

it is evident that 1 cb.c. deci-normal thiosulphate corresponds to 5·6 m.gm. of iron. The reduction is accomplished the more rapidly the greater is the excess of sodium thiosulphate. This process of iron estimation is very applicable for dilute solutions of ferric chloride, but cannot be used when the solution contains nitric acid.

The present method is more especially serviceable when it is necessary to estimate small quantities of ferric salt produced by some chemical reaction from ferrous salt, the measurement of such ferric salt serving for the determination of the amount of oxidising substance present. We shall see in the next paragraph an application of the method to the estimation of nitric acid.

§ 39.

Nitric Acid Estimation.

Nitric acid may be very well estimated by the ordinary alkalimetric methods, but the following process is even more simple. A solution of ferrous chloride containing free hydrochloric acid is converted into ferric chloride by means of nitric acid.

$$3Fe_2Cl_4 + 6HCl + 2HNO_3 = 3Fe_2Cl_6 + 4H_2O + 2NO$$
$$(6FeCl + 3HCl + NO_5 = 3Fe_2Cl_3 + 3HO + NO_2)$$

168 parts of iron converted into ferric salt
= 63 parts of nitric acid (HNO_3).

In old notation,

168 parts of iron converted into ferric salt
= 54 parts of nitric acid (NO_5).

A solution of ferrous chloride perfectly free from ferric salt is required for this process. This may be prepared by dissolving two or three grams of thin bright iron wire in strong hydrochloric acid. The solution is brought into a flask fitted with a caoutchouc stopper which carries two tubes, one reaching nearly to the surface of the liquid, the other merely passing through the stopper. About 0·5 grams of the nitrate under examination is weighed into this flask, the stopper is placed in position, and a stream of carbonic acid free from air is passed through the flask, the contents being boiled, until the liquid becomes of a pure yellow colour, and the issuing fumes cease to produce a blue colour on paper soaked in potassium iodide and starch. The liquid, having been allowed to cool in the current of gas, is transferred to a measuring vessel, and the amount of ferric salt is determined (by one of the methods described in the preceding paragraph), in an aliquot part, after neutralising the free acid by means of sodium carbonate.

A determination of the residual ferrous salt by permanganate would also enable us to calculate the amount of nitric acid, provided the original amount of ferrous salt were known. The iodometric method is, however, more direct and more exact.

As one part of nitric acid is able to convert nearly three times its own weight of iron from the state of ferrous to that of ferric chloride, the method becomes of great service in the determination of small quantities of nitric acid. The application to the analysis of well water will be found in Part III.

§ 40.

Estimation of Mercury and Chlorine.

Hempel's method for the estimation of mercury is as follows: The mercury, in the form of a mercurous salt, is precipitated as mercurous chloride by means of hydrochloric acid or common salt. The precipitate is washed by decantation, and brought into a glass-stoppered flask. A deci-normal iodine solution is added from a measuring instrument, along with potassium iodide, until the liquid, after thorough shaking, becomes perfectly clear and the colour of dissolved iodine is apparent. The amount of free iodine is then determined by means of thiosulphate:

$$Hg_2Cl_2 + 2KI + 2I = 2HgI_2 + 2KCl.^{1}$$
$$(Hg_2Cl + KI + I = 2HgI + KCl).$$

1 cb.c. of deci-normal iodine = 20 m.gm. mercury,
or iodine × 1·5748 = mercury (same in old notation).

Mercuric salts must be reduced to mercurous by means of ferrous chloride in solutions made alkaline by potash or soda. By dissolving the precipitated ferroso-ferric salt by means of dilute sulphuric acid, mercurous chloride is obtained.

Mercuric and mercurous salts if simultaneously present in solution, may be determined by estimating the latter in a portion of the liquid, then warming another portion with ferrous chloride and excess of caustic soda, acidulating with sulphuric acid, and filtering off the precipitated mercurous chloride when it has become perfectly white. The mercurous salt is then determined by the process described.

Combined chlorine may likewise be determined by this process. It is only necessary to acidify the solution with nitric acid, and to add a solution of mercurous nitrate so long as a precipitate forms. The precipitate, after washing by decantation, is treated as already described.

1 cb.c. iodine = 3·55 m.gm. chlorine.

The solution of mercurous nitrate employed should be as free as possible from mercuric salt, and must not contain any other metal precipitable by chlorine. If *much* sulphuric acid be present, the removal of this acid by means of barium nitrate is to be recommended. This method gives very good results. The final point of the reaction is easily determined.

[1] Mercurous bromide undergoes a similar reaction.

§ 41.

Estimation of Free Chlorine and Bromine.

Free chlorine may be estimated, as we have already seen, by determining the quantity of iron which it is able to convert from ferrous into ferric salt.

Small quantities of chlorine may, however, be more exactly estimated by determining the amount of iodine liberated by their action.

A measured volume of the liquid containing free chlorine is shaken up with an excess of potassium iodide, and the amount of iodine thus liberated is determined by means of thiosulphate solution.

$$KI + Cl = KCl + I.$$

Iodine used × 0·2795 = chlorine (same in old notation.)
or 1 cb.c. thiosulphate = 3·55 m.gm. chlorine.

Free bromine may be estimated by an exactly similar process.

Iodine used × 0·63 = bromine,
or 1 cb.c. thiosulphate = 8·0 m.gm. bromine.

§ 42.

Estimation of the Oxyacids of Chlorine, Bromine, and Iodine.

The oxyacids of chlorine, with the exception of perchloric acid, are decomposed by hydrochloric acid with formation of free chlorine and water. The following equations express the reactions:—

$$\begin{array}{lll}
HClO + HCl = H_2O + Cl_2 & (ClO + HCl = HO + Cl_2). \\
HClO_2 + 3HCl = 2H_2O + Cl_4 & (ClO_3 + 3HCl = 3HO + Cl_4). \\
HClO_3 + 5HCl = 3H_2O + Cl_6 & (ClO_5 + 5HCl = 5HO + Cl_6).
\end{array}$$

By allowing the liberated chlorine to react upon potassium iodide an equivalent quantity of iodine is set free. The solution containing the chlorine acid (or salt) is acidulated with hydrochloric acid, an excess of potassium iodide is added, and the liberated iodine is determined by means of thiosulphate.

If old notation be employed $n+1$ equivalents of liberated iodine $= n$ equivalents of oxygen in the acid under examination.

The oxyacids of iodine and bromine may be estimated by a similar process.

This method can only be carried out in acid solutions; it does not suffice for the estimation of hypochlorous acid in presence of chloric acid, and can, therefore, only be applied for the examination of such samples of bleaching powder as are free from chlorates. The method just described is especially applicable for the estimation of small quantities of the acids under consideration, because it is carried out by a direct titration.

Iodates cannot be estimated by oxydimetric methods, because of the indifference of iodine towards ferrous chloride; by the present method they may, however, be determined with exactness. For the examination of bleaching powder see Part III.

§ 43.

Estimation of Combined Iodine.

I prefer Pisani's above the other methods for estimating small quantities of combined iodine because it can be applied in presence of chlorides and bromides.

The principle of Pisani's method is as follows: If a solution of iodide of starch be brought into a neutral solution of silver nitrate, the iodide is decolorised, silver iodide, and probably iodate, being simultaneously produced. The amount of iodide used is proportional to the quantity of silver nitrate present. If the relation between the iodide of starch solution and a silver solution of known strength be determined, these liquids may be employed for estimating iodine generally.

Field has shown that the iodide of starch solution may be replaced by a dilute solution of iodine, to which a little starch is added before it is used. A fresh solution need not then be prepared for each analysis. Iodine is determined in metallic iodides by this method as follows:—

About $\frac{1}{2}$ cb.c. of titrated iodine solution containing starch is added to the perfectly neutral liquid containing the iodide; titrated silver nitrate solution—preferably $\frac{1}{2}$-normal—is added drop by drop until the blue colour is destroyed. The quantity of silver required, minus the amount needed to decolorise the iodine and starch employed, represents the iodine in the compound.

All substances, such as metallic sulphides, cyanides, &c., capable of precipitating silver, must, of course, be absent. Bromides and chlorides, however, exercise no prejudicial action, inasmuch as the iodine only is precipitated so long as the blue colour remains, and it is only after this has been removed that precipitation of chloride and bromide of silver commences.

Another process especially applicable for the estimation of large quantities of combined iodine is detailed in § 37. Iodine may also be estimated in most iodides by the process of § 38.

§ 44.

Silver Estimation.

Small quantities of silver may be very accurately determined by reversing the process just described for the estimation of combined iodine. For this purpose the solution, which must not contain more than 0·03 gram silver, is treated with precipitated calcium carbonate, whereby excess of acid is neutralised, and the subsequent colorimetric change rendered more apparent. Titrated iodine solution, containing starch, is then slowly added; the colour at once quickly decreases in intensity, the liquid becomes of a yellowish tint, and finally blue-grey. When this point is reached the process is finished. The amount of silver is calculated.

The iodine solution should be diluted, so that 50 cb.c. precipitate 10 m.gm. of metallic silver.

Substances which decolorise iodide of starch, as also those which are precipitated by iodine, must be absent.

If large quantities of silver are to be estimated, the greater part, perhaps 90 per cent, must be precipitated by means of a titrated common salt solution (a process to be explained in Section IV.); the remainder may then be determined by the iodometric method.

§ 45.

Estimation of Chlorine, Bromine, and Iodine in Salts.

Chlorine, bromine, and iodine cannot be estimated by *purely* volumetric processes when all three are simultaneously present in a solution. Chlorides and iodides, or iodides and bromides, on the other hand, may be volumetrically determined in the same liquid. If, for example, a solution contains an iodide and a chloride, the former may be determined by decomposing by means of ferric chloride or sulphate, free from nitrate, and estimating the iodine according to § 38. Or the iodine may be precipitated in the form of cuprous iodide, and determined as directed in § 37. Iodine may be estimated by the same method in presence of bromine with good results. No good method, however, of separating chlorine from bromine has yet been proposed. The analysis of substances containing chlorine and bromine, or the three halogens, must, therefore, be carried out by *indirect* methods.

The following process, although indirect and involving gravimetric procedure, is nevertheless simple and exact.

The whole of the chlorine, bromine, and iodine is precipitated in a portion of the liquid by means of a measured volume of silver solution of known strength; the precipitate is collected on a filter and washed; excess of silver is estimated in the filtrate by § 44, or by one of the methods described in Section IV. The amount of silver in the precipitate is obtained by deducting the excess from the total silver added. The precipitate is now dried at 100°, ignited and weighed. Iodine is determined in another portion of the liquid according to § 43. The iodine is calculated to silver iodide, and this is deducted from the total weight of precipitated chlor-brom-iodide. The weight of chloride and bromide of silver is thus obtained, and the total silver being known, as also the silver combined with iodine, the silver combined with chlorine and bromine is readily found.

We have thus determined:—

Total weight of AgCl, AgBr, and AgI . . . $= G$
Total weight of silver contained in G . . . $= S$
Amount of iodine . . . . $= I$
Amount of silver iodide . . . . $= g$
Amount of chloride and bromide of silver . . $= G - g = \alpha$
Amount of silver in chloride and bromide . . $= S - (g - I) = \beta$

Assuming that the chloride and bromide of silver was all in the form of chloride, the amount of the chloride would be

$$\text{AgCl} = \frac{\beta\ 143{\cdot}47}{107{\cdot}97} = \beta\ 1{\cdot}329$$

The silver in the chloride and bromide multiplied by 1·329 gives the amount of chloride of silver, supposing the whole of the silver to exist in this form; this is subtracted from α, and the residue is noted.

Remembering that the difference between AgBr and AgCl = 44·50, and that this corresponds to an equivalent of bromine = 80 (contained in a mixture of bromide and chloride), then $\frac{80}{44{\cdot}5} = 1{\cdot}798$ becomes the factor by which the difference which has been found between the silver chloride and the silver chloride + bromide is to be multiplied in order to find the amount of bromine. By adding this to β, and deducting the sum from α, the amount of chlorine is found.

The following example will help to make the calculation clearer:—

The chlorine, bromine, and iodine in a mixture of the potassium salts of the three halogens, are precipitated by means of a measured quantity (excess) of silver nitrate solution; after filtration the excess of silver is determined by means of iodine (§ 44).

0·6478 grams silver is required for the complete precipitation.

The mixed precipitate of silver chloride, bromide, and iodide weighs 1·041 grams. The iodine, determined in another portion of the solution, is found to amount to 0·127 gram; 0·127 iodine = 0·235 AgI : 1·041 − 0·235 = 0·806 = weight of silver chloride and bromide.

The amount of silver in this quantity of silver chloride and bromide amounts to 0·6478 − (0·235 − 0·127) = 0·5398 grams, which, multiplied into 1·329, gives 0·717 as the quantity of silver chloride in the mixed precipitate.

Then 0·806 − 0·717 = 0·089, which multiplied by 1·798 = 0·160 gram bromine.

In order, finally, to determine the amount of chlorine, we have, weight of silver in the precipitate of silver chloride and bromide (= 0·5398) + weight of bromine (= 0·16) = 0·6998: by deducting this from the weight of mixed silver chloride and bromide, viz., 0·806, we have 0·1062 as the amount of chlorine. The result of the analysis is then—

0·127 gram iodine
0·160 „ bromine
0·1062 „ chlorine.

Silver bromide may be separated from chloride, in absence of iodide, by means of ammonia of 0·98 sp. gravity previously digested with silver bromide. Such a solution dissolves no bromide of silver, but readily dissolves chloride. This separation is useful when the quantities of chloride and bromide are very unequal, and the bromine estimation is the more important. The process may also be applied in the estimation of the three halogens as follows:—

Iodine is distilled off with ferric sulphate and determined as in § 38. Iron is precipitated in the residue by means of potassium carbonate, and in the filtrate, after acidification with nitric acid, chlorine and bromine are thrown down by means of silver nitrate. The mixed precipitate is washed with ammonia which has been saturated with silver bromide, and the residue, consisting of silver bromide, is dried, ignited, and weighed.

Chlorine, bromine, and iodine are precipitated in a second portion of the solution by means of $\frac{1}{10}$-normal silver solution, the excess of silver being determined by iodine; from the difference between total silver salt and silver bromide plus silver iodide, the quantity of silver chloride is found, and from this the amount of chlorine is calculated. For solutions containing much chlorine this process is to be prefered to the indirect method.

§ 46.

Estimation of Traces of Heavy Metals.

Certain commercial substances, such as citric and tartaric acids, and certain chemical reagents, such as sodium acetate, not unfrequently contain traces of heavy metals precipitable by sulphuretted hydrogen, too small to admit of being estimated by the ordinary gravimetric methods. Such minute quantities of heavy metals may be determined by adding perfectly pure sodium acetate to an aqueous solution of the substance under examination, followed by the addition of a measured volume of freshly-prepared sulphuretted hydrogen water. After a few minutes the excess of sulphuretted hydrogen is determined by means of iodine. An equal volume of the same sulphuretted hydrogen water is now added, and the liquid is again titrated with iodine. The difference between the two titrations represents the quantity of iodine corresponding to the heavy metal present. Small quantities of lead, copper, zinc, arsenic (as arsenious salt), antimony, mercury, and bismuth may be determined by this method with considerable exactness. Care must be taken not to add a very large excess of sulphuretted hydrogen water. Ferric salts interfere with the accuracy of the method: the presence of ferrous salts is immaterial. Oxidising acids must be absent.

The method does not afford absolutely accurate results, but it is of great use in the examination of those chemicals, or commercial substances, the value of which is materially altered by the presence of small quantities of heavy metals.

SECTION IV.

ANALYSIS BY PRECIPITATION.

IN § 1 I have insisted upon the necessity of possessing some means of determining with accuracy the final point of all volumetric reactions. A colorimetric indication is to be preferred.

In analyses by precipitation the possession of such a means of determining the end of the reaction becomes of paramount importance.

The principle of the analyses to be considered in the present section is very satisfactory in itself. No one doubts the possibility of completely precipitating silver by means of common salt, lead salts by means of alkaline chromates, and copper by means of sodium sulphide. What patience is, however, required to enable one to wait until the precipitate has completely settled after each addition of the standard liquid! Several years ago I described a filter by the use of which it might readily be determined whether or not the end of the reaction had been reached. Now, however, I have abandoned all precipitation analyses except those the termination of which can be determined by a sudden change in colour, or those which may be used in conjunction with a saturation or oxidation method.

Certain estimations which may be performed by means of precipitation analyses, in which, however, the final points of the reactions cannot be accurately determined, are much better carried out by the aid of other methods. It is better, for instance, to determine lead by precipitation with an alkaline chromate and subsequent oxidation of a ferrous salt by the chromic acid, than by precipitation with titrated sulphuric acid.

Conversely, chromic acid is better determined in potassium chromate by an oxydimetric method than by titration with a standardised lead solution, and so on.

There are a number of precipitation methods which are practically useless, because they may be replaced by ready and very accurate oxydimetric or saturation processes.

Those estimations, for example, of heavy metals (zinc, cadmium, lead, &c.) depending upon precipitation by means of sodium sulphide are better altogether done away with, because the metals which can be determined by this method can also be estimated with greater accuracy, and in presence of other metals, by methods which have been already described. Sodium sulphide is, moreover, a most disagreeable liquid to work with, and the final points of the reactions in which it is used are often very difficult of determination.

I have therefore omitted any description of those processes in which sodium sulphide is employed, and have contented myself with detailing precipitation methods in which a distinct colorimetric change enables us to determine with accuracy the final point of the reaction.

§ 47.

Estimation of Chlorine and Silver.

Chromate of potassium precipitates dark-red silver chromate from a neutral or slightly alkaline solution of a silver salt. From a liquid containing sodium chloride and potassium chromate, silver nitrate precipitates the whole of the chlorine in the form of silver chloride before the production of any precipitate of silver chromate. On these facts Mohr has based a process for the estimation of chlorine in soluble chlorides, the neutral solutions of which are not precipitated by potassium chromate.

The liquid, if acid, is completely neutralised by addition of potassium carbonate. Four or five drops of a solution of pure potassium chromate—1 : 10—are added, and normal, or deci-normal silver solution is run in from a burette until a permanent dark-red precipitate is produced.[1]

108 parts of silver precipitate 35·5 parts of chlorine.

The process is best carried out by gaslight; or, if performed in daylight, the flask containing the solution should be placed within a large porcelain basin.

This process may be applied to the estimation of chlorine in those metallic chlorides which are precipitated by potassium chromate (chlorides of lead, bismuth, barium, &c.) by previously precipitating the warm solution by means of an alkaline carbonate, filtering and determining the chlorine in the filtrate. The solution must not contain other metals than those of the alkalies, and alkaline earths with the exception of barium.

The converse of this process may be applied for the estimation of silver, in absence of other metals. It is only necessary to run the neutral silver solution from a burette into a measured quantity of deci-normal sodium chloride solution until the whole of the chlorine contained therein is thrown down as silver chloride.

If silver has been precipitated as chloride, it may be determined by this process by dissolving the precipitate in ammonia, precipitating with ammonium sulphide, dissolving the silver sulphide in nitric acid, and after neutralising by means of potassium carbonate, titrating against sodium chloride.

The standard liquids may be prepared by dissolving 5·85 grams of pure, semi-fused sodium chloride ($\frac{1}{10}$th atom) and 17 grams ($\frac{1}{10}$th atom) of silver nitrate, respectively, in 1000 cb.c. of water.

It is sometimes recommended to use pure silver instead of the nitrate, and if really pure silver can be obtained, it is well to adopt this method. Recent experiments have, however, convinced me that sal-

---

[1] Solutions which contain ammonia should be rendered alkaline by means of a small excess of potassium carbonate, and calcium acetate solution should then be added until the liquid is neutral.

ammoniac is the best substance for the determination of the strength of the standard liquids.

Sal-ammoniac can be readily obtained in a state of purity by subliming the commercial salt: it must leave no residue when ignited on platinum foil, nor must it cause a turbidity in warm baryta water. Traces of iron may be recognised by testing the solution with ammonium sulphide.

A solution of pure sal-ammoniac is made in distilled water of a strength such that 20 cb.c. = 0·2675 gram NH_4Cl = 0·1775 gram Cl: 20 cb.c. of this solution are placed in a 150 or 200 cb.c. flask; a few drops of potassium chromate, and of pure potassium carbonate solutions are added; the liquid is rendered neutral by means of a little acetate or nitrate of calcium, and silver solution (prepared as before described) is run in until a faint red precipitate is produced. If 50 cb.c. of silver solution are required, the liquid is exactly deci-normal: if a greater or less amount is used, the liquid must be adjusted in accordance with the results of the titration, and another experiment, similar to that just described, must be performed. The deci-normal sodium chloride solution is now to be titrated against the standard silver. Sal-ammoniac cannot be itself employed in the place of sodium chloride as a standard liquid, on account of the readiness with which its solution undergoes decomposition.

The method for the estimation of chlorine and silver just described is much to be preferred to the old process, in which sodium chloride was run in until precipitation was complete.

Silver may be determined in presence of other metals, as follows: The whole of the silver is precipitated from an acid solution by means of a measured volume—slight excess—of deci-normal sodium chloride. To the whole, or to an aliquot part of the liquid, pure potassium carbonate is added to alkaline reaction; after boiling, the precipitate is filtered off, and washed with hot water. The alkaline filtrate is rendered neutral by means of calcium acetate solution, potassium chromate is added, and the excess of chloride of sodium is determined by means of deci-normal silver. If ammonium salts are present, the process is modified either by weighing the precipitated silver chloride, or by dissolving it, after careful washing, in ammonia, adding ammonium sulphide, dissolving the precipitated silver sulphide in nitric acid, and estimating by the method already described.

The standard silver solution should be kept in dark-coloured bottles.

§ 48.

Estimation of Chlorine in the Oxyacids of Chlorine.

The methods for determining the oxygen in these acids have been described in §§ 25 and 43. The chlorine may be determined by reducing with ferrous sulphate, free from chlorides, in presence of sulphuric acid, precipitating the iron by boiling with pure potassium carbonate, filtering, and applying the process described in the last paragraph to the filtrate.

This process determines the *total* chlorine in such substances as bleaching powder.

§ 49.

Cyanogen Estimation.

Cyanogen forms a precipitate with silver analogous to those produced by chlorine, bromine, and iodine. When, however, silver solution is added to the solution of an alkaline cyanide, no precipitate is formed until the half of the cyanogen which is present has entered into combination with the silver. This phenomenon occurs also in presence of metallic chlorides, bromides, and iodides. Cyanogen may be determined by adding a little sodium chloride to the liquid containing potassium cyanide, rendering the liquid alkaline by means of potash, and running in centi-normal silver solution until a permanent slight turbidity is produced.

$$2KCy + AgNO_3 = AgCy\ KCy + KNO_3$$

2 equivalents of cyanogen correspond to 1 equivalent of silver; or silver used × 0·4816 = cyanogen.

This method may be applied to the estimation of cyanogen in organic substances, such as oil of bitter almonds, laurel water, &c. Metallic sulphides, if present, must be removed by adding zinc sulphate to the alkaline liquid and filtering off the precipitate which forms, before titrating with silver. Double cyanides, if present, must be decomposed by boiling with mercuric oxide in a solution containing potash, filtering, removing mercury by precipitation with sulphuretted hydrogen, again filtering, and precipitating sulphuretted hydrogen by addition of zinc sulphate. The filtrate from the last precipitate is then titrated with silver solution.

The presence of certain metals interferes with the exact estimation of cyanogen by means of silver solution. Mercury, iron, and cobalt compounds must especially be removed. Mercury may be removed by means of sulphuretted hydrogen. Double cyanides of iron may be decomposed by the method just described. Double cyanides of cobalt are, however, most readily analysed by heating in a combustion tube with cupric oxide, and determining the carbon dioxide and nitrogen evolved, by the methods of organic analysis.

Cyanides are poisonous when they yield prussic acid on distillation with boric acid.

§ 50.

Phosphoric Acid Estimation.

Phosphoric acid is most readily determined by means of a titrated uranium solution. The process is carried out in hot solutions containing acetic acid by running in the test liquid until a drop of the solution under examination gives a dark reddish brown colour when spotted on a porcelain slab, in contact with a drop of potassium ferrocyanide solution.

The uranium solution is prepared by dissolving yellow uranium oxide in acetic acid.

A solution of sodium ammonium phosphate ($Na(NH_4)HPO_44H_2O$), a salt easily obtained in a pure state, is prepared by dissolving 20·9 grams of the salt in 1000 cb.c. of water (old notation, 20·9 grams). 1 cb.c. of this solution contains 7·1 m.gm. of P_2O_5 (7·1 m.gm. PO_5, old notation). The solution is therefore $\frac{1}{20}$-normal (deci-normal in old notation). 20 cb.c. of this solution are brought into a quantity of very dilute acetic acid, the liquid is heated to boiling, the lamp is removed, and the uranium solution is run in, five drops or so at a time—until a drop of the liquid gives the required reaction with potassium ferrocyanide. 2 cb.c. of the $\frac{1}{20}$-normal phosphate solution are now added, the liquid is again heated to boiling, and carefully titrated with uranium solution. The total quantity of uranium liquid employed corresponds to 22 cb.c. of $\frac{1}{20}$-normal phosphate solution. The uranium solution is adjusted so that it exactly corresponds with the phosphate solution; 1 cb.c. is then equal to 7·1 m.gms. P_2O_5 (7·1 m.gm, PO_5 in old notation).

The process for the estimation of phosphoric acid is carried out in the manner just described: a couple of cb.c. of the $\frac{1}{20}$-normal phosphate solution may be used for determining the exact close of the reaction; the phosphoric acid in these must of course be deducted from the total phosphoric acid found.

The estimation of phosphoric acid by this process demands the absence from the liquid containing phosphoric acid of all bases except the alkalies, alkaline earths, and manganous oxide. All non-volatile or reducing organic acids, such as citric, tartaric, oxalic, and formic acids, must also be absent. The presence of sulphuretted hydrogen, sulphurous oxide, hydriodic acid, or the acids of arsenic, likewise interferes with the process. The presence of a very large quantity of acetates must also be avoided.

A method of separating phosphoric acid from other acids, and bringing it into a form in which it may be determined, will be found in Part II.

The following modification of the uranium method affords exceedingly accurate results. The alkaline or alkaline earth phosphate is dissolved in acetic acid, the liquid is made up to a fixed volume (say to 200 cb.c.), and a portion of it is placed in a burette. 20 cb.c. of $\frac{1}{20}$-normal uranium solution are heated almost to boiling, with addition of a few drops of acetic acid. The liquid should remain perfectly clear; if a turbidity occurs, more acetic acid must be added. The phosphate solution is then run in until a drop of the hot liquid ceases to give a reddish-brown colour with potassium ferrocyanide, and the number of cb.c. used is noted. The liquid is again heated nearly to boiling, and $\frac{1}{20}$-normal uranium liquid is cautiously added from another burette until the brown colour is again obtained with ferrocyanide. The number of cb.c. of uranium solution used is added to the 20 cb.c. originally taken; the sum represents the amount corresponding to the quantity of phosphate liquid run in from the burette. This process, originally suggested by Fresenius for the estimation of phosphoric acid in calcium phosphate, possesses two distinct advantages over the older method. It is more easy to determine the exact termination of the reaction by this method; the decomposing action of the alkaline acetates is much decreased by the great dilution of the liquid, and entirely removed by the device of titrating back with uranium solution. This modification may also be applied in standardising the two liquids. I have not, however, found any appreciable difference between the results and those obtained by the usual method. This was doubtless because of the small amount of alkaline acetates present.

The uranium process is only applicable to estimations of tribasic phosphoric acid; the other phosphoric acids must be transformed into tribasic acid, by prolonged boiling with strong acids, before they can be determined by means of this process.

§ 51.

Aluminium Estimation.

The estimation of this metal by volumetric methods was until lately a most tedious process. The method which I shall describe is a modification of that originally described by me in 1865 (*Zeits. für Anal. Chem.*, part 1).

The acid solution containing aluminium is mixed with sodium acetate; a measured volume—excess—of $\frac{1}{20}$-normal phosphate solution (see preceding paragraph) is added, and the liquid is heated to boiling. The excess of phosphoric acid is then determined, without filtration, by means of uranium solution as described in the preceding paragraph, and from this the amount of phosphoric acid corresponding to the aluminium present is found. The aluminium is precipitated as $AlPO_4 . 4H_2O$ $(Al_2O_3 . PO_5)$. Each cb.c. of $\frac{1}{20}$-normal phosphate solution which has combined with aluminium = 5·13 m.gms. Al_2O_3 (same in old notation). If much free mineral acid be present in the solution containing aluminium, it must be neutralised with sodium carbonate, the precipitate which forms dissolved in a drop of hydrochloric acid, and a solution of sodium acetate containing acetic acid added. Excess of lime may be removed by precipitation with sodium sulphate; filtration from precipitated gypsum is not necessary. Small quantities of ferric salts do not materially affect the estimation. The iron may be determined in another portion of the liquid. Iron, if present in somewhat large quantities, may be removed by adding a little sodium sulphite, boiling, adding considerable excess of caustic potash, and filtering from precipitated ferroso-ferric oxide. Hydrochloric acid having been added to the filtrate until the precipitate which forms is entirely redissolved, the solution is mixed with excess of sodium acetate. In the event of magnesia being present in quantity, it is better to precipitate iron and aluminium with ammonium sulphide, and to dissolve the alumina from the precipitate by means of caustic potash.

It is necessary to bear in mind that those substances detailed in the preceding paragraph as interfering with the estimation of phosphoric acid must be removed from solutions in which aluminium is to be determined by the uranium process. All bases except the alkalies and alkaline earths must be absent.

Aluminium phosphate is somewhat soluble in aluminium acetate and also in ammonia; but it is quite insoluble in excess of phosphates: these salts are present in excess in carrying out the process as described above. It can be easily shown by experiment that uranium acetate does not decompose aluminium phosphate.

§ 52.

Estimation of Magnesia and Manganese.

These metals may be completely precipitated from solutions containing ammonia and ammonium chloride by means of sodium phosphate—the precipitates having the composition $Mg(NH_4)PO_4.6H_2O$ and $Mn(NH_4)PO_4.H_2O$ respectively, ($2MgO.NH_4O.PO_5.12HO$ and $2MnO.NH_4O.PO_5.2HO$).

The manganese salt is obtained in a crystalline form by boiling the liquid: the magnesium salt is precipitated very slowly. If, however, microcosmic salt be employed as precipitant, or if the liquid be acidified with hydrochloric acid after adding sodium phosphate, and a considerable excess of ammonia be then added, the magnesium ammonium phosphate is precipitated immediately and completely.[1]

After washing the precipitates with hot water containing ammonia, they are dissolved in dilute hydrochloric acid, the liquids are saturated with sodium acetate, and the phosphoric acid is determined by means of uranium solution.

1 cb.c. $\frac{1}{20}$-normal uranium solution
= 7·1 m.gm. MnO = 4·0 m.gm. MgO.

Old notation,

1 cb.c. $\frac{1}{10}$-normal uranium solution
= 7·1 mg.m. MnO = 4·0 mg.m. MgO.

Manganous oxide exerts no influence upon the reaction between uranium and ferrocyanide of potassium. The ferro- must be perfectly free from ferri-cyanide.

This method is particularly adapted for the estimation

---

[1] Mohr, *Zeits. für. Anal. Chem.*, XII., part 1.

of magnesium, as it is in the form of ammonium-magnesium phosphate that this metal is generally separated from the alkalies. Manganese is, however, generally better determined by the oxydimetric process described in § 23.

§ 53.

Sulphuric Acid Estimation.

Of the methods which have been published for the estimation of combined sulphuric acid, I look upon that of Mohr (described in § 14) and that of Wildenstein, in which titration is effected by a standarised potassium chromate solution, as the best.

The circumstance that barium chromate is insoluble in ammoniacal liquids, in which many other metallic salts are soluble, induced me to make experiments with the view of rendering Wildenstein's method of more general application.

It was necessary to find a reagent capable of indicating the presence of very small traces of chromic acid, the indications of which should not be interfered with by the presence of barium chromate or other salts likely to be present in carrying out the estimation.

Preparation of Standard Liquids.

Solutions of potassium dichromate and barium chloride are required. These I make $\frac{1}{8}$-normal, so that each cb.c. of barium chloride solution is equal to 12·25 m.gm. H_2SO_4, or 10 m.gm. SO_3, and is also equal to 1 cb.c. potassium dichromate solution. (If old notation be employed, the liquids are made $\frac{1}{4}$-normal. 1 cb.c. barium chloride is then equal to 10 m.gm. SO_3.)

Potassium dichromate may be prepared free from sulphate by dissolving the ordinary salt, along with $\frac{1}{100}$th of its weight of barium chloride, in boiling water, filtering and crystallising. The crystals are washed with cold water, and dried first in the water-bath, and then at 200°. About 20 40 grams of the pure salt are dissolved in 1000 cb.c. of water, and the amount of chromic acid is determined in

10 cb.c. of this solution by means of the ferrous sulphate and permanganate method described in § 26. From the results of this determination the liquid is adjusted so as to be $\frac{1}{8}$-normal.

12·5

1 cb.c. = 14·525 m.gm. CrO_3.

$\frac{1}{4}$-normal in old notation, then 1 cb.c. = 12.5 m.gm. CrO_3.

The barium chloride solution is prepared by dissolving about 30 grams of the recrystallised salt in a little hot water acidulated with a few drops of hydrochloric acid, pouring the solution into a quantity of water, and making up to 1000 cb.c.

The liquids are then compared as follows: About 100 cb.c. of water, containing a considerable quantity of ammonia (free from sulphate), are heated to boiling, a couple of drops of calcium chloride solution (also free from sulphates) are added, in order to precipitate any carbonic acid present; the lamp is removed, and 20 cb.c. of barium chloride, and the same volume of potassium dichromate solution, are added. The liquid having been again heated to boiling is removed from over the lamp, and the dichromate solution is cautiously run in from a burette, with constant shaking, until the supernatant liquid appears of a yellow tinge. The number of cb.c. of dichromate run in from the burette, multiplied by 49, gives the number of cb.c. of water, which must be added to the 980 cb.c. of barium chloride solution in order to make it of such a strength as that 1 cb.c. shall be equal to 1 cb.c. dichromate solution.

The liquids may also be compared by titrating a solution of barium chloride against another of potassium dichromate, and then determining the strength of the barium chloride by precipitating a known weight of pure potassium sulphate, dissolved in water, and mixed with calcium chloride and ammonia, with a measured volume of the barium chloride solution, and estimating the excess of this salt in the filtrate by means of the dichromate solution. The liquids may then be adjusted by a method analogous to that described in § 6. This method of standardising is to be recommended as a control on the other.

a. *Estimation of Sulphuric Acid in Alkaline Sulphates, in absence of all other bases, and of all Acids which are precipitated by Barium Chloride in Alkaline Solutions (Phosphoric, Oxalic, Tartaric, Citric, Silicic, Sulphurous, Chromic, Arsenious, and Arsenic Acids).*

Wildenstein's method is applicable in its original form. The acid solution is saturated with ammonia, heated to boiling, an excess of barium chloride solution is added, and the excess is estimated by means of dichromate solution. The sulphuric acid may be estimated to within 1 m.gm. of the exact amount. Neither ammonium salts nor salts of the alkalies interfere with the precipitation of the barium chromate.

It is very difficult to obtain a solution of ammonia which is absolutely free from carbonate. Before adding barium chloride I, therefore, pour a couple of drops of pure calcium chloride, or calcium acetate solution, into the boiling liquid, then remove the lamp, and proceed with the titration.

In determining the final point of the reaction, the vessel should be placed upon a white surface, in a position where the light falls fully upon it. The hotter the liquid and the more it is shaken, the more quickly does the precipitate settle. It is well not to work with more than 150 cb.c. of liquid, which is about the amount used in determining the strength of the standard solutions.

b. *Estimation of Sulphuric Acid in Sulphates of Magnesium, Zinc, Cadmium, Nickel, Cobalt, and Copper, in absence of other bases (except the Alkalies) and of the acids mentioned under* a.

Inasmuch as the sulphates of magnesium, zinc, and cadmium are soluble in ammonia containing sal-ammoniac, and as these solutions are colourless, and are not acted upon by potassium dichromate, it follows that the sulphuric acid in these three salts may be determined by the process described under *a.* It is only necessary to dissolve in ammonia, add sal-ammoniac, heat to boiling, add a little chloride of calcium, and proceed as already directed. (Silver sulphate may also be examined by this method.) The results are very accurate.

Although the sulphates of nickel, cobalt, and copper are soluble in ammonia containing sal-ammoniac, their solutions are coloured, and hence it is not possible to determine with accuracy the final point of the reaction if the sulphuric acid be determined by method *a*. By taking advantage of the formation of a new compound of lead chromate with lead chloride it becomes possible to determine the point at which sufficient dichromate has been added. By adding lead acetate solution to a liquid containing sal-ammoniac, potassium chromate, or dichromate and ammonia, a flesh-red precipitate is produced. This precipitate is only formed in ammoniacal liquids. If a considerable quantity of lead acetate be added to a liquid containing dichromate and a little ammonia, the ordinary yellow chromate of lead is precipitated. The flesh-red precipitate has a shade of brown in it when it is formed in coloured liquids.

I am not as yet able to state the exact composition of the new salt. If a solution of lead acetate be poured into tolerably strong ammonia, free from carbonate, the liquid becomes slightly opalescent, but no precipitate is produced for some time. If a drop of this liquid be placed on a porcelain plate, and a couple of drops of a solution of potassium chromate, containing only $\frac{1}{300,000}$th of its weight of chromic acid, and mixed with a considerable quantity of sal-ammoniac and ammonia, be added, the flesh-red precipitate is at once produced. If a couple of drops of barium chloride be added to the same very dilute chromate solution, and the liquid be boiled, the reaction with lead solution just mentioned is no longer obtained, but a precipitate of lead chloride only is formed, which shows that barium chromate is not soluble in 300,000 parts of this liquid.

The presence of considerable quantities of nitrates, of copper, nickel, cobalt, zinc, cadmium, magnesium, or calcium salts does not interfere with the reaction of the chromate liquid with the ammoniacal lead solution. Sulphates, oxalates, and phosphates, if not present in very large quantities, are also without influence upon the reaction. (A method for removing phosphates before the titration will be described hereafter.)

Sulphuric acid may be estimated in the sulphates of nickel, cobalt, and copper by dissolving in water acidulated with hydrochloric acid, adding sal-ammoniac, a couple of drops of calcium chloride solution, and an excess of ammonia. The liquid is heated to boiling, the sulphuric acid is precipitated by means of a measured volume of barium chloride solution, and the excess of this liquid is determined by running in dichromate solution very cautiously until a drop of the liquid, when spotted on a slab with prepared lead solution, gives the characteristic flesh-red precipitate. After each addition of dichromate the liquid should be well shaken, and allowed to settle for a few seconds before it is tested. When the reaction is obtained, the liquid is again shaken up, and another drop is tested with lead solution; if the reaction is again obtained, the titration is finished.

A mere darkening of the lead solution (showing that too little ammonia is present) may be disregarded.

In the case of copper sulphate, the original blue ammoniacal liquid assumes a green tint as the dichromate is run in; the colour becoming decidedly green when an excess of chromate is present.

I had supposed it possible to base a method for determining the end of the reaction on this circumstance, but found it impracticable.

c. *Estimation of Sulphuric Acid in presence of the foregoing bases, of Aluminium, Chromium, Ferrous, Manganous, Tin, Mercury, Bismuth, and Antimony Oxides: also in presence of Oxalic, Chromic, and Silicic Acids, the acids of Arsenic and Phosphorus, and in difficultly-soluble Sulphates.*

In the absence of organic acids yielding a residue of carbon on heating, all sesquioxides, as also the oxides of tin, bismuth, and antimony, may be precipitated by the addition of sodium acetate to boiling solutions.[1] Ferrous and manganous salts are precipitated on addition of sodium hypochlorite Oxalic acid may be converted by the same reagent, in hydrochloric acid solutions, into carbonic acid, which may be removed. Phosphoric and arsenic acids are precipitated along with the sesquioxides. If too small a quantity of sesquioxide be present, it is only necessary to add ferric chloride. Chromic acid is converted into a chromic salt by adding ferrous chloride or by dissolving a little iron wire in the liquid. Sodium hypochlorite does not act upon chromic salts in acetic acid solutions.

As none of the precipitates enumerated above contains sulphuric acid, this acid may be estimated in the filtrate, which can only contain calcium[2] in addition to the bases mentioned under *a* and *b*. It is not necessary to wash the precipitates before titrating the filtrate. The precipitation may be advantageously carried out in a 250 cb.c. flask, which is afterwards filled to the mark with water, and from this a measured volume of liquid is withdrawn after the precipitate has settled, and the sulphuric acid therein determined by the method described under *a* or *b*.

It is to be noted that ferrous and manganous salts reduce chromic acid in ammoniacal solutions, the former salts being precipitated as oxide, the latter as peroxide.

---

[1] Silicic acid may also be perhaps precipitated here. The presence of this acid would prevent the rapid settling of the precipitated barium chromate, but would not interfere with the final reaction with the lead solution.

[2] In the presence of such quantities of calcium salts as suffice to produce a precipitate of gypsum, it is well to add ammonium carbonate after precipitating the sesquioxides, &c., and to allow the liquid to remain at rest for a few minutes before filtering. This process is also to be recommended in presence of alumina and chromium oxide, unless much ferric oxide be also present. Uranium oxide is precipitated by means of ammonia, or by sodium phosphate, excess of which is afterwards removed by means of ferric acetate.

Stannous chloride must be converted into stannic salt before precipitating with sodium acetate.

This method is applicable in presence of mercury. Mercuric sulphate is dissolved in hydrochloric acid, and the mercury is precipitated by means of ammonia or ammonium carbonate; sulphuric acid is determined in the filtrate by method *a*. If mercuric chloride be present along with other metals, the solution is precipitated by sodium acetate, and excess of ammonia and ammonium carbonate are added. Any manganese which may be present is thus precipitated as peroxide.

Difficultly-soluble sulphates are decomposed by boiling with potassium carbonate (lead sulphate by digesting with sodium bicarbonate or ammonium carbonate), and sulphuric acid is determined in the filtrate. Gypsum, as also freshly-precipitated strontium sulphate, may be treated as sulphates of the alkalies.

d. *Estimation of Sulphuric Acid in presence of Sulphides of the Alkalies, Sulphites and Thiosulphates, also of Cyanogen Compounds of the Alkalies.*

Although sulphites and thiosulphates do not reduce the ammoniacal dichromate solution, yet I think that the estimation of sulphuric acid in presence of these salts cannot be exactly carried out by precipitation with barium chloride, inasmuch as oxygen is being continually absorbed, and the quantity of sulphuric acid as continually increased.

I prefer to add a few pieces of zinc to the solution after acidification with hydrochloric acid; sulphurous acid is thus destroyed. The sulphuretted hydrogen formed may be readily removed by boiling. Ammonia is then added, and the liquid is filtered from precipitated sulphur. The filtrate, which contains sulphuric acid and perhaps a very little pentathionic acid, is titrated by method *a*.

Sulphuric acid may be determined in presence of an alkaline cyanide or ferrocyanide by method *a*. Ferricyanides must, however, be removed before titration.

This may be done by acidifying with hydrochloric acid, adding zinc, and allowing the reduction to proceed in the warm liquid until all colour is discharged; ammonia is then added in excess, whereby zinc is precipitated as ferrocyanide. Sulphuric acid is determined in the filtrate.

e. *Estimation of Sulphuric Acid in presence of Tartaric, Racemic, and Citric Acids.*

Inasmuch as barium chromate is somewhat soluble in these acids, the method of Wildenstein cannot be directly applied.

By adding calcium chloride to the hydrochloric acid solution containing sulphuric acid, and alcohol of 95 per cent to the amount of twice the volume of liquid, the whole of the sulphuric acid may be precipitated as calcium sulphate. The precipitate is filtered off after a little time, washed with alcohol,—if potassium tartrate be present, the alcohol should contain a little hydrochloric acid,—and sulphuric acid is determined therein by method *a*.

Gypsum in presence of free sulphuric acid may be removed by this process, and estimated apart from the free acid.

§ 54.

Barium Estimation.

By precipitating barium with a measured volume of normal sulphuric acid, and determining the excess of acid as described in the foregoing paragraph, *without* previous filtration, barium may be very accurately estimated.

The method is especially applicable when all bases other than alkalies and alkaline earths are absent. Inasmuch as barium may be readily separated from other bases by means of ammonium sulphide—as we shall hereafter see—this condition is readily fulfilled.

Strontium and calcium, if present, are precipitated as sulphates, but as an excess of barium chloride must be employed in the determination of the sulphuric acid, these salts are decomposed thereby on warming, and therefore do not interfere with the results. If phosphoric or oxalic acid be present, a little calcium chloride is added after precipitating the barium with sulphuric acid, ammonia is then added in excess, and the excess of sulphuric acid is determined.

This process for the estimation of barium is of very general application, inasmuch as it may be carried out in presence of the alkaline earths. The excess of sulphuric acid is to be always determined by method *a* of the preceding paragraph.

PART II.

METHODS OF SEPARATION PRECEDING VOLUMETRIC ESTIMATIONS.

INTRODUCTION.

In Part I. we have learned by what processes single substances may be determined volumetrically, after separation from those bodies which would exert a hurtful influence upon the estimation. We have now to describe processes by means of which such separations may be carried out. I shall only describe processes of separation which I have found, by careful experiment, to be specially suitable in volumetric analysis.

In describing methods of separation I have divided the metallic salts into groups, in accordance with their behaviour towards sulphuretted hydrogen and alkaline sulphides; and the acids into groups, in accordance with analogies of decomposition. I have described methods for the separation of the groups, and also methods for the separation of the members of each group from one another.

Section I. of the present part is concerned with the separation of metallic compounds; Section II. with that of non-metallic compounds.

It is, however, possible to determine many substances volumetrically without previous separation. For instance, we have already learned that ferrous salts may be determined in presence of all other substances, except those which exert a reducing or oxidising action; that sulphurous acid may be determined in presence of acetic, sulphuric, or hydrochloric acid; and that the estimation of chlorine may be carried out in presence of sulphates, nitrates, or acetates.

Separation, previous to estimation, need only be adopted when substances are present which would interfere with the proper carrying out of the method of estimation.

The group separations may be regarded as a complete scheme of systematic analysis; nevertheless the analyst will often wish only to determine one substance present along with many others by the quickest and simplest method which he can devise. To find, if possible, a method for the estimation of bases, *without* previous separation of groups or of single bases, has long been my wish, and I believe that the processes described in Section II. of the present part will serve this purpose. It is only by employing volumetric processes that such a system becomes possible.

I must premise that every quantitative analysis presupposes a knowledge of all the substances present in the substance to be examined. This is especially to be insisted upon in practising volumetric methods, inasmuch as each substance is determined by titration of a liquid, and is not obtained in a visible form as in gravimetric analysis. False results are not unfrequently obtained because of the influence exerted upon the process of analysis by substances which are not known to be present.

SECTION I.

SEPARATION OF THE BASES FROM ONE ANOTHER.

§ 55.

Solution of the Inorganic Substances to be Separated.

EVERY volumetric process presupposes that the substance to be determined is in solution. All substances are not soluble in water. Many substances insoluble in water are dissolved by dilute or concentrated hydrochloric acid at ordinary temperatures: to this class belong phosphates, arsenates, and carbonates, most basic silicates (solution being attended with separation of silica), many metals, metallic sulphides, oxides, &c. Other substances are better dissolved by nitric acid. Such are most metallic sulphides, and those metals which are not, or not wholly, dissolved by hydrochloric acid. Other substances, again, are only soluble in aqua regia. Such are platinum, gold, mercuric sulphide, &c. Hydrochloric acid and potassium chlorate may often advantageously replace aqua regia as a solvent. Nitric acid along with potassium chlorate exerts a yet more energetic action.

A considerable number of substances resist the solvent action of all the reagents mentioned. Many silicates and aluminates, alumina, chromium oxide, ferric and stannic oxides after being strongly heated, barium sulphate, and the haloid silver compounds, belong to this class. Such substances are brought into a soluble form by fusion. This process is carried out by heating the finely powdered substance, along with three or four times its weight of a mixture of equal parts of potassium and sodium carbonates, in a platinum crucible (porcelain, if substances which affect platinum be present), until the mass fuses calmly, dissolving the fused mass in hot water, filtering, acidifying the filtrate with hydrochloric acid, and treating the residue insoluble in water with nitric acid. Any reduced metal present in the residue may be separated, and subsequently examined. In many cases filtration may be dispensed with, and the fused mass at once dissolved in dilute hydrochloric acid. Filtration is indispensable in cases where treatment with hydrochloric acid would produce a substance insoluble in acids—for instance, in the fusion of barium sulphate with sodium carbonate.

All silicates undecomposed by hydrochloric acid may be brought into a fit form for analysis by fusion with a mixture of equal equivalents of Na_2CO_3 and K_2CO_3. If such silicates contain alkalies they should be fused with baryta or lime, or, better, with 3 parts calcium chloride and $\frac{1}{2}$ to 1 part caustic lime.

Silicates containing but small quantities of alkalies must be decomposed by methods which do not necessitate the use of very high temperatures, inasmuch as chlorides of the alkalies are somewhat volatile at high temperatures.

As a rule, only monosilicates are decomposed by hydrochloric acid, *i.e.*, silicates containing one equivalent of silica to one of base. In the zeolites the chemically-contained water appears to play the part of a base; by driving off the water by means of heat the zeolite becomes a bisilicate, and is no longer decomposed by hydrochloric acid. Generally, then, those minerals which are converted by heating into acid silicates are unattacked by acids, while basic silicates which remain basic after heating are more readily decomposed by acids after than before heating. If it be desired, for instance, to determine the amount of alkali in such a substance as *lepidolite*, which is not decomposed by hydrochloric acid, it is only necessary to heat it to redness for some time, in order to obtain it in a state in which hydrochloric acid readily attacks it with solution of the whole of the alkali. The amount of alkali may be determined by this method in many of the granitic minerals, such as *epidote, wernerite, idocrase, granite, tourmaline,* most of the *micas,* &c. This method for determining alkali is applicable to all silicates containing no more silica than corresponds with the formula of a monosilicate.

Bisilicates are very frequently decomposed by sulphuric acid after ignition. The alkali in *kaolin,* for instance, may be determined by heating the finely powdered substance, and treating the mass with sulphuric acid. If this silicate, however, be very strongly ignited, it is scarcely decomposed by sulphuric acid. The first effect of ignition appears to be the conversion of the silica into a less dense form in which it is more readily attacked by acids; but on continued heating the alumina is rendered very compact and dense, and becomes insoluble in acids. This is also the effect of great heat upon chromic and ferric oxides.

The following process serves for the determination of the alkalies in such bi- and tri-silicates as are not entirely decomposed by hydrochloric acid (*felspar, basalt,* &c). The mineral is mixed with hydrofluoric and sulphuric acids in a platinum basin, and the basin is heated in a water-bath until its contents are dry (the operation must, of course, be carried out under a hood with a strong draught). The whole of the silica is thus driven off in the form of silicon fluoride, and the alkalies remain as sulphates. Another method consists in heating the finely powdered substance along with very concentrated sulphuric acid to 200° in a sealed tube. As a part of the alkali of the glass is, however, generally dissolved, this process is not so exact as the other; it may be applied for the estimation of ferrous salts in silicates.

A very good method is to fuse one portion of the mineral with three or four times its weight of sodium carbonate (perfectly free from potash salts), and to estimate potash in the fused mass; to fuse another portion with four times its weight of pure potassium carbonate, prepared from the tartrate, and to estimate soda in the residue. In order to separate small quantities of soda from large quantities of potash the two alkalies are evaporated to dryness with sulphuric acid, the residue is dissolved in a little hot water, and after adding a quantity of calcium acetate, free from soda salts,[1] equal in amount to the weight of mineral used for the analysis, the whole is treated with 3 or 4 volumes of 95 per cent alcohol. The potash is almost entirely precipitated, along with the lime, as sulphate, the whole of the soda, along with a very little potash, remains in solution in the form of acetate.

In order to separate much soda from little potash the alkalies are transformed into chlorides, and the potash is precipitated as tartrate according to § 12.

Bases other than alkalies can be determined in silicates by the methods described; but fusion with carbonates of sodium and potassium is the readiest method for the general analysis of these minerals. In the event of a silicate containing only one alkali, the carbonate of the other may be employed as a flux.

Platinum crucibles are employed for processes of fusion, unless easily reducible metals or other substances which injure platinum are present. In such cases porcelain crucibles, or if these be attacked by the alkaline carbonates, silver crucibles, must be used. If the alkalies only are to be determined, light iron crucibles may be employed. The fused mass must not be treated with acid in such crucibles.

Silicates containing fluorides may be decomposed by the methods detailed. *Fluorspar* must be fused with four times its weight of sodium carbonate, and its own weight of silica, in order to obtain the whole of the fluorine in soluble form. *Cryolite* is decomposed by continued boiling with milk of lime, the whole of the fluorine entering into combination with the calcium, and remaining, after treating the washed precipitate with acetic acid, in the form of calcium fluoride, in which form it may be weighed.

---

[1] These are tested for by heating the salt in an open platinum crucible until all volatile matter is removed, moistening the residue with ammonium carbonate, and gently warming, adding distilled water, and placing the moistened mass on red litmus paper; if no blue colorisation is produced, soda salts are absent.

Spinel, gahnite, corundum, as also strongly heated sesquioxides (Al_2O_3, Fe_2O_3, &c.), are but little acted upon by alkaline carbonates. They may be decomposed by fusion with caustic potash in a silver crucible, a method which is also applicable to the analysis of *titanium dioxide* and *tin ore.* These sesquioxides are, however, most readily brought into a form suitable for analysis by fusion with four times their weight of dehydrated borax, or potassium bisulphate; the former salt is to be preferred.[1]

Those substances, such as sulphur, &c., which are not acted on by acids, but are volatilised on heating, may be brought into a soluble form by fusion, in a porcelain crucible, with 3 parts of potassium nitrate, and 2 parts of dehydrated sodium carbonate. This method is also applicable to the analysis of chrome iron ore (see footnote).

I can recommend the following method for the solution of such metallic sulphides and arsenic compounds as are with difficulty oxidised by acids. 1 part of the mineral is mixed with 4 parts of potassium chlorate, 3 parts of sodium carbonate, and 2 parts of sodium chloride, and the mixture is slowly heated to redness in a porcelain crucible. So soon as the mixture fuses quietly, it is allowed to cool, and the mass is dissolved in hydrochloric acid, or the alkalies are first dissolved out with water. This method possesses the advantage of introducing no salt of the nitrogen acids into the solution; the presence of these acids interferes with the subsequent manipulations, such as passage of sulphuretted hydrogen through the liquid, titration with iodine, &c. Sulphur is also quickly oxidised

---

[1] Fusion with borax is not to be recommended for the analysis of acid silicates: it may be applied to the estimation of ferrous salts in silicates, but the fusion must be carried out in a covered crucible, through the lid of which a tube passes connected with an apparatus evolving carbon dioxide. Borax is an exceedingly good reagent for the decomposition of chrome iron ore. Seven parts of dehydrated borax are employed for each part of the ore; sodium carbonate is slowly added during the fusion, until effervescence no longer occurs, chromium is finally oxidised by means of saltpetre, and the chromate is dissolved out with water.

by this method, which is not the case by the ordinary processes of evaporation with fuming nitric acid or aqua regia. It is well to use double the above quantity of sodium carbonate, or in place of this to employ 6 parts of a mixture of equal equivalents of sodium and potassium carbonates, in the case of minerals rich in arsenic or antimony. Mercuric sulphide, as also arsenic and antimony sulphides, and electronegative metallic sulphides generally, may be very readily analysed by boiling with caustic potash, and leading chlorine into the liquid, or cautiously adding bromine. This method is especially to be recommended in the case of mercuric sulphide. If it be desired to determine only the metal in arsenic or antimony sulphide, the mineral is best fused with 3 parts of sodium carbonate and 3 parts of sulphur flowers, the fused mass is treated with water, which dissolves out all arsenic, antimony, and tin, if present, while other metals which the mineral may have contained remain behind, and may then be oxidised by nitric acid and potassium chlorate, or by fusion with oxidising agents.

§ 56.

Division of the Metals into Groups, and Separation of these from one another.

Before describing the methods for the separation of metals into groups, I will make a few remarks concerning precipitation in general. In precipitation by means of gases, or reagents in solution, it is very necessary to be provided with a means of determining when a sufficient quantity of the reagent has been added. Excess of sulphuretted hydrogen is readily detected by the smell after closing and shaking the vessel in which precipitation is performed. Where this method is inapplicable a few drops of the separated liquid must be removed (filtered, if necessary), tested with a little of the precipitant, and then returned to the main liquid. In some cases precipitates form very slowly. Warming the liquid generally hastens precipitation; the presence of other soluble salts also sometimes aids precipitation. With a small excess of the precipitant precipitation is generally sooner complete than when the exact quantity required for formation of the precipitated salt is added.

The metals are divided into three groups: those not precipitable by sulphuretted hydrogen under any circumstances; those precipitable by the same reagent in alkaline solutions; and those precipitable in acid solutions. The first group is divided into two classes, (1) those metals which are precipitable by ammonium carbonate in boiling solutions, and (2) those which are not thus precipitated. The second group comprises (1) those metals which are precipitated by ammonium sulphide in the form of sulphides, and (2) those which are precipitated by the same reagent as oxides. The metals of the third group are divided into (1) those which are soluble in alkaline sulphides, and (2) those which are not dissolved by these reagents. The following table represents the grouping of the more important metals:—

I. NOT PRECIPITATED BY SULPHURETTED HYDROGEN.		II. PRECIPITATED BY SULPHURETTED HYDROGEN IN ALKALINE SOLUTIONS.		III. PRECIPITATED BY SULPHURETTED HYDROGEN IN ACID SOLUTIONS.			
1. Not precipitated by $(NH_4)_2CO_3$, in presence of NH_4Cl.	2. Precipitated by $(NH_4)_2CO_3$, in presence of NH_4Cl.	3. Precipitated as oxides, soluble in Potash.	4. Precipitated as Sulphides.	5. Precipitated in Acid and Alkaline Liquids.		6. Precipitated in Acid Liquids only.	
Potassium	Barium	Aluminium	Manganese	Cadmium	Insoluble in Alkaline Sulphides.	Mercury[2]	Soluble in Alkaline Sulphides.
Sodium	Strontium	Chromium	Iron	Lead		Tin	
Ammonium	Calcium		Nickel	Copper		Antimony	
Magnesium			Cobalt	Silver		Arsenic	
			Zinc	Bismuth		Gold	
			Uranium[1]			Platinum	

[1] In absence of $(NH_4)_2CO_3$.

[2] Partially precipitated in Alkaline Liquids.

This division of the metals into groups corresponds in certain points with the division into alkalies, alkaline earths, earths, &c. I have placed mercury in sub-group 6, although mercuric sulphide is not soluble in ammonium sulphide, nor indeed in pure sulphides of the alkalies. Mercuric sulphide, however, like the other sulphides of sub-group 6, is dissolved in sulphides of the alkalies in presence of caustic potash; but this sulphide, alone of the metallic sulphides mentioned in sub-group 6, is precipitated from such solution on addition of sal-ammoniac. This fact presents us with a method of separating mercury from the metals both of sub-groups 5 and 6.

The metals mentioned in the foregoing table may be separated into groups, in a solution containing them all, by the following process: Sulphuretted hydrogen is passed into the warm acidified solution, the precipitate is collected on a filter, and digested with potassium sulphide containing a little caustic potash, whereby the members of sub-group 6 are dissolved. The filtrate from the first precipitate is neutralised by means of ammonia, and mixed with ammonium sulphide; the precipitate, containing the members of sub-groups 3 and 4, is digested with gentle heating with caustic potash, whereby the metals of sub-group 3 pass into solution. By boiling the filtrate from group II. with ammonium carbonate, the members of sub-group 2 are precipitated, while those of sub-group 1 remain in solution.

The following precautions must be attended to in carrying out this separation: In acidifying the original solution the addition of a large excess of acid must be avoided.[1] Sulphuretted hydrogen is passed through the cold liquid until the latter smells strongly of the gas; the liquid is then heated almost to boiling, and the passage of the gas is resumed until no further precipitate forms.[2]

If arsenic, gold, or platinum compounds are present, it is advisable to add ammonium sulphide instead of passing

---

[1] Nitric acid should not be employed as the acidifying reagent. —*Tr.*

[2] It is well to allow the liquid and precipitate to remain at rest in a warm place for an hour or so before filtration.—*Tr.*

sulphuretted hydrogen into the liquid. The metals of sub-groups 1, 2, and 6, with the exception of mercury, remain in solution, while the others are precipitated. The precipitate is dissolved in aqua regia (nitric acid, if silver be present), and the sub-groups are separated by the process described. The solution containing sub-groups 1, 2, and 6 is acidified with hydrochloric acid, whereby the members of sub-group 6 are precipitated. Phosphoric acid, if present, must be removed after precipitation of the metals of sub-group 5. In such a case it would be necessary to add the filtrate from the precipitate obtained by acidifying the solution in ammonium sulphide, to the liquid obtained by dissolving the precipitate by ammonium sulphide in aqua regia.

Inasmuch as nickel sulphide is not perfectly soluble in ammonium sulphide, it is advisable to acidify the filtrate from the precipitate of group II. with acetic acid, to collect any precipitate produced, and to add it to the group precipitate.[1] The ammonium sulphide employed must be of a yellow colour, and must also be free from carbonates. During the filtration of the precipitated sub-groups 3 and 4 the funnel should be covered with a glass plate to prevent free access of air. The presence of ammonium chloride aids the precipitation of these metals, and also prevents the simultaneous precipitation of the alkaline earths.

Precipitation of the metals of sub-group 2 by means of ammonium carbonate, should be carried out in boiling

---

[1] If chromium be present, it is better to add an excess of caustic potash to the liquid containing the first four sub-groups, followed by the addition of bromine water, and warming. Chromic salts are thus converted into chromates. When the liquid has become perfectly yellow, nitric acid is added in excess, and the whole is warmed until a clear solution is obtained. Ammonium acetate and lead acetate are then added, the precipitate of lead chromate is removed by filtration, and excess of lead is precipitated in the filtrate by means of sulphuretted hydrogen. The filtrate from this precipitate is treated as has been already directed. Alkalies must be determined in a separate portion of the original solution. Chromic acid is determined in the precipitated lead chromate, after washing with nitric acid and water, according to § 27. I have found the method given above for the oxidation of chromium salts preferable to any other.

solutions in presence of sal-ammoniac. A little ammonia should be added to the ammonium carbonate employed. If much magnesia be present, the precipitate must be dissolved in hydrochloric acid and reprecipitated. If the alkalies are not to be determined, it is advisable to add such an amount of sodium acetate as may serve to convert all ammonium salts (except the carbonate) into acetates. The carbonates of barium, strontium, and calcium, which are somewhat soluble in ammonium chloride, are thus more completely precipitated.

§ 57.

Removal and Estimation of those Substances which interfere with the separation of the Bases.

Before proceeding to a consideration of the special methods for the separation of the members of the various groups, I will describe processes whereby certain substances which prevent the proper carrying out of these methods may be removed. Such substances are removed in part before commencing the individual group-separations, and in part during the processes of separation.

The substances alluded to are these: *Silicic, titanic, phosphoric,* and *oxalic acids, cyanogen compounds* and *non-volatile organic compounds.* Silicic and titanic acids are removed by evaporating the liquid to dryness on a water bath after acidification with hydrochloric acid, again adding hydrochloric acid to the residue, and repeating the evaporation. On now moistening with the same acid and adding water, silicic and titanic oxides do not dissolve. They may be collected and weighed. The titanic oxide may be removed by boiling with concentrated sulphuric acid, and the remaining silica may be again weighed.

Hydrocyanic and oxalic acids must be removed when metals are present which would be precipitated by these substances. Hydrocyanic acid and cyanides are removed by evaporation with concentrated sulphuric acid, or by fusion with potassium bisulphate. Oxalic acid is removed by the same processes or by boiling with chlorine water.

Non-volatile organic compounds are destroyed by fusion with nitre and soda. Phosphoric acid must be removed after the precipitation of those metals which are thrown down by sulphuretted hydrogen in acidified solutions. In presence of sesquioxides (alumina, ferric, and chromic oxides), the removal of this acid presents certain difficulties. These sesquioxides are precipitated by boiling their neutral or nearly neutral solutions with excess of sodium acetate. The precipitate does not contain the proto-salts of the same metals, if these are present, nor any of the other members of the first four sub-groups. Phosphoric acid is, however, precipitated along with the sesquioxides, more especially in presence of ferric oxide. The precipitation is carried out by boiling the neutral and somewhat dilute solution with excess of sodium acetate. The formation of a white precipitate shows that there is not a sufficient quantity of ferric salt present; ferric chloride must be added drop by drop until the colour of the precipitate becomes reddish-brown. If there be a large amount of ferric salts present relatively to the quantity of phosphoric acid, it is advisable to reduce the greater part to ferrous salts by passing sulphuretted hydrogen through the liquid before precipitating with sodium acetate. If the reduction should be carried too far, the addition of a few drops of chlorine water will serve to oxidise a sufficient quantity of the iron.

The solution in which the precipitation by sodium acetate is carried out is best rendered neutral by adding ammonia until a slight precipitate forms, and then adding a couple of drops of dilute hydrochloric acid. If alkalies are to be estimated, ammonium acetate is used as precipitant in place of sodium acetate. The precipitate is filtered hot, and washed with hot water containing a few drops of ammonium acetate until a small portion of the washings ceases to leave a residue when evaporated on platinum foil.

Aluminium and phosphoric acid may be determined in the precipitate by sodium acetate by means of the following process.

The addition of ferric chloride during the precipitation has of course rendered an estimation of iron in this precipitate useless. Iron may, however, be readily determined in presence of phosphoric acid by § 19.

The precipitate is dissolved in hydrochloric acid, ferric salts are reduced by addition of potassium sulphide or sodium sulphite, and considerable excess of caustic potash is added. The whole of the iron is thus precipitated, while phosphoric acid and alumina remain in solution. If it be not desired to estimate phosphoric acid, but only to remove it, this may be effected by adding baryta water and filtering. The precipitate is washed with hot water containing caustic potash, and alumina is determined in the filtrate according to § 51. If it be desired to estimate the phosphoric acid, the iron must be filtered off after precipitation, the phosphoric acid thrown down in the filtrate by means of baryta water, and the barium phosphate determined by § 50.

In the event of chromic oxide being present, the precipitate by sodium acetate is treated as described, only in place of adding baryta water, the alkaline filtrate is boiled along with sodium hypochlorite or bromine, until the chromic salt is converted into chromic acid. Barium chloride is then added, and the precipitated barium chromate (containing phosphate) is determined according to §§ 26 and 27. If phosphoric acid is to be determined in presence of chromium and aluminium, sodium silicate solution is added after conversion of the chromic salt into chromic acid, whereby aluminium silicate is thrown down free from phosphoric acid. This precipitate is dissolved in hydrochloric acid, the solution is evaporated to dryness to render silica insoluble, and after taking up with hydrochloric acid the alumina is determined by § 50. The alkaline filtrate from the precipitate of aluminium silicate is neutralised with hydrochloric acid, magnesia mixture (magnesium chloride with sal-ammoniac and ammonia) is added, followed by addition of ammonia; the liquid is heated to boiling, the double phosphate of magnesium and ammonium which precipitates is filtered off, washed with ammonia water, and phosphoric acid is determined therein according to § 50.

The chromic acid in the filtrate may be determined at once by § 26, but it is better to precipitate by means of barium chloride, and determine by § 27.

Uranic salts, if present, are reduced by means of copper turnings. The solution is poured off along with any small quantity of uranic phosphate which may have precipitated, saturated with caustic potash, whereby uranous oxide is thrown down, filtered, and phosphoric acid is determined in the filtrate.

If those metals which are precipitated by ammonium sulphide (sub-groups 4 and 5) are alone present along with phosphoric acid, a separation of the acid may be effected by means of ammonium sulphide; after filtration, phosphoric acid is determined by means of magnesia mixture. This method of separation is available also in presence of alkalies—not in presence of magnesia—or of the metals of sub-groups 2 and 3.

It is necessary that chromium should be converted into chromate and entirely removed before the members of sub-group 1 can be estimated. This may be done by the method described, or by gently warming the liquid with strong nitric acid in a porcelain crucible, and adding successive very small quantities of potassium chlorate (the crucible may be covered with a funnel); when the oxidation is complete, potash is added in excess, the liquid is filtered, any dissolved alumina precipitated by addition of sal-ammoniac, and chromium precipitated in the filtrate. Lead, if present, may be also precipitated as chromate by acidifying with nitric acid and adding excess of sodium acetate; the whole of the chromic acid may be thus eventually thrown down in the form of lead chromate.

§ 58.

Separation and Estimation of Bases of the First Group (Potassium, Sodium, Ammonium, Magnesium).

These four metals, if present together in solution, may be determined by the following process: A tolerably concentrated solution of caustic baryta[1] is added in excess, and the liquid is boiled for some time. Ammonia is thus driven off, and may be determined by § 11. Magnesia is precipitated; after washing and dissolving in sulphuric acid, it may be determined by § 52.

The filtrate from precipitated magnesia is boiled, and excess of baryta is precipitated by means of sulphuric acid. The filtrate is evaporated, after addition of a little pure sulphuric acid, in a weighed platinum dish, the dry residue is heated to incipient redness for some time (a piece of ammonium carbonate being held in the crucible), and the whole is weighed. The sulphates of potassium and sodium are then dissolved in water, and the amount of sulphuric acid is determined in these salts by titration with barium chloride solution, according to § 53.

By deducting the weight of sulphuric acid (SO_3) from the total weight of the two sulphates, the weight of potash and soda (K_2O and Na_2O) is obtained.

94·2 parts K_2O require 80 parts SO_3 to form K_2SO_4;

Old notation,

47·1 require 40 to form $KOSO_3$.

62 parts Na_2O require 80 parts SO_3 to form Na_2SO_4;

Old notation,

31 require 40 to form $NaOSO_3$.

The unknown amount of potash (x) and the unknown amount of soda (y) must be united with $\frac{80}{94 \cdot 2} . x$ and $\frac{80}{62} . y$ parts sulphuric acid (SO_3).

If G = total weight of sulphates, then

$$G = x + y + \frac{80}{94 \cdot 2} . x + \frac{80}{62} . y.$$

Or if the constant factors be reduced to decimal fractions, then

$$G = x + y + 0 \cdot 85\, x + 1 \cdot 29\, y \ldots\ldots\ldots (1)$$

---

[1] This must be free from alkalies. After precipitation with pure sulphuric acid, the filtrate must leave no appreciable residue when evaporated on platinum.

As the total weight of potash and soda is

$$x+y=G-SO_3,\ldots\ldots\ldots\ldots(2)$$

the values of x and y may be calculated from equations (1) and (2) thus—

$$\text{For soda,}\quad y=\frac{1{\cdot}85.\,SO_3-0{\cdot}85\,G}{0{\cdot}4387},\quad\text{and}$$

$$\text{For potash,}\ x=\ G-(SO_3+y).$$

An example will make the process of calculation more apparent:—

Let the total weight of potassium and sodium sulphates be 1·581 grams = G; let the amount of sulphuric acid (SO_3) found by titration be 0·80 gram, then the amount of soda (Na_2O) is $y=\frac{1{\cdot}85\,.\,0{\cdot}80-0{\cdot}85\,.\,1{\cdot}581}{0{\cdot}4387}=0{\cdot}310$ grams, and the amount of potash (K_2O) is $x=1{\cdot}581-(0{\cdot}80+0{\cdot}310)$ $=0{\cdot}471$ grams.

Adding these quantities to the number expressing the amount of SO_3, we get 1·581, which corresponds with the total amount of sulphates originally found. (If old notation be employed, the same factors hold good for the calculations.)

The following process serves for the determination of potash, soda, and magnesia, if it be desired to determine these only: The solution containing these three substances along with ammonia is evaporated to dryness with sulphuric acid; the residue is gently ignited and weighed ($K_2SO_4Na_2SO_4MgSO_4$). It is then dissolved in water, and the whole of the sulphuric acid and magnesia are precipitated by means of clear baryta water, in the boiling liquid. The precipitate is washed with boiling water, dissolved in a measured volume of hydrochloric acid, and the magnesia titrated by means of ammonia.

A little sulphuric acid is added in order to precipitate any baryta which may be present. If a considerable precipitate be obtained, it is collected and weighed; the amount of baryta is to be calculated to magnesia, which is then to be deducted from the magnesia found. Baryta is removed from the filtrate by means of carbonic acid, and, after filtration, potash and soda are determined by titration with hydrochloric acid. From the amount of hydrochloric acid used, the amount of SO_3 formerly combined with K_2O and Na_2O may be determined.

The following data have now been determined:—

(1.) Weight of sulphates of potassium, sodium, and magnesium (by direct weighings).
(2.) Weight of magnesia (calculated).
(3.) Weight of potassium sulphate and sodium sulphate (calculated).
(4.) Weight of potash and soda—K_2O and Na_2O—combined with sulphuric acid—SO_3—(calculated).

The amounts of potash and soda respectively present in the original substance may be calculated from (3) and (4) by the method already explained.

In the foregoing processes magnesia has been precipitated as hydrate; this precipitate is not easy to filter and wash on account of its being gelatinous. If the amount of magnesia exceed 0·25 gram, I am in the habit of precipitating by means of ammonium phosphate from the solution containing ammonium chloride and ammonia, and determining according to § 52. If it be desired to estimate potash and soda in the filtrate after precipitating magnesia in this form, phosphoric acid must be first of all removed by acidifying with acetic acid and boiling with a little ferric chloride. The filtrate may then be evaporated to dryness with sulphuric or hydrochloric acid. A mixture of potassium and sodium chlorides may be analysed by the indirect method, after ignition to remove all volatile substances, by determining the total weight, and then titrating with silver according to § 47.

This method of determination possesses many advantages over the determination as sulphates. It is not at all easy to obtain neutral sulphates by evaporation with sulphuric acid; there is less danger from spirting in evaporating with hydrochloric than with sulphuric acid, and the estimation of chlorine by means of silver is a most accurate process, and necessitates no filtration after the mixed chlorides have been once obtained. Sulphuric and phosphoric acids may also be readily removed by precipitation with barium chloride and removal of excess of barium by means of ammonium carbonate. The method dependent upon the transformation of the salts into sulphates is to be recommended only when a solid substance containing potash, soda, and magnesia has to be examined, inasmuch as magnesium chloride cannot be obtained perfectly dry without loss of chlorine. If magnesia be absent, or can be readily removed by means of sodium phosphate, then the other method, in which the potash and soda are converted into chlorides (after removal of phosphoric and sulphuric acids), is preferable.

Indirect methods of analysis can only be applied to the examination of pure substances, and in cases where the substances to be estimated are present in something like equal quantities. In the case of potash and soda the amount of one of these bases must not, at the utmost, exceed that of the other by one-fifth part.

It is often necessary to separate potash from soda: this may be best done by precipitating the former in the form of tartrate. (See § 12.) The soda may be precipitated in the filtrate by addition of hydrofluosilicic acid, or it may be converted into chloride by evaporation with hydrochloric acid. Magnesia must have been previously removed by means of caustic baryta or ammonium phosphate. Acids other than hydrochloric, nitric, and acetic must be absent. Ammonia, if present, must always be determined in a separate portion of the liquid, either by boiling with caustic baryta and estimating the ammonia evolved, or by boiling off ammonia and applying the process described in the last part of § 11.

§ 59.

Separation and Estimation of Bases of the Second Group (Barium, Strontium, and Calcium).

The separation of barium from strontium and calcium is a matter of no great difficulty.

The solution containing the three bases may be boiled with a mixture of 1 part sulphate and 2 parts carbonate of potassium, whereby barium is entirely precipitated as sulphate, which is insoluble in hydrochloric acid, while strontium and calcium are precipitated as carbonates which are soluble in the same acid. The barium sulphate may be collected and weighed. The bases may be determined by a purely volumetric method by precipitating all three as carbonates by means of ammonium carbonate and ammonia, in presence of much ammonium chloride, and addition of sodium acetate to a hot solution, dissolving the precipitate, after washing, in a measured quantity of normal hydrochloric acid, boiling off carbon dioxide, dividing the solution into two equal parts, titrating one part with half-normal ammonia until neutral, precipitating the other half with a mixture of 1 part sulphate and 2 parts carbonate of potassium, dissolving the precipitated strontium and calcium carbonates in a measured quantity of normal hydrochloric acid, and determining excess of acid by means of half-normal ammonia. The difference between total acid required to convert the three carbonates into chlorides, and that required to convert the strontium and calcium carbonates only into chlorides, gives the amount of acid corresponding with the quantity of barium carbonate in the first precipitate. From this the amount of barium is readily calculated.

$$BaCO_3 + 2HCl = BaCl_2 + H_2O + CO_2.$$
$$(BaOCO_2 + HCl = BaCl + HO + CO_2.)$$

If barium and strontium, or barium and calcium, only are present, they may both be determined by the preceding method.

Barium may be easily separated from calcium and strontium, and also determined, by precipitation as chromate in a solution containing ammonia and sal-ammoniac. (See § 27 or 54.)

Hydrofluosilicic acid is also applicable for the separation of barium, but the metal cannot be thus determined volumetrically.

The separation of strontium from calcium is a matter of very considerable difficulty.

Stromeyer's method consists in evaporating both substances to dryness, with addition of nitric acid. This process must be repeated until all chlorine, if any were originally present, is removed. The residue is treated with absolute alcohol containing a little ether; calcium nitrate alone goes into solution. This method does not yield altogether accurate results.

The method of H. Rose is preferable, but more tedious. It is based on the fact that strontium sulphate is insoluble in a concentrated solution of ammonium sulphate, while calcium sulphate is slightly soluble in this liquid. The method necessitates the use of very large quantities of liquid, and the presence of so much ammonium sulphate interferes with the subsequent precipitation of calcium. The method is scarcely applicable for the separation of much calcium from a small quantity of strontium; its results are most reliable when it is desired to separate a small quantity of calcium salt from a considerable quantity of strontium salt, but not to determine the former. A concentrated solution of the two salts is poured into a liquid prepared by dissolving 1 part of ammonium sulphate in 4 parts of water: this liquid must contain at least fifty times as much ammonium sulphate as there is calcium, calculated as sulphate, in the original solution. The precipitate is collected, washed with a concentrated solution of ammonium sulphate, and either ignited and weighed, or decomposed by boiling with potassium carbonate, and the amount of strontium carbonate so produced determined by alkalimetric methods.

The following process is based upon my own experiments: The two bases are precipitated in ammoniacal solution by means of an excess of ammonium oxalate; the precipitation is carried out either in hot or cold solutions, preferably in the latter if magnesium salts are present. Barium, if present, is removed, in the form of chromate, previous to addition of ammonium oxalate. Strontium oxalate is easily and completely decomposed by potassium carbonate, even in presence of potassium oxalate; this is not the case with calcium oxalate.

A mixture of 4 equivalents of potassium oxalate with 5 equivalents of potassium carbonate is without action upon calcium oxalate, but brings about the complete conversion of strontium oxalate into carbonate. A solution containing such a mixture is prepared by dissolving equal parts of crystallised oxalic acid and potassium carbonate in a little hot water, boiling off all carbon dioxide, adding $1\frac{1}{2}$ times the original quantity of potassium carbonate, and diluting.

The direct addition of the full quantity of potassium carbonate to the oxalic acid is liable to lead to the formation of bicarbonate, and should not therefore be practised. A little more than $2\frac{1}{2}$ parts of potassium carbonate to 1 part of oxalic acid may be employed, but the proportion should not exceed 3 to 1. The addition of a small quantity of ammonia is to be recommended. A quantity of this solution, containing at least 5 times as much oxalic acid as the sum of the calcium and strontium present, must be employed. The precipitated oxalates are boiled with this liquid for five minutes, the solution is filtered off, and the precipitate is washed until the filtrate ceases to render turbid a solution of calcium acetate. The precipitate is now transferred to a beaker, strontium carbonate is dissolved by means of dilute acetic acid, and determined in the solution by § 8. Calcium is determined in the residue as oxalate according to § 21. (Barium and lead oxalates behave towards potassium carbonate in the same manner as strontium oxalate.)

I have lately modified this process by boiling the precipitated and washed oxalates of strontium and calcium with a concentrated solution of potassium sulphate for five minutes, filtering, washing with hot water, and determining oxalic acid in the filtrate, after acidification with sulphuric acid, according to § 20. The amount of oxalic acid found is proportionate to the amount of strontium present. The calcium oxalate in the residue is now dissolved by gentle warming with dilute hydrochloric acid, and the amount of oxalic acid is again determined after filtering from undissolved strontium sulphate. From the second quantity of oxalic acid found the amount of calcium is calculated.[1]

---

[1] The fact that strontium sulphate is insoluble in potassium sulphate solution, while calcium sulphate is slightly dissolved by this

If it be desired to estimate calcium only in presence of strontium, the solution may be boiled for a few minutes after addition of a considerable quantity of solid potassium sulphate, along with a little ammonium oxalate, and ammonia sufficient to bring about an alkaline reaction; the precipitate, after filtration, may be heated with hydrochloric acid, and the calcium oxalate which is thereby dissolved may be determined without filtration by titration with permanganate (§ 21).

Barium, strontium, and calcium may be determined by an indirect method. They are precipitated as carbonates, the barium is determined, and simultaneously separated as sulphate, by means of two titrations as explained in the first part of the present paragraph. Strontium and calcium are again precipitated as carbonates in the liquid freed from barium, and weighed. From this weight, and from the quantity of acid required for their saturation, the amount of each may be calculated by the help of the table in the appendix. This method is only applicable when the carbonates of strontium and calcium are obtainable in a perfectly pure state, and when the amount of either does not exceed that of the other by more than one-fifth part.

§ 60.

Separation and Estimation of Bases of the Third Group (Aluminium and Chromium).

To the solution caustic potash is added, in quantity sufficient to redissolve the precipitate which forms, bromine water is added, and the liquid is boiled. Chromic oxide is thus converted into chromic acid, which is precipitated from the alkaline liquid by addition of barium chloride, and determined by § 26. (Any phosphoric acid

liquid, may be applied to the qualitative separation of the two metals. It is only necessary to boil the solution containing calcium and strontium salts after addition of a considerable quantity of solid potassium sulphate, and to test the filtrate for calcium by addition of ammonia and ammonium oxalate. The whole of the strontium remains in the precipitate.

present is precipitated along with the barium chromate.) Aluminium is determined in the filtrate by § 51 without previous removal of barium.

Chromic acid may be determined in presence of chromic oxide by precipitating the former in a cold solution containing acetic acid by means of a lead salt. Chromic oxide is determined in the filtrate by the foregoing method.

Chromic acid is separated from acids which exert an oxidising action upon ferrous salts by precipitation as lead chromate in solutions containing acetic acid, or as barium chromate in alkaline solutions.

Minerals containing chromium are best decomposed by fusion with borax, with successive additions of soda and nitre. Any alumina is removed from the aqueous solution by addition of ammonium chloride, and chromic acid is precipitated and determined as barium chromate in the filtrate.

§ 61.

Separation and Estimation of Bases of the Fourth Group (Uranium, Iron, Zinc, Manganese, Nickel, and Cobalt).

The members of the third group are precipitated along with those of this group, but the former go into solution on treating the precipitate with concentrated caustic potash.

Uranium may be separated from the metals of the second, third, and fourth groups, and determined, by precipitating with a mixture of ammonium sulphide and carbonate, filtering, strongly acidifying the filtrate with nitric acid, boiling for some time, and after filtering from evaporated sulphur, applying the process given in § 50. The precipitation by means of ammonium carbonate and sulphide must be carried out in cold solutions; the precipitate should be allowed to settle before filtration, and should be washed several times with the reagents used for precipitation. If it be desired to precipitate uranium as sulphide along with the other metals of the fourth group, colourless ammonium sulphide, free from carbonate, must be employed as precipitant; the addition of sal-ammoniac is also to be recommended.

If the metals of the group now under consideration have been precipitated as sulphides (the metals of the third group, as also uranium, are supposed absent), they may be separated by dissolving the precipitate in aqua regia, or in hydrochloric acid if nickel and cobalt are absent, measuring the volume of liquid, determining iron in an aliquot portion after reduction of ferric to ferrous salts by means of pure zinc (§ 19), and treating the remainder of the liquid as follows: The iron salts are completely oxidised by boiling with nitric acid, the solution is boiled with addition of ammonia and ammonium acetate until the precipitate settles readily; after filtration, washing of the precipitate with hot water, and addition of a few drops of acetic acid, zinc is precipitated by means of sulphuretted hydrogen gas. (If the precipitated zinc sulphide is gray-coloured—from presence of nickel sulphide—it must be dissolved in hydrochloric acid, and re-precipitated as sulphide after addition of sodium acetate, the filtrate being added to that formerly obtained.[1]) The precipitated zinc sulphide is determined according to § 30. The filtrate from the precipitate of zinc sulphide is saturated with ammonia—if any precipitate form, it is to be dissolved by addition of ammonium chloride, —gently warmed, and manganese precipitated therein as manganese-ammonium phosphate, by addition of microcosmic salt. If much cobalt be present it is necessary to dissolve this precipitate in hydrochloric acid, and reprecipitate by means of ammonia along with phosphoric acid. (Henry.) Manganese is determined in this precipitate by the method described in § 52; or manganese, cobalt, and nickel may be precipitated together as sulphides by the addition of ammonia and ammonium sulphide to the filtrate from the zinc sulphide; the precipitate may be digested with acetic acid, whereby manganese only goes into solution. From this solution manganese may be thrown down

---

[1] If formic acid be employed in place of acetic, the precipitated zinc sulphide is quite free from nickel sulphide.—*Delffs.*

as peroxide by addition of sodium hypochlorite, and determined according to § 23. The sulphides of nickel and cobalt are dissolved in aqua regia, and determined according to § 24.

A convenient method consists in adding excess of ammonium carbonate to the solution containing the three metals, precipitating cobalt and nickel by sulphuretted hydrogen gas, filtering, acidifying with hydrochloric or acetic acid, and precipitating the manganese as phosphate or peroxide. Manganese may also be separated from nickel—but not from cobalt—by boiling the solution of the three metals, containing acetic acid, after addition of bromine.

The method described in § 24 for the separation of cobalt and nickel is the most to be recommended for the purposes of volumetric estimations.

Stromeyer and Fischer's method is also applicable. In this method the cobalt is precipitated in the form of potassium-cobalt nitrite by the addition of potassium nitrite to the solution containing acetic acid; after standing twenty-four hours the precipitate is collected, washed with potassium acetate solution, and boiled with caustic soda or baryta (not with potash), whereby the whole of the cobalt is precipitated as Co_2O_3, in which form it may be determined by oxydimetric methods. Nickel may be precipitated and determined in the filtrate by means of bromine and potash.

This method of separation has been shown by Gauhe to be very accurate; it may also be employed for the separation of cobalt from manganese and zinc.

The separation of the members of the present group becomes less complicated when cobalt and nickel are absent. Iron is determined in a portion of the solution; the remainder is boiled with sodium acetate, the precipitated ferric oxide is filtered off, and the filtrate is mixed with a large excess of ammonia and microcosmic salt, whereby the manganese is completely precipitated, while the zinc remains in solution. The precipitate is washed with ammonia, and the manganese determined by the method already described. Zinc is determined in the filtrate as sulphide; or manganese may be precipitated as peroxide in the solution after throwing down ferric oxide, by addition of bromine, care being taken that acetic acid is present in excess.

Ferrous and ferric salts, if existing together in a solution, may be determined by titrating a portion of the liquid with permanganate, reducing ferric to ferrous salts, determining the total iron in another portion, deducting the iron existing as ferrous salt, and calculating the remainder to ferric.

If it be desired to determine ferrous and ferric oxides in a silicate, the mineral is preferably decomposed by the method of A. Mitscherlich, which consists in heating the finely-powdered substance along with three times its weight of concentrated sulphuric acid, diluted with 1 part by weight of water, in a sealed tube of hard glass to a temperature of 200° for a couple of hours; or the mineral may be fused with borax in a platinum crucible, into which a stream of carbon dioxide is passed, and the fused mass dissolved in sulphuric acid.

It is often necessary to determine the amount of manganous and higher oxides in manganese ores; this is best effected by estimating the quantity of disposable oxygen, which may be done by warming the finely-powdered substance with a measured volume of standarised ferrous sulphate solution, with addition of sulphuric acid, and determining the quantity of ferric salt produced.

The quantity of oxygen evolved on heating manganese ores to redness is somewhat less than that which reacts upon ferrous salt in the foregoing process, inasmuch as manganese oxides are all converted into Mn_3O_4 by heat, while they are reduced to MnO by the action of ferrous salts.

§ 62.

Separation and Estimation of Bases of the Fifth Group (Cadmium, Lead, Copper, Silver, and Bismuth).

The precipitated sulphides are warmed with nitric acid (free from hydrochloric) of not higher sp. gravity than

1·20,[1] the liquid is filtered off, the precipitate washed by decantation, and digested with ammonium acetate in order to dissolve any lead sulphate which may have been produced. The liquid is mixed with sulphuric acid, the precipitated lead sulphate is collected, washed with dilute sulphuric acid, and the lead determined as follows: The precipitate is boiled with potassium carbonate, whereby the lead is converted into carbonate, the residue is washed, dissolved in a measured volume of normal hydrochloric acid, decomposed by sodium sulphate, and determined according to § 8; or the quantity of sulphuric acid in the precipitated lead sulphate is determined by boiling the precipitate (after washing with alcohol) with normal potassium carbonate solution, filtering, and determining sulphuric acid in the filtrate according to §§ 8 and 53.

$$Pb = 2·588 \times SO_3.$$

From the solution containing no lead, silver is precipitated as chloride by addition of hydrochloric acid. The precipitate is dissolved in ammonia, the silver is thrown down as sulphide by adding sulphuretted hydrogen, dissolved in nitric acid (free from hydrochloric), and determined according to § 47; or the silver may be determined in an aliquot part of the solution filtered from the lead precipitate by the process described at the close of § 47. If bismuth salts are present in large quantity, they must be removed by partially neutralising with potash, and adding a large volume of water.

The solution containing bismuth, cadmium, and copper, is mixed with ammonia in excess, whereby the whole of the bismuth is precipitated. In the event of copper being present in quantity, the bismuthous hydrate is dissolved in nitric acid and reprecipitated by ammonia. The bismuthous hydrate is dissolved in nitric acid, and bismuth is determined according to § 27.

Copper and cadmium are precipitated as sulphides, by passing sulphuretted hydrogen through the liquid, after removing the greater part of the free acid by evaporation,

---

[1] A stronger acid would convert the greater part of the lead sulphide into insoluble sulphate.

or after addition of sodium acetate. The precipitated sulphides are boiled with dilute sulphuric acid (1 part concentrated acid to 5 parts water by volume), or with dilute hydrochloric acid (1 part strong acid to 4 parts water), whereby the whole of the cadmium is dissolved. The filtrate is partially neutralised with ammonia, sodium acetate is added, and the cadmium is precipitated as sulphide, and determined according to § 30.

The copper sulphide is dissolved in nitric acid, and the copper is determined by one of the methods described in §§ 22 and 37 (most quickly by precipitation as cuprous oxide or iodide).

Copper may be readily separated from cadmium by precipitation in the form of sulphocyanide. For this purpose the ammoniacal solution is acidified by means of hydrochloric acid, sodium sulphite or sulphurous acid is added, and the copper is precipitated by adding potassium sulphocyanide; the precipitate is then treated according to § 22. Sulphurous acid is removed from the filtrate by addition of chlorine water or sodium hypochlorite, sodium acetate is added, free chlorine is removed by means of ammonia or sal-ammoniac, and cadmium is precipitated by sulphuretted hydrogen.

I can recommend the following method of separation when bismuth is absent: The precipitated sulphides of copper, silver, lead, and cadmium are boiled with pure dilute hydrochloric acid (1 volume strong acid to 3 to 4 volumes water); the lead and cadmium are converted into chlorides, while the copper and silver sulphides are unchanged. The amount of acid employed must not be less than 100 times the quantity of lead sulphide present, otherwise a portion of the lead will probably remain undissolved. The residue is washed with hot water containing hydrochloric acid until the washings are no longer rendered turbid by addition of potassium chromate. Lead is precipitated as chromate (§ 27) in the filtrate after partial neutralisation with ammonia and addition of sodium acetate, chromic acid is removed from the filtrate by addition of barium chloride and ammonia, and cadmium is precipitated as sulphide and determined according to

§ 30. The sulphides of silver and copper are dissolved in pure nitric acid, the silver is thrown down as chloride by addition of hydrochloric acid; this precipitate, as also the liquid containing copper, is treated as already described.

This process is not trustworthy if bismuth be present, inasmuch as bismuth sulphide is partially but not altogether soluble in hydrochloric acid of the strength named above; stronger acid acts upon copper sulphide without effecting a total solution of the bismuth. This method is to be preferred to that first described when much lead is present, because the lead sulphate formed during oxidation of the sulphides by means of nitric acid may then amount to a considerable quantity.

§ 63.

Separation and Estimation of Bases of the Sixth Group (Mercury, Tin, Arsenic, Antimony, Platinum, and Gold).

Before describing the methods for separating these metals, I will make a few remarks concerning the separation of the members of this group from the foregoing groups.

If arsenic oxide (As_2O_5), gold, or platinum be present, it is advisable not to precipitate with sulphuretted hydrogen in acid solutions, but rather to render the liquid nearly neutral by addition of ammonia, to add a mixture of ammonium carbonate and yellow ammonium sulphide, to warm, and filter. The precipitate is then washed with water containing the precipitants, and dissolved in nitric acid.[1]

The filtrate, containing only the metals of the first and sixth groups, with the exception of mercury (and perhaps uranium), is acidified with hydrochloric acid, and the precipitated sulphides of the sixth group are collected, washed with water, dried at 100°, and heated in a weighed bulb tube through which a stream of chlorine is passed; the tin, antimony, and arsenic are converted

---

[1] If mercury were present it would remain with the metals of the fifth group, but would not be soluble in nitric acid.

into chlorides, which are volatilised and absorbed in a mixture of tartaric and hydrochloric acids contained in a three-bulbed U tube. The gold and platinum sulphides are reduced to the state of metals; the increase in the weight of the bulb tube therefore represents the weight of these two metals. The platinum may be determined by dissolving the mixed metals in aqua regia, boiling down, precipitating with potassium chloride and alcohol, and weighing the potassium-platinic chloride produced. The gold may be precipitated in the metallic form by boiling the filtrate from the platinum precipitate with oxalic acid.

If gold and platinum are accompanied by tin only, the sulphides may be dissolved in aqua regia, the gold and platinum precipitated from this liquid by means of copper foil, and removed as far as possible from the copper, which is then dissolved in nitric acid, leaving any small quantities of the noble metals which may have adhered thereto undissolved; the gold and platinum are finally dissolved in aqua regia, separated, and determined by the gravimetric method already described. The liquid decanted from the precipitated gold and platinum contains the tin. The noble metals may be separated from the members of the fifth group by this process.

In the absence of gold and platinum, tin antimony arsenic and mercury may be separated and estimated by the following process:—

Tin and mercury must be present as stannic and mercuric salts respectively, inasmuch as stannous and mercurous sulphides are not soluble in potassium sulphide. Stannous are converted into stannic salts by addition of nitric acid, mercurous into mercuric salts by adding sodium hypochlorite or chlorine water.

The greater part of the free chlorine is removed from the liquid by boiling, or by addition of ammonia, the acid being also for the most part removed, and sulphuretted hydrogen is passed through the hot liquid until this smells strongly of the gas. The liquid should be maintained at about 70° during the passage of sulphuretted hydrogen, in order to insure the complete precipitation of arsenic which may be present as arsenic oxide (As_2O_5); the addition of a few grains of sodium sulphite hastens the precipitation in such a case. The precipitated sulphides of the metals of the fifth and sixth group are collected on a filter, washed, and warmed for a few minutes with a little potassium sulphide (or liver of sulphur) solution, along with a considerable quantity of caustic potash. The metals of the sixth group are thus completely dissolved. After filtration, and washing with hot potash solution containing potassium sulphide, the filtrate is heated to boiling with addition of a considerable quantity of ammonium chloride. Mercury is thus completely precipitated as sulphide; the precipitate may be dried and weighed, or dissolved in hydrochloric acid and potassium chlorate, and the mercury determined according to § 40. The filtrate from the precipitated mercuric sulphide is slightly acidified with hydrochloric acid, whereby tin, arsenic, and antimony are thrown down as sulphides; tin and antimony are removed by treating the precipitate with hydrochloric acid diluted with three vols. of water. Arsenic is determined in the residue by dissolving it in cold ammonium carbonate, precipitating the sulphur by addition of silver nitrate, removing excess of silver (without filtration) by addition of hydrochloric acid, filtering and applying the iodometric process of § 36. Or, arsenic may be removed from the precipitated sulphides of tin, antimony, and arsenic by solution in ammonium sesquicarbonate, and the residue may be dissolved in hydrochloric acid. This solution, after removal of sulphuretted hydrogen by boiling, may be divided into two portions, in one of which tin, and in the other antimony, may be determined.

Tin may be determined by precipitating with granulated zinc, decanting and washing, dissolving the zinc with adhering tin in hydrochloric acid in a flask furnished with a cork carrying a tube drawn to a point. When gas (SbH_3, and H) has ceased to be evolved even on warming, the liquid is decanted from any precipitated antimony (which is washed with water), mixed with Rochelle salts, saturated with sodium bicarbonate, and the tin is estimated with iodine solution according to § 36; or the stannous may be converted into stannic chloride by addition of ferric chloride, the amount of ferrous chloride simultaneously produced being determined by means of permanganate. If this method be adopted, it is not necessary to decant the liquid containing tin from the small quantity of precipitated antimony.

The remaining half of the liquid containing tin and antimony is mixed with Rochelle salts, saturated with sodium bicarbonate, and the amount of antimony is determined by iodine solution according to § 35.

This process for the estimation of antimony and tin is based on the fact that hydrochloric acid converts stannic sulphide into stannic chloride, which is without action upon free iodine; while antimonious sulphide is converted into antimonious chloride ($SbCl_3$), which reacts upon free iodine. It is therefore essential that the tin be present only in the form of stannic salt before passing sulphuretted hydrogen through the original liquid. The solubility of arsenious sulphide in ammonium carbonate may be taken advantage of for the separation of arsenic from other metals; the arsenic is obtained in the form of an arsenious salt, in which form it may readily be determined.

Arsenious and arsenic acids, if combined with alkalies, may be determined, when present together, by § 36.

If alkaline earths are present, the substance is dissolved in nitric acid, sodium acetate is added, and arsenic acid is titrated with uranium solution in a manner similar to that described for phosphoric acid in § 50.

In presence of other metals the arsenic salt is dissolved in nitric acid, the solution is neutralised with ammonia, and ammonium sulphide is added in excess. The whole of the arsenic is precipitated by addition of hydrochloric acid (the arsenic oxide is precipitated in the form of As_2S_5, the arsenious in the form of As_2S_3); the precipitate is dissolved in ammonium sesquicarbonate; sulphur is removed from the liquid by addition of silver nitrate; the liquid is divided into two parts—in one arsenious oxide is determined according to § 36; the other is reduced with sulphur dioxide, and treated as described in § 36.

A solution of ammonium sesquicarbonate, for use in the separation of arsenic, may be readily obtained by dissolving commercial ammonium carbonate in 10 parts of warm water at 50° to 60°.

SECTION II.

ESTIMATION OF THE BASES WITHOUT SEPARATION OF GROUPS OR OF INDIVIDUAL METALS.

IN the introduction to Section I. of the present part I have briefly indicated the possibility of determining the various bases by volumetric processes without previous separation of groups or of individual metals.

The fact that such a scheme of analysis is possible, at once shows the pre-eminent advantage possessed by volumetric over gravimetric methods. Nevertheless, chemists have busied themselves but little with attempts to systematise the volumetric methods, but have for the most part been content to possess a knowledge of special processes for the estimation of the individual metals and acids. Some chemists have brought forward methods in which the substances to be volumetrically determined are only obtained in a proper state after long and tedious processes of gravimetric separation. We may agree with Fresenius, when he says, that in such cases it is frequently easier to weigh the substances than to dissolve them and to titrate the solutions. Many appear to hold that analytical chemistry is but a compilation of receipts for the examination of various compounds, and of commercial products. For my part, I look on volumetric analysis as a branch of chemical science, not as an art of prescription; and I shall endeavour to describe methods which are of general application, and not such as are only applicable in one or two instances. I trust that other workers will enter this field: there is much and valuable fruit to b gathered.

It will be well that we should clearly understand th general principles which are to guide us in framin methods of estimation which may be of wide applicability.

In the ordinary processes of analysis the metals ar separated into groups, each of which is again subdivide into its constituent members. Gravimetric processe necessitate the conversion of each substance which is t be determined into the form of a chemical compound o definite and known composition; volumetric processes d not require this. The volumetric processes described i the preceding section have been based upon group-separations: these we must now for the most part renounce We must endeavour to separate each base from a solutio of all the bases; we must generally revert to the origina solution, which we must divide into as many portions a there are separate bases, or groups of bases, to be determined.

The process of analysis is thus much shortened, no only by the omission of group-separations, but also b the fact that but one, or two filtrations at the most, ar necessary; in many instances no filtrations are required The precipitates do not require the same long-continue washing which consumes so much time in the ordinar processes. Two circumstances more especially recommend the methods under consideration. Every estimatio is readily controlled by repeating the process on th original liquid; the analyses of technical products i which one or more, but not all of the constituents, is t be determined, becomes a matter of ease, and can b carried out much more rapidly than when it is necessary to make a systematic separation of the metalli groups.

As the processes are based upon general principles there is no difficulty in deducing from them methods which become available under particular circumstances.

§ 64.

Preliminary Remarks.

Those substances mentioned in § 57 as exerting a prejudicial action upon the base separations must be removed by the methods described in the paragraph referred to before applying the methods detailed in the following table, pp. 168, 169. Acids other than sulphuric, hydrochloric, nitric, acetic, and perhaps oxalic (which is readily removed by means of chlorine water), must be absent from the solution. Phosphoric acid is not generally prejudicial to the determination of the bases; I have noted those cases in which it must be removed. Those metals which are precipitable by sulphuretted hydrogen in acid solutions must be removed before determining zinc, cobalt, and nickel in certain special cases; the removal of these metals is *essential* when the metals of the sixth group are present.

The general method is applicable to the metals of the first five groups only; the metals of the sixth group are always precipitated by sulphuretted hydrogen along with those of group 5, from which they are separated by solution in potash and potassium sulphide; they may then be determined according to § 63. In a few special cases (for instance, in the analysis of arsenites and antimonites of the alkalies and alkaline earths) it is possible to determine the members of this group by direct titration with iodine; but such cases are exceptional.

§ 65.

Explanation of the Table.

The following table contains methods for the determination of twenty bases, which are divided into eight sections. It may frequently happen that a liquid contains one member of each section, although the analysis of a substance containing all the bases will be a matter of very rare occurrence.

1. Bismuth, Silver, Copper, Cadmium.	2. Lead.	3. Zinc.	4. Cobalt, Nickel, Manganese, Barium, Strontium, Calcium, Magnesium.
Partial neutralisation with soda. Addition of a little sodium chloride and much hot water. Precipitate of bismuth oxychloride, and silver chloride washed and treated with nitric acid. Silver chloride filtered off and weighed, or converted into sulphide by treatment with ammonium sulphide, dissolved in nitric acid, and determined by § 47. If much lead be present, it must be removed from original liquid by means of sulphuric acid. Solution containing bismuth precipitated with potassium chromate, and bismuth determined by § 27, or bismuth may be determined by § 101. Filtrate free from silver and bismuth, mixed with sodium sulphite and potassium sulphocyanide, if lead be present also with sodium sulphate; precipitate boiled with caustic potash, and residual cuprous oxide determined by § 22. Filtrate free from lead and copper partially neutralised with ammonia, saturated with sulphuretted hydrogen, and cadmium sulphide determined by § 30. In absence of cadmium, copper may be determined, even in presence of sodium sulphate, by precipitating with stannous chloride and potassium iodide as cuprous iodide, and treating according to § 22 or 37.	Precipitation with excess of sulphuric acid. Precipitate washed, gently warmed with ammonium acetate; addition of potassium dichromate; filtration, and determination by § 27. Filtrate, free from lead, may be partially neutralised with soda, and employed for determination of bismuth, silver, copper, and cadmium.	Metals of the 5th group, if present, must be first removed by saturating with sulphuretted hydrogen in acid solution. Saturation of acid liquid with ammonium acetate, addition of sulphuretted hydrogen, determination of zinc sulphide by § 30. If zinc sulphide be grey, resolution in hydrochloric acid, and re-precipitation as described above is necessary.	If cobalt and nickel are to be determined, the metals of the 5th group must be first removed by passing sulphuretted hydrogen through the acid solution; otherwise this is not necessary. Neutralisation with ammonia. Addition of ammonium sulphide. After a few minutes strong acidification with acetic acid, heating to boiling, filtration, and washing with hot ammonium acetate. Solution of precipitate in hydrochloric acid with a little potassium chlorate: division of solution into 2 parts, and precipitation of each with chlorine or bromine water and caustic potash, and treatment according to § 24. Filtrate containing manganese, calcium, barium, strontium, and magnesium divided into 3 parts, 1 part warmed with sodium hypochlorite, MnO_2 collected and determined by § 23. Filtrate mixed with much solid potassium sulphate; ammonium oxalate, microcosmic salt, and excess of ammonia added; liquid boiled and filtered. Lime and magnesia in precipitate dissolved in hydrochloric acid; solution divided into 2 parts; in one part lime titrated according to § 21; in other part magnesia, according to § 52, by determining phosphoric acid. Undissolved sulphates remain behind. Second portion of filtrate from precipitate by ammonium sulphide, &c., decomposed by measured volume of normal sulphuric acid, rendered ammoniacal, and excess of acid determined by § 53, whence barium calculated. Third portion of filtrate precipitated by ammonium carbonate ($BaCO_3$, $SrCO_3$, $CaCO_3$), titrated according to § 8, and strontium determined from difference. Phosphoric acid must be previously removed by means of ferric chloride: manganese also by means of sodium hypochlorite in acetic acid solution.

5.	6.	7.	8.
Iron.	Aluminium, Chromium.	Uranium.	Potassium, Sodium, Ammonium.
Reduced in hot solution containing sulphuric acid by excess of zinc: solution decanted from undissolved zinc, and titrated by § 19. In presence of much nitric acid, previous precipitation by ammonium sulphide, solution in dilute sulphuric acid, and removal of sulphuretted hydrogen by boiling, is necessary.	Partial neutralisation of free acid with soda. Addition of acid potassium oxalate; addition of mixture of potassium sulphide and potassium carbonate until alkaline; addition of much caustic potash (free from silicic acid), and warming to 50°-60° for some minutes, measuring liquid, filtration of aliquot parts. Filtrate boiled with bromine water or sodium hypochlorite until sulphur, oxalic acid, and chromium oxide entirely oxidised. Acidification with nitric acid to expel carbon dioxide. Addition of caustic potash until all dissolved; addition of barium chloride, whereby all chromic and phosphoric acid, if present, is precipitated. Filtration; determination of chromic acid in precipitate by § 27. Aliquot part of filtrate acidified with nitric acid, measured volume of microcosmic salt solution added, and a little potassium sulphate to precipitate barium. Saturation with sodium acetate and determination of excess of phosphoric acid by means of uranium, according to §§ 50 and 57, whereby alumina is determined. Alumina may be directly determined, in absence of chromium and phosphoric acid, by acidifying alkaline filtrate, and adding calcium chloride and sodium acetate; also in acid solutions, if only alkalies and alkaline earths are present.	Addition of much ammonium carbonate and a little ammonium sulphide. Filtrate, or aliquot part thereof, boiled, acidified with nitric acid, saturated with sodium acetate, and titrated with microcosmic salt solution until disappearance of the potassium ferrocyanide reaction, according to § 50. Phosphoric acid, if present, may be precipitated with magnesia mixture according to § 52.	Ammonia is determined in a special portion according to § 11. For estimation of sodium and potassium, the whole is evaporated to complete dryness with sulphuric acid, treated with warm water, mixed with caustic baryta, and a little freshly-prepared barium sulphide solution, heated to boiling and saturated with carbon dioxide. After again boiling, the liquid is filtered: an aliquot part of filtrate divided into 2 parts. One-half is titrated according to § 8; the other half is mixed with tartaric acid and 2 volumes of alcohol. The precipitate is filtered, washed with cold saturated solution of potassium tartrate, and residue titrated with soda according to § 12, whereby potassium is determined. Sodium is found by calculation. In presence of silver, a little silver chloride is formed, and remains on dissolving the sulphates.

Uranium is seldom met with in ordinary analysis; the alkalies are most easily determined in a special portion of the substance; hence, in general, the liquid will be divided into six parts. It is, however, preferable to make allowance for accidents and for controlling analyses, and to divide the liquid into a greater number of parts than are actually required according to the table.

Let us suppose that the whole of the bases mentioned in the table are present, and that the liquid is to be divided into 10 parts. 5 grams of the substance are dissolved in nitric acid, the solution is made up to 500 cb.c., and 50 cb.c.$=0·5$ grams are withdrawn for each determination. We may begin with the determination of the metals in any section we please: let us take the first. By "partial neutralisation" I mean the addition of such a quantity of alkali or alkaline carbonate as causes a turbidity which disappears on addition of a drop of nitric acid. Potash or soda may generally be employed indifferently for neutralisation, but the fixed alkalies cannot be always replaced by ammonia or by ammonium carbonate. The addition of a large excess of sodium chloride in Section I. is to be avoided, inasmuch as silver chloride is slightly soluble in a solution of sodium chloride. Hot water must be used for dilution to insure the resolution of any precipitated lead chloride. Ferric oxide, alumina, or traces of phosphoric acid, may accompany the precipitated silver chloride and bismuth oxychloride; the presence of these salts does not, however, interfere with the accuracy of the subsequent processes. This fact illustrates the superiority of the present method over that which involves group-separations.

So also in the estimation of copper, considerable quantities of barium, strontium, and calcium sulphates—as also more or less lead sulphate—may accompany the cuprous oxide, but these substances exert no reducing action on ferric chloride or sulphate.

Copper may be precipitated as cuprous iodide in presence of cadmium, but the filtrate then contains tin (stannous chloride being employed as reducing agent), which necessitates a separation of the cadmium; it is therefore better to precipitate the copper as sulphocyanide.

The cadmium is better precipitated in a hot solution; this obviates the co-precipitation of zinc, which might occur if too much soda had been added to the original liquid.

In the second section sulphates of barium, strontium, and calcium may be precipitated along with the lead sulphate, but these sulphates are insoluble in ammonium acetate, while the chromates of these three metals are soluble in this liquid. Lead sulphate, on the other hand, is soluble in ammonium acetate, while lead chromate is insoluble; hence treatment with ammonium acetate, followed by warming with potassium dichromate, converts the lead sulphate only into chromate.

In the third section care must be taken to obtain the zinc sulphide free from nickel salts. This is best accomplished by passing sulphuretted hydrogen through the *cold* liquid the mineral acids in which have been almost completely neutralised, then adding ammonium acetate, warming, and continuing the passage of the gas.

In the fourth section, after removal of manganese (and iron), the alkaline earths are precipitated as sulphates; calcium sulphate is alone affected by the addition of ammonium oxalate; the addition of microcosmic salt and ammonia causes a precipitation of the magnesia present.

The determination of the alkalies is best carried out in a fresh portion of the original substance.

SECTION III.

SEPARATION AND ESTIMATION OF THE MORE IMPORTANT ACIDS.

THE acids must be combined with bases capable of forming soluble salts with those reagents which are employed in the separation processes—that is to say, with the alkalies.

Various methods may be adopted for forming combinations of the acids with the alkalies. Long-continued boiling with potassium or sodium carbonate sometimes suffices; freshly precipitated strontium sulphate, for instance, is converted into carbonate by this means, while potassium sulphate is simultaneously produced; lead phosphate, oxalate, and sulphate are also decomposed by this method. Barium sulphate and many silicates, on the other hand, are only decomposed by fusion with an alkaline carbonate.

Sulphuretted hydrogen or ammonium sulphide may very frequently be employed as a means for separating the acids from those metals which are precipitable by these reagents.

The acids must be separated and determined in a special portion of the liquid under examination.

§ 66.

Division of the Acids into Groups.

The acids may generally be determined without previous separation from one another. Sulphuric acid may, for instance, be determined in presence of phosphoric, nitric, hydrochloric acid, &c. The chlorine in soluble chlorides may be determined with accuracy in presence of sulphuric, nitric, or phosphoric acid. It sometimes happens, however, that the acids cannot be determined in separate portions of the same liquid without previous removal of some of themselves. Thus chlorine cannot be determined by titration with silver nitrate in a liquid containing sulphuretted hydrogen or alkaline sulphides. The presence of chromic acid interferes with the estimation of phosphoric acid by the uranium process. In such cases a separation becomes necessary. I have therefore divided the more important acids into three groups. Groups I. and II. include those acids which may be *directly* estimated by means of silver nitrate; Group III. includes those which can only be estimated by *indirect* processes. This division into groups is not, however, meant to suggest the idea that the acids *must* be separated before estimation; they are much more frequently determined in separate portions of the same liquid, thus carrying out the principle enunciated in last section for the determination of the bases.

GROUPING OF THE MORE IMPORTANT ACIDS.

Acids which may be directly estimated.		*Acids which can only be estimated indirectly.*
I. Not precipitated by silver nitrate in nitric acid solutions.	II. Precipitated by silver nitrate in nitric or sulphuric acid solutions.	III.
Arsenic acid.	Hydrochloric acid.	Nitric acid.
Arsenious „	Hydrobromic „	The oxyacids of
Chromic „	Hydriodic „	Chlorine,
Sulphuric „	Hydrocyanic „	Bromine,
Phosphoric „	Sulphydric „	Iodine.
Boric „	Sulphurous „	
Oxalic „	Thiosulphuric „	Tartaric acid.
Carbonic „	(Hyposulphurous)	Citric acid.
Silicic „		
Hydrofluoric „		

These acids cannot be all simultaneously present in a solution. Most of the acids of Group III. are decomposed, in acid liquids, by those of Groups I. and II., &c.

The acids of the first and second groups are determined in their own form, those of the third group in the form of products of decomposition. Looked at from this point of view, tartaric and citric acids belong to Group I.; as they are organic acids, I have, however, placed them as an appendix to Group III.

§ 67.

Estimation of the Acids of Group I. (Arsenic, Arsenious, Chromic, Sulphuric, Phosphoric, Boric, Oxalic, Carbonic, Silicic, Hydrofluoric Acids).

No separation is required, for the most part, before determining these acids.

I will describe the methods by which the acids enumerated above may be determined in presence of each other, or of the acids belonging to Groups II. and III. I will also point out the modifications which must be applied when the acids are combined with bases other than the alkalies.

A. *In alkali salts, and in absence of hydrofluoric and boric acids.*

Silicic Acid is first determined by evaporating to dryness after addition of ammonium chloride, filtering, washing, and applying the method of § 57.

The *arsenic acids* may be separated from all others by precipitation in the form of arsenious sulphide from an acid solution, the amount of arsenic being determined in the precipitate by § 63. If arsenious and arsenic acid are both to be determined, the following method may be employed: Arsenious acid is determined in one portion of the alkaline liquid by titration with iodine according to § 36; another portion is acidulated with hydrochloric acid, and warmed after addition of sodium sulphite until the arsenic is reduced to arsenious oxide. Excess of sulphurous acid is removed by boiling, the liquid is rendered alkaline by addition of sodium carbonate, and the total arsenious oxide is determined by the iodine method. The difference between the two results represents the amount of arsenious, to be calculated to arsenic oxide.

The removal of arsenic acids generally renders the subsequent determinations more easy; it is indispensable before determining phosphoric acid by uranium solution, or oxalic acid by permanganate. In these cases, instead of precipitating arsenic by means of sulphuretted hydrogen, yellow ammonium sulphide may be added, so as to retain the arsenic in solution, and the phosphoric and oxalic acids may be precipitated from this liquid by addition of calcium chloride.

Chromic acid may be determined, in absence of other oxidising or reducing substances, by means of ferrous salt and permanganate, according to § 26. Oxalic acid, if simultaneously present—which is only possible in alkaline liquids—may be removed by precipitation as calcium oxalate. If other acids of Group I. are to be determined in a liquid containing chromic acid, the latter must be reduced by boiling with alcohol, and the chromium must be precipitated as oxide by addition of ammonia, and removed; oxalic and phosphoric acids, if present, having been previously precipitated from the alkaline liquid in the form of calcium salts.

The remaining acids of Group I.—supposing hydrofluoric acid absent—may be determined in separate portions of the liquid without previous separation.

Sulphuric acid may be precipitated in acid liquids by adding strontium chloride and alcohol, and determined according to § 14. If only alkalies, oxalic, and phosphoric acid are present, sulphuric acid may be determined after addition of calcium chloride, without filtration, according to § 53.

Phosphoric acid may be determined, in absence of chromic and arsenic acids, by titration with uranium solution as described in § 50; oxalic acid, if present, having been previously oxidised to carbonic acid by heating with bromine. Or phosphoric acid may be precipitated by magnesia mixture from an alkaline solution, and determined in the precipitate by § 52. If arsenic acids are present, ammonium sulphide must be added so as to retain these in solution.

Oxalic acid may be directly determined in absence of chromic acid. In other cases this acid may be precipitated as calcium oxalate, which may then be dissolved in hydrochloric acid, and the solution titrated with permanganate, according to § 20.

Carbonic acid is determined by § 13 in the original liquid.

B. *In presence of hydrofluoric and boric acids, and without paying regard to carbonic acid which may be present.*

We assume the absence of bases other than the alkalies, and the previous removal of silicic acid, if present, by boiling in a platinum basin with ammonium bicarbonate.

Sodium carbonate is added, followed by addition of excess of calcium acetate solution; phosphoric, oxalic, and hydrofluoric acids are thus completely precipitated; sulphuric and boric acids are partially precipitated. After a considerable time the precipitate is filtered off, and digested with acetic acid, whereby calcium phosphate and borate, and any calcium carbonate present, are alone completely dissolved.[1] The residue is washed with a large quantity of hot water in order to dissolve any calcium sulphate, dried, ignited, and weighed. The mixture of calcium carbonate and fluoride so obtained is dissolved in a measured quantity of normal hydrochloric acid, and after filtering from undissolved calcium fluoride, the calcium is determined by the method detailed in § 6. From the results of this determination the quantity of oxalic acid originally present in the liquid may be calculated $CaC_2O_4 = CaCO_3 + CO$ ($CaOC_2O_3 = CaOCO_2 + CO$). The difference between the weight of calcium carbonate and the total weight of the ignited residue represents the weight of calcium fluoride; from this the amount of hydrofluoric acid is readily calculated.

The liquid filtered from the precipitate by calcium acetate is now mixed with that obtained by digesting this precipitate with acetic acid (if a precipitate form it

---

[1] If arsenic acid was originally present, it would also be found in this solution.

is dissolved by adding acetic acid), and the individual acids, with the exception of boric acid, are determined by the processes already described.

In order to determine boric acid, the liquid containing lime and acetic acid, from which chromic acid and the arsenic acids have been separated as in *A*, is mixed with oxalic acid, whereby the lime is completely precipitated; after filtration, magnesia mixture is added, and the phosphoric acid precipitated. The precipitate is filtered off, and well washed with hot water; the filtrate is evaporated to dryness in a weighed platinum basin, the residue is ignited, treated with hot water, again ignited, and weighed. It is then dissolved in a measured quantity of normal hydrochloric acid, the magnesia is determined according to § 8, and deducted from the total weight; the difference represents boric acid.

Inasmuch as magnesium borate is soluble in an ammoniacal solution of ammonium chloride, while magnesium-ammonium phosphate is insoluble in the same liquid, care must be taken to add a large quantity both of ammonia and of ammonium chloride when precipitating phosphoric acid.

If the filtrate and first washings from the ignited residue be themselves evaporated to dryness, ignited, washed with hot water, and the residue be treated as directed, the results are more accurate.

C. *In presence of other acids and bases.*

It may be laid down as a general rule that the estimation of the greater number of the acids of group I. necessitates that these acids shall not be in combination with metals precipitable by sulphuretted hydrogen or by ammonium sulphide, with the exception perhaps of lead. In the absence of those acids which exert a prejudicial effect on the estimation of the acids of the group now under consideration, the following method is applicable: The *arsenic acids* are determined iodometrically in alkaline liquids. The presence of those bases which become soluble in alkaline liquids in presence of tartaric acid, but which do not, under these conditions, reduce arsenic acid, nor are oxidised by free iodine, nor impart a colour to the liquid, is without effect upon the titration. Arsenious acid may therefore be determined in presence of alkalies, of small quantities of alkaline earths, of aluminium, zinc, cadmium, and tin, by means of iodine solution. In presence of alumina, or of the oxides of the heavy metals, it is necessary to add Rochelle salts or tartaric acid, so that these compounds may go into solution on addition of sodium carbonate. Alkaline earth arsenites are simply dissolved in hydrochloric acid, and the solution is mixed with excess of sodium bicarbonate; the precipitate which forms is without influence upon the subsequent titration, and as it may contain a small quantity of arsenious oxide, it should not be removed by filtration. The estimation of arsenic need then only be prefaced by a process of separation when the salts under examination are compounds of the arsenic acids with certain of the heavy metals. After reduction of arsenic acid by means of sulphur dioxide, in an acid liquid, the whole of the arsenic is precipitated along with the metals of the fifth and sixth groups by means of sulphuretted hydrogen from a warm solution; the arsenious sulphide is removed by solution in ammonium carbonate, the liquid so obtained is decomposed by addition of ammoniacal silver nitrate solution, acidified with hydrochloric acid, and filtered. The filtrate is saturated with sodium bicarbonate, and the arsenic is determined by titration with iodine.

I have already pointed out, in the beginning of this paragraph, how arsenic acids may be separated from the other acids of group I. by precipitation as arsenious sulphide.

Chromic acid may be determined in solutions containing hydrochloric or sulphuric acid in presence of almost all metals, provided that those substances which influence the reduction of this acid by a measured quantity of ferrous sulphate solution ($H_2S, H_2SO_3, H_2S_2O_3, H_2C_2O_4$, As_2O_3, HNO_2, and other reducing acids; HNO_3, HCl, HBr, $HClO_3$, $H_2Mn_2O_8$, and other oxidisers) be absent.

Only the metals of the sixth group, with the exception of stannic (not stannous) salts, mercury, and copper,[1] need be removed before determining chromic acid. These metals may be separated by saturating the liquid with sulphuretted hydrogen. The chromium in the filtrate is oxidised by boiling with bromine, after saturating with potassium carbonate and caustic potash (any precipitate which forms being removed by filtration), and is then precipitated by the addition of barium chloride. Cupric chromate may be directly decomposed by means of potash. Separation of chromic acid is also necessary in presence of those reducing and oxidising agents enumerated above. The reducing agents can only be present along with chromic acid, in alkaline liquids. Arsenious or arsenic oxide is removed by precipitation with calcium acetate, the chromic acid in the filtrate being precipitated as barium chromate. Chromic acid may also be similarly separated from oxidising agents in alkaline solutions, provided that metals of the fourth, fifth, and sixth groups are absent. It is to be noticed that manganese, present as manganic or permanganic acid, should be removed as MnO_2 from the alkaline liquid after addition of alcohol.

In the event of metals of the fourth and fifth groups being present along with oxidising acids, it is advisable first to remove the metals of the fifth group by passing sulphuretted hydrogen through the acid liquid, to render the filtrate alkaline by addition of potash, and *after* converting the chromium into chromic acid by boiling with bromine, to filter, and to precipitate the filtrate by means of barium chloride.

Sulphuric acid may be precipitated by addition of strontium nitrate and a volume of alcohol of 95 per cent, equal to the volume of liquid, from a solution of any sulphate soluble in nitric acid, and in presence of other acids: § 14 directs how to proceed with the determination. Or the acid may be thrown down and directly determined according to § 53 by means of barium chloride.

Lead, calcium, and strontium sulphates are completely decomposed by boiling with potassium carbonate; the

---

[1] If this metal be present in large quantity, it must be removed.

filtrate contains the whole of the sulphuric acid. If pure, or if containing substance unacted on by boiling potassium carbonate, the acid in either of these three sulphates may be determined by using a measured volume of normal potassium carbonate solution, and proceeding according to § 17.

I have already described, in § 57, the methods for separating *phosphoric acid* from the bases. If the phosphoric acid estimation be alone of importance, a separation from iron and aluminium salts may be carried out by mixing the solution with tartaric acid, and adding ammonia in excess, followed by addition of magnesia mixture. The phosphoric acid is determined in the precipitate by § 52; ferric and aluminic oxides remain in solution.

Boric acid is determined as magnesium borate: it must be previously separated from all bases other than magnesia and the alkalies. This may be effected by precipitating the metals of the fifth and sixth groups from an acid solution by means of sulphuretted hydrogen, adding ammonium chloride, carbonate, and sulphide, and filtering. In the event of magnesia being absent, an ammoniacal solution of magnesium sulphate is added to the filtrate, and the boric acid is determined as already described.

Oxalic acid is precipitated as calcium or lead oxalate from ammoniacal solutions, or from solutions slightly acidified with acetic acid, the metals of the fifth and sixth groups having been previously removed by means of sulphuretted hydrogen.

If oxidising and reducing acids are absent, oxalic acid may be estimated by means of permanganate solution, in presence of lead, zinc, cadmium, nickel, cobalt, manganese, aluminium, chromium, and the alkaline earths.

Carbonic acid and *silicic acid* may be determined in presence of all bases—the former by § 13, the latter by § 57.

Hydrofluoric acid is always determined by weighing as calcium fluoride (CaF_2; old notation, CaF), in which form it is thrown down from solutions of all soluble fluorides by means of calcium chloride and ammonium carbonate. The precipitate must be freed from other co-precipitated bases by treatment with dilute hydrochloric acid. Insoluble fluorides are decomposed by the method of § 56.

Silicic may be separated from hydrofluoric acid by addition of ammonium carbonate to the alkaline liquid. If an alkali fluoride be present in solution along with silicic acid—as after fusion of fluorspar—the liquid may be acidified with acetic acid, an equal volume of alcohol may be added, and the precipitated alkaline silico-fluoride may be determined, after separation and washing, by titration with standardised caustic potash or soda; or the precipitate may be decomposed by boiling with milk of lime, and after passing carbon dioxide into the liquid, and filtering, the amount of alkali may be determined in the filtrate; the amount of hydrofluoric acid is readily calculated.

In the first case (as also in the direct titration with alkali), two equivalents of potash, used for neutralisation, correspond with three equivalents of fluorine present, so that $1\frac{1}{2}$ times the amount of potash used represents the amount of fluorine present.

$$K_2SiF_6 + 4KHO = SiO_2 + 6KF + 2H_2O.$$
$$(KFSiF_2 + 2KO = SiO_2 + 3KF.)$$

In the latter case (as also in the decomposition by lime, and subsequent titration of alkaline carbonate), the hydrochloric acid used corresponds with 3 equivalents of fluorine, so that 36·5 parts of hydrochloric acid are equal to 57 parts of fluorine; or 1 cb.c. normal acid = 60 m.gm. HF. (Same for old notation.) Compare also § 12.

§ 68.

Estimation of the Acids of Group II. (Hydrochloric, Hydrobromic, Hydriodic, Hydrocyanic, and Sulphydric Acids).

The acids of this group are all precipitated from solutions containing nitric acid, by addition of silver salts; by this reaction they may be separated from the acids of group I.

The acids of group II. can, as a rule, be determined in presence of those of group I.

In the event of the acids of the group now under consideration being present in combination with alkalies, it is advisable to remove the *sulphydric acid* by addition of ammoniacal zinc sulphate solution. The precipitated zinc sulphide is determined according to § 30, and the amount of sulphydric acid originally present is calculated. The filtrate, free from sulphydric acid, is divided into two portions: in one *cyanogen* is determined by § 49; the other is saturated with potash, ferrous sulphate is added, and, after warming, the liquid is acidified by addition of hydrochloric acid. The precipitate so produced, containing the whole of the cyanogen, is removed by filtration, and *hydrochloric*, *hydriodic*, and *hydrobromic* acids are determined in the filtrate in accordance with § 45.

A few remarks may be made here concerning the estimation of the acids of group II. in insoluble compounds, in presence of the acids of group I., and also in presence of any bases.

In those silicates which are decomposed by heating with concentrated sulphuric acid, hydrochloric acid may be determined by titrating the clear solution directly with silver nitrate. If the silicate is only decomposable by fusion, silicic acid must be removed after fusion, by boiling with ammonium carbonate; the liquid must be filtered, acidified with nitric acid, and titrated with silver.

Hydrofluoric acid is separated from hydrochloric by precipitation with calcium acetate; the filtrate is acidified with nitric acid before determining hydrochloric acid.

Metallic chlorides, bromides, and iodides—with the exception of those of silver, lead, and bismuth—are decomposed by boiling with potassium carbonate, the whole of the halogen going into solution in combination with potassium. The silver, lead, and bismuth haloid salts are decomposed by means of sulphuretted hydrogen. Bismuth salts are dissolved in sulphuric acid; lead salts in caustic potash; silver chloride in ammonia; silver bromide and iodide are fused with potassium and sodium carbonates.

This preliminary separation of the bases is to be generally recommended, although it is not always absolutely required, inasmuch as silver nitrate precipitates the halogens in presence of any metals (mercuric and chromium chlorides excepted). The fact that chlorine, bromine, and iodine may be determined in presence of all the acids of group I., with the exception of the arsenic acids and of phosphoric acid, also renders the separation mentioned above desirable. *Hydrocyanic acid* may be determined in presence of almost all the acids of group I., and also in presence of hydrochloric, hydrobromic, and hydriodic acids, by the method described in § 49. The same paragraph contains directions for separating this acid from the bases.

Sulphur is determined volumetrically either as sulphuretted hydrogen or as sulphuric acid. The first method is only applicable in the case of those sulphur compounds which are free from all substances capable of oxidising sulphuretted hydrogen, and in which the whole of the sulphur is converted into sulphuretted hydrogen by addition of hydrochloric acid. The sulphuretted hydrogen is passed into ammoniacal zinc or cadmium solution, and the precipitated sulphide is treated in accordance with § 30.

Finely-powdered sulphides are completely oxidised by fusion with a mixture of 4 parts potassium nitrate and 3 parts calcined sodium carbonate; the whole of the sulphur goes into solution, as alkaline sulphate, on treating the fused mass with water. A mixture of potassium chlorate, sodium carbonate, and sodium chloride may also be employed, these salts being mixed in the proportion of 5 : 4 : 3.[1]

Sulphides cannot generally be thoroughly oxidised by treatment with aqua regia.

---

[1] Compounds which lose sulphur on heating—iron pyrites, for instance—should be fused with a mixture of 4 parts sodium carbonate, 8 parts potassium nitrate, and 24 parts pure fused sodium chloride; or a mixture of 6 parts potassium chlorate, 4 parts sodium carbonate, and 2 parts common salt may be employed.

§ 69.

Estimation of Sulphurous and Thiosulphuric Acids in presence of Alkaline Sulphides.

Although these acids do not strictly belong to group II., nevertheless, on account of the frequency with which their alkaline salts occur in commerce, I have added an account of the methods for their estimation as an appendix to this group.

§§ 32 and 34 contain descriptions of the processes to be adopted for determining sulphurous and thiosulphuric acids. The methods therein described assume the presence of but one of these acids, and the absence of alkaline sulphides.

In the event of both acids being present, and of the mixture containing alkaline sulphides (as in liver of sulphur, crude soda liquors, &c.), the following process may be adopted.

The substance is dissolved in water, and the solution is shaken with freshly-precipitated zinc or cadmium carbonate in a well corked flask. The whole of the sulphur present as alkaline sulphide is thus thrown down in the form of zinc or cadmium sulphide. When the precipitate has completely settled, it is collected on a filter and dissolved in fuming nitric acid, or in more dilute acid to which a crystal of potassium chlorate is added from time to time. The sulphuric acid produced is determined by § 53, and from this the amount of sulphur originally present is calculated. In the event of alkaline monosulphides only being present, the zinc or cadmium sulphide may be directly determined by § 30. The filtrate from precipitated cadmium sulphide is divided into two parts; one part is warmed, and decomposed by addition of silver solution.

$$Na_2S_2O_3 + Ag_2O = Na_2SO_4 + Ag_2S.$$
$$(NaOS_2O_2 + AgO = NaOSO_3 + AgS.)$$

The precipitate, which may contain a little silver carbonate, is filtered off and digested with ammonia, the residue is dissolved in nitric acid, and the silver is determined in accordance with § 44. Silver found × 0·577 = $H_2S_2O_3$ (old notation, silver found × 0·444 = S_2O_2).

Sulphurous acid may be determined by difference in the second part of the liquid filtered from cadmium sulphide. This is effected by titrating with iodine, and deducting from the total amount used that corresponding with the thiosulphuric acid present. (1 equivalent iodine = 1 equivalent $H_2S_2O_3$; old notation, 1 equivalent iodine = 2 equivalents S_2O_2.)

Iodine converts sulphurous into sulphuric acid, but thiosulphuric into tetrathionic acid: a method of separating the two acids may be based upon this fact. The liquid which has been freed from sulphides is divided into two parts: one part is titrated with iodine, a measured volume of standardised barium chloride solution is added, the excess of barium is precipitated by passing in carbon dioxide, the precipitate is collected, washed until the washings cease to affect turmeric paper, dissolved in normal hydrochloric acid, and the liquid titrated with $\frac{1}{2}$-normal ammonia; the sulphuric acid present after treatment with iodine is thus determined. The second half of the liquid is acidulated with hydrochloric acid, and boiled until the whole of the sulphur dioxide is removed; the amount of sulphuric acid is then determined according to § 53, without removing the precipitated sulphur. The difference between the two sulphuric acid determinations represents the amount of this acid produced by the action of iodine upon the sulphurous acid present; from this the amount of the latter acid is calculated. By deducting the amount of iodine corresponding with sulphurous acid from the total iodine employed in the titration, the quantity of iodine corresponding with thiosulphuric acid is found.

I have already described a process for determining sulphuric acid in presence of sulphurous and thiosulphuric acids; the method is also applicable in presence of alkaline sulphides (after acidifying with hydrochloric acid, boiling off SO_2, &c.).

Carbonic acid is most readily determined in presence of the sulphur acids and sulphides, by addition of potassium chromate and sulphuric acid, and precipitation as barium carbonate (§ 13).

§ 70.

Estimation of the Acids of Group III. (Nitric Acid and the Oxyacids of Chlorine, Bromine, and Iodine).

These acids must be combined with alkalies (which is easily done by adding excess of sodium carbonate), and a determination of each must be effected in a separate portion of the liquid.

In presence of other oxidising acids, nitric acid is preferably determined in the form of ammonia, according to § 11. The oxyacids of chlorine, bromine, or iodine, if not simultaneously present, may be determined by § 42. If, however, oxyacids of chlorine are accompanied by those of bromine and iodine, the following method may be adopted.

The solution is evaporated to dryness after addition of sodium carbonate, and the residue is gently ignited, so that the chlorates, bromates, iodates, &c., are converted into chloride, bromide, and iodide, which are then examined by § 45.

Chlorides, bromides, and iodides, if present in the original liquid along with the oxyacids, may be separated by digestion with freshly-precipitated silver phosphate (Ag_3PO_4); the precipitate, on treatment with ammonia and a little ammonium sulphide (excess of which is removed by zinc sulphate), yields the halogens in solution.

The amount of chlorine, bromine, and iodine in the oxyacids having been determined, the oxygen may be estimated by titration with sodium thiosulphate, according to § 42. Hypochlorites may be directly determined by titration with sodium arsenite in alkaline solutions, as described in Part III. under analysis of bleaching salts.

Before leaving the subject of the estimation of acids, I will describe methods for determining tartaric and citric acids, the most important organic acids (with the exception of acetic and oxalic, the determination of which has been already described) which are made use of in analytical chemistry.

§ 71.[1]

Estimation of Tartaric and Citric Acids in presence of different Bases and Acids, and in Fruit-Juices.

The frequency with which tartaric and citric acids are met with in commerce renders it very desirable that we should be provided with a ready and accurate method for their determination.

Tartaric acid may be accurately determined as potassium hydrogen tartrate, a salt which is quite insoluble in a mixture of 1 part water and 2 parts alcohol, even in presence of acetic acid or of acetates.

If it be desired to determine *tartaric and citric acids* in a tolerably-concentrated solution containing the *free acids or their compounds with the alkalies*, acetic acid is added to acid reaction (if the liquid be not already acid), followed by the addition of excess of potassium acetate solution, and a quantity of alcohol of 95 per cent, equal to twice the volume of the liquid. After stirring well, and allowing to stand for an hour, the clear liquid is poured off from the precipitate; a mixture of 2 volumes of alcohol and 1 volume of water is added, and the precipitate is collected on a filter. Potassium citrate and acetate are readily soluble in water. The potassium hydrogen tartrate is dissolved in hot water, and the solution is titrated with $\frac{1}{2}$-normal ammonia. (1 cb.c. $\frac{1}{2}$-normal ammonia = 75 m.gm. crystallised tartaric acid; same for old notation.)

The filtrate containing the whole of the citric acid, accompanied by acetic acid, is neutralised with soda, and the citric acid is precipitated in the form of lead citrate by addition of a solution of neutral lead nitrate.[2] (Acids other than those mentioned are supposed absent.)

---

[1] Described by me in *Archiv für Pharmacie* [2], ii. 2, 1874.

[2] I have found that lead citrate is somewhat soluble in ammonium acetate.

The lead citrate is filtered off, and after washing with a mixture of equal volumes of alcohol and water, is suspended in water through which sulphuretted hydrogen is passed. After the precipitation of the whole of the lead, the liquid is boiled until excess of sulphuretted hydrogen is removed, and the citric acid is determined by titration with $\frac{1}{2}$-normal ammonia.

1 cb.c. $\frac{1}{2}$-normal ammonia=32 m.gm. $C_6H_8O_7$.

Old notation,

1 cb.c. $\frac{1}{2}$-normal ammonia=35 m.gm. crystallised citric acid.

Addition of a lead salt produces a turbidity in 100 cb.c. of water containing 2 m.gm. of citric acid The lead citrate must not be washed with water, else it undergoes a slight decomposition.

The method just described is also applicable for the determination of *tartaric and citric acids in presence of those metals which are precipitated from acid solutions by sulphuretted hydrogen*, provided that no other bases but the alkalies, and no other acids but acetic, be present. The method is applicable for the analysis of tartar emetic, or of Fehling's solution if prepared from copper tartrate in place of copper sulphate.

Estimation of Tartaric and Citric Acids in presence of acids other than Acetic, and of those Bases which are not precipitated in Acetic Acid Solutions by any of the Acids present (Oxalic, Sulphuric, Hydrochloric, Nitric Acids; Alkalies, Magnesia, Alumina, Iron and Zinc Oxides, &c.).

Metals precipitable by sulphuretted hydrogen in acid solutions, if present, are removed after saturating the liquid with sodium acetate. If potassium hydrogen tartrate separate out during this saturation, it need not be regarded, as it may be again dissolved by washing the precipitated sulphides with hot water containing a very little acetic acid. The filtrate is nearly neutralised with sodium carbonate, and an excess of lead nitrate is added. Tartaric, citric, oxalic, and sulphuric acid are thus precipitated, along with a considerable quantity of lead chloride. The precipitate is washed with the alcoholic mixture already described, removed to a beaker, and treated with ammonia, whereby the lead tartrate and citrate are alone dissolved.

After filtration, and washing the residue with dilute ammoniacal water, ammonium sulphide is added to the filtrate, which is then acidified with acetic acid, and boiled until the whole of the sulphuretted hydrogen is driven off. The precipitated lead sulphide is filtered off and washed with hot water; potassium acetate and two volumes of alcohol are added to the filtrate. After an hour the precipitate of potassium hydrogen tartrate is collected and treated as already described. The filtrate contains the citric acid and a little hydrochloric acid (if this acid were originally present), because lead chloride is partially decomposed by ammonia. Citric acid is precipitated by addition of lead nitrate. On account of the presence of lead chloride, it is more advisable to precipitate the citric acid first as calcium citrate. This is done by adding calcium chloride to the alcoholic filtrate containing the acid, removing any precipitate of calcium sulphate or oxalate which is produced, heating to boiling, adding more alcohol, and rendering the liquid alkaline by addition of ammonia. Every trace of citric acid is thus thrown down in the form of calcium citrate; the precipitate is collected on a filter, washed with alcohol, and dissolved in acetic acid. The liquid is mixed with lead nitrate, boiled and filtered. The precipitate is washed with alcohol, decomposed by sulphuretted hydrogen, and the citric acid is determined as already described. The calcium citrate may also be dissolved in nitric acid, and the acid thrown down by addition of basic lead acetate.

This method is applicable, with slight modifications, in almost every case.

In the event of lime and phosphoric acid being present, the liquid should be mixed with sal-ammoniac, and should also be boiled after addition of sodium acetate, and any precipitate of aluminium or iron phosphate, or calcium oxalate, filtered off. As this precipitate may contain small quantities of calcium tartrate, it is to be washed with water and then with a hot solution of sal-ammoniac; the latter washings are to be tested for tartaric acid by adding excess of potassium acetate and alcohol. If tartaric acid be found, its quantity is to be determined. The rest of the process is the same as that just described.

The bases present in solution may be for the most part determined after removal of the majority of the acids by means of lead. Aluminium and iron, for instance, may be determined in the liquid from which lead has been removed by means of sulphuretted hydrogen, by adding excess of sodium acetate, and boiling: in the filtrate calcium may be precipitated as oxalate, and magnesium as double phosphate. So also the oxalic, phosphoric, and sulphuric acids remaining in the lead precipitate after treatment with ammonia, may be readily determined. It is only necessary to dissolve the residue in caustic potash, to add ammonium sulphide, to acidify with acetic or hydrochloric acid, to boil and filter. The filtrate is then divided into three parts: to the first excess of calcium chloride and ammonia are added, a measured volume of normal barium chloride solution is run in, the liquid is heated, and excess of barium is determined by titration with normal potassium dichromate liquid. Sulphuric acid is calculated according to § 53. Oxalic acid is determined in the second portion after acidification with sulphuric acid (§ 20). The third portion is mixed with sodium hypochlorite, boiled, and saturated with sodium acetate; phosphoric acid is then determined by § 50.

Estimation of Tartaric and Citric Acids in Fruit-Juices.

The acids characteristic of the juices of fruits are tartaric, citric, and malic; fruit-juices also contain gummy substances and colouring matter.

The juice is to be partially clarified by filtration; if the liquid be very thick and gelatinous, an equal volume of alcohol should be added, whereby a precipitate is produced, which may then be filtered off and washed with hot water.

Acetate of lead is added, whereby citric, tartaric, and malic acids are precipitated along with phosphoric and oxalic acids and colouring matter. The precipitate is washed with dilute alcohol and treated with ammonia. After filtration, a liquid is obtained containing the three organic acids and more or less colouring matter. This liquid is mixed with ammonium sulphide, acidified with acetic acid, and filtered: the filtrate is colourless. Tartaric acid is precipitated by adding potassium acetate and alcohol to the filtrate. The liquid filtered from precipitated potassium hydrogen tartrate contains citric and malic acids; it is mixed with calcium chloride, ammonia, and a little alcohol, warmed and filtered. The precipitate, after washing with boiling lime-water, is free from malic acid; it is dissolved in nitric acid, the solution is precipitated by addition of lead acetate, and the citric acid is determined as already described.

Phosphoric, oxalic, and sulphuric acid, if present in the juice, remain in the lead precipitate after treatment with ammonia, and may be determined therein. Racemic acid is present in certain fruit-juices; it is precipitated along with tartaric acid, but may be removed by dissolving the precipitate formed on addition of potassium acetate, in hydrochloric acid, adding excess of ammonia and calcium chloride solution, whereupon calcium racemate is precipitated free from tartrate. The precipitate, after washing with hot sal-ammoniac solution, and then with distilled water, may be dried, ignited, and weighed as calcium carbonate.

Tartaric and citric acids may be determined in such difficultly-soluble or insoluble substances as crude argol, calcium citrate, &c., as follows: Argol is dissolved in hot water containing a little hydrochloric acid; the liquid is saturated with ammonium acetate, the calcium is precipitated by addition of ammonium oxalate, and removed by filtration. The calcium oxalate is determined by titration with permanganate. Tartaric acid is precipitated from the filtrate by adding potassium acetate and alcohol.

Alkalies in combination with tartaric acid are determined by igniting the substance, dissolving in water, and titrating by the alkalimetric method.

Calcium citrate may be dissolved in hydrochloric acid, and the citric acid precipitated by addition of lead acetate; if calcium tartrate were also present, the lead precipitate is to be treated as already directed.

§ 72.

Concluding Remarks concerning Volumetric Separation Methods.

We have seen how various substances may be determined, when simultaneously present, by volumetric processes; and we have learned how few are the separations required in this branch of analysis as compared with those demanded in gravimetric processes. In every analysis four points are to be chiefly attended to:—

1. A knowledge of the qualitative composition of the substance.
2. A method for dissolving the substance.
3. Methods of separation.
4. Methods for estimating the individual substances.

The separation and titration methods should be as simple as possible. By constantly asking one's self *why* is this done, and by following the reactions which occur throughout the analytical process, it is often possible, under special circumstances, to shorten the various methods, or otherwise to adapt them to the requirements of peculiar cases.

I have endeavoured to describe only those methods of separation and of estimation which are capable of general application.

PART III.

QUANTITATIVE ANALYSIS OF SUBSTANCES WHICH ARE OF TECHNICAL IMPORTANCE.

INTRODUCTION.

WHAT is generally required in the quantitative analysis of a commercial product is the estimation of only one or two of the constituents, as the value of the substance may generally be then fairly assessed.

The technical analysis of a manganese ore, for instance, consists in determining the amount of available oxygen; of chromate of potash, in determining the amount of chromic acid, and so on.

In many cases the technical analysis of a substance does not seek to determine the total amount of that constituent which is of especial importance in reference to the purpose for which the substance is to be used, but to estimate the quantity of this constituent which can be obtained under the special conditions of the manufacture.

I cannot in this work give detailed directions for carrying out such technical analyses, but would only impress upon the analyst the necessity of obtaining a fair average sample of the substance to be analysed, of determining, by suitable means, the moisture in the sample, and of endeavouring to acquaint himself with the principles upon which the analytical methods which he employs are based. In general the volumetric processes of separation and estimation detailed in the foregoing pages may be followed, with slight modifications according to special circumstances.

I will now show how the foregoing processes may be applied to the analysis of some of the more important technical products.

§ 73.

Potashes.

COMMERCIAL potashes generally contain,—besides potassium carbonate,—sulphuric, silicic, sulphydric, and hydrochloric acids, alkaline earths, iron and manganese. The amount of potassium carbonate is determined in the solution in hot water, after filtration, by titrating with normal hydrochloric acid according to § 8. Sulphuric acid may be determined by § 14 or 53, and hydrochloric acid as directed in § 47, after acidifying with nitric acid. Alkaline sulphide, if present, may be determined by adding ammonium chloride, precipitating with ammoniacal zinc sulphate solution, and treating the precipitate as directed in § 30. Silicic acid may be gravimetrically determined by § 57. If necessary, the bases other than potassium may be determined by the methods already detailed. Soda, if present, is best estimated by separating the potash as potassium tartrate (§ 12), evaporating the filtrate to dryness with sulphuric acid, igniting, and weighing the residue as sodium sulphate.

§ 74.

Soda.

It is generally sufficient to determine the total alkalinity of commercial soda by the ordinary process. Caustic soda, if present, may be determined by dissolving a weighed portion of the sample in hot water in a closed flask, precipitating with barium chloride, making up to a certain volume, and after the precipitate has settled, withdrawing an aliquot portion and determining the alkali with normal hydrochloric acid. The process must be conducted with as little access of air to the liquid as possible.

Soda frequently contains sulphide, sulphate, and thiosulphate of sodium. The sulphate may be determined by § 53, after acidification with hydrochloric acid. The sulphide and thiosulphate are estimated by titrating a portion of the soda solution with iodine, after addition of sodium bicarbonate and starch paste. The amount of iodine used in order to produce a blue colour being noted, a second equal portion of the soda solution is mixed with sal-ammoniac, precipitated with ammoniacal zinc sulphate solution, and filtered; the filtrate is titrated with iodine. The amount of iodine used in the second titration corresponds with the thiosulphate present; from the difference between the two quantities of iodine used the sulphide present is calculated (compare § 69). If the total alkalinity has been determined by the ordinary saturation process, the amount of sodium existing as sulphide must be deducted from the total sodium found.[1]

Sodium chloride, which is not unfrequently present in crude soda, may be determined in accordance with § 47.

The amount of iron in the soda or other liquor may be found by boiling for some time with sulphuric acid, filtering from sulphur, reducing with zinc, and titrating with permanganate (§ 19.)

§ 75.

Common Salt.

The technical analysis of salt consists in determining the quantities of those substances other than sodium chloride which are present. The most important of these substances are lime, magnesia, sulphuric acid, and traces of water.

Lime is determined by precipitating the solution with

---

[1] The amount of sodium carbonate may be estimated by determining carbonic acid in the filtrate; this is effected by precipitating with barium chloride, and titrating the precipitated barium carbonate.

ammonium oxalate, after addition of ammonium chloride, filtering, and dissolving the precipitate in hydrochloric acid, &c., according to § 21. Magnesia may then be determined in the filtrate by § 52.

These substances may also be determined by successive additions of ammonium oxalate and phosphate to the ammoniacal solution, according to § 65.

Sulphuric acid is determined in another portion by means of standard barium chloride (§ 53).

Water is estimated by noting the loss incurred on heating a weighed portion of the sample to incipient redness in a platinum crucible.

Potash, if present, is determined as tartrate according to § 12.

§ 76.

Soap Analysis.

The value of soap varies with the amount of water, alkali, and fatty acids contained in it. Water may be determined by exposing a weighed quantity (10 to 15 grams), cut into small pieces, to a temperature of 110° to 120°, until it ceases to lose weight.

A considerable quantity (50 to 60 grams), cut from the centre of a large mass of the sample, is dissolved in distilled water, and the solution is made up, when cold, to 1000 cb.c.

50 cb.c. are withdrawn, placed in a beaker, and a few drops of eosin solution are added; normal hydrochloric acid is then run in until the liquid becomes colourless. From the amount of acid used the total alkali is calculated.[1]

Another portion of 50 cb.c. is added to 300 cb.c. of a saturated solution of common salt, which must itself be neutral to test-paper, and the liquid is made up to 400 cb.c. The true soap (neutral alkaline salts of the fatty

---

[1] The fatty acids, at the instant of their complete liberation, apparently combine with the eosin; the upper layer of semi-solid fat therefore retains a pink colour, but the liquid underneath i totally decolorised.

acids) is precipitated, while any uncombined alkali remains in solution. An aliquot portion of the liquid is passed through a dry filter, and the alkali is determined by the ordinary process. The amount found, deducted from total alkali, gives alkali in combination. If soda and potash be both present, the process of § 12 may be applied after removing the fat.

50 cb.c. of the soap solution are run into a stoppered separating funnel, and there decomposed by excess of acid; the fatty acids so separated are agitated with carbon disulphide until completely dissolved; this solution, which forms the lower layer in the funnel, is run into a small weighed flask; the carbon disulphide is distilled off, and the residue is heated at 100° until it ceases to lose weight.[1]

Soap is very frequently adulterated with mineral matter. The following substances are those most commonly employed: borax, water glass, Glauber's salt, soda, oxide and sulphide of iron, white vitriol, clay of different kinds, pumice-stone, verdigris, &c.; starch and potato-meal, and such substances as gum, turpentine, &c., are also sometimes used as adulterants. Mineral impurities may be detected by treating the soap with strong alcohol, filtering, and examining the residue.

Ordinary soap contains from 20 to 30 per cent of water, 7 to 8 per cent combined, and 2 to 5 per cent free alkali—the latter generally as carbonate—and 60 to 70 per cent of fatty acids. According to Stockhardt, 100 parts by weight of fatty acids neutralise 12 to 14 parts of soda. The same authority gives the following figures as representing the solidifying points of the fatty acids of different soaps.[2]

---

[1] As the fatty acids exist in the soap as anhydride, but are weighed as hydrate, a correction is necessary. If the amount of fatty acid found be multiplied by 0·937, an approximately correct result is obtained.

[2] In the process for soap analysis I have for the most part adopted a method published in the *Chem. News.*, vol. 35, p. 2. The method is there communicated by Mr. C. F. Cross, a student in the laboratory of this college. The use of eosin as an indicator is a decided improvement upon that of litmus tincture or paper, as recommended by Dr. Fleischer.—*Tr.*

Fatty acids from	Solidifying points.
Pure tallow, ...	44° to 45° C.
Pure palm oil, ...	38° „ 39°
1 part tallow and ½ part cocoa-nut oil, .	29° „ 30°
Equal parts of tallow and cocoa-nut oil, .	27° „ 28°
1 part palm and ½ part cocoa-nut oil, .	27° „ 28°
Pure cocoa-nut oil, ...	23° „ 24°

§ 77.

Saltpetre.

Nitric acid is determined according to § 39. Hydrochloric and sulphuric acids are usually present; the former is determined by § 47, the latter by § 53.

Lime, if present, is estimated by dissolving in dilute nitric acid, adding ammonia and ammonium oxalate in excess, and treating the precipitate according to § 21.

If potash and soda are simultaneously present, the former is determined as tartrate (§ 12), after precipitating the lime by means of ammonium carbonate.

§ 78.

Gunpowder.

Water is determined by drying a portion in an exsiccator over sulphuric acid until the weight is constant for some hours.

The saltpetre is separated from the other constituents (sulphur and charcoal) by washing a weighed portion of the gunpowder on a filter with hot water until a few drops of the washings cease to leave a residue when evaporated on platinum foil. The washings are then evaporated somewhat, and the nitric acid is determined according to § 39. Sulphur is determined by gently warming a mixture of 1 part of the powder, 1 part of pure sodium carbonate, 1 part of pure saltpetre, and 6 to 8 parts of pure potassium chloride in a platinum crucible, and gradually increasing the temperature until the mass fuses quietly and becomes colourless. The fused mass is dissolved in water acidified with hydrochloric acid, and the sulphuric acid is determined by means of barium chloride (§ 53).

Carbon is determined either by drying that portion of the powder from which the nitre has been removed, at 100°, until it ceases to lose weight, and deducting the amount of sulphur contained therein; or by removing the sulphur by means of carbon disulphide, and drying and weighing the residue.

§ 79.

Crude Molasses Potash.

When molasses are fermented, and the alcohol is distilled off, a residue is obtained, which, after being heated in an oven, contains alkaline carbonates and other salts, especially salts of calcium, mixed with varying quantities of carbon.

The main point in the technical analysis of this residue consists in determining the amount of potassium carbonate. Inasmuch as soda is present along with potash and alkaline sulphates and chlorides, the potash cannot be determined by direct titration.

A portion of the sample is dried at 100° and weighed. A second portion is boiled for a few minutes with 50 to 100 parts of water, dried, and weighed. The residue, consisting of carbon, silicates of aluminium, iron, and calcium, calcium carbonate, and sometimes iron sulphide, is treated with hydrochloric acid; the residue is dried, weighed, ignited, and again weighed. The loss on ignition represents carbon, while the difference between the total weight insoluble in water and the carbon *plus* ash represents the portion soluble in acid.

The aqueous solution is generally coloured brown; this, if due to the presence of organic matter, may be overlooked, but if due to the presence of iron sulphide, probably points to the simultaneous presence of alkaline sulphides which have an alkaline reaction.

The aqueous solution is divided into two portions; in one the total carbonic acid is determined, in the other the respective quantities of soda and potash. If alkaline sulphides are present in any quantity, the aqueous liquid must be divided into three portions. Carbonic acid is determined according to § 8. In the event of alkaline sulphides being present, the liquid is precipitated with neutral barium chloride, and the precipitated barium carbonate (containing sulphate) is treated as directed in § 8. The second portion of the aqueous solution is acidified with hydrochloric acid, boiled to expel carbon dioxide, and precipitated with barium chloride. (If it be desired to determine sulphuric acid, a measured quantity of normal barium chloride is employed; excess of barium is precipitated by adding ammonia and ammonium carbonate, and from the amount of barium carbonate so obtained, determined alkalimetrically, the sulphuric acid is found.—§ 14). The filtrate, freed from barium, is evaporated to dryness in a weighed platinum dish, the ammonium salts are expelled by heating, and the residue, consisting of potassium and sodium chlorides, is weighed. The chlorine is then determined in the residue according to § 47, and the soda and potash calculated according to § 58. The sodium is calculated to carbonate, the amount of carbonic acid required is deducted from the total acid, and the residue is calculated to potassium carbonate.

Chlorine may be determined, according to § 47, in a portion of the aqueous solution, after acidification with nitric acid and removal of sulphuretted hydrogen.

Alkaline sulphides may be determined by precipitating the aqueous solution with ammoniacal zinc sulphate, and treating the precipitate according to § 30. Hydrochloric acid is added to the filtrate, but not in quantity sufficient to neutralise the whole of the alkali (sodium bicarbonate may be added if necessary), and any thiosulphate present is determined by titration with iodine (§ 33).

§ 80.

Liver of Sulphur.

Liver of sulphur is a mixture of different alkaline polysulphides with various alkaline sulphates and carbonates. A weighed portion is dissolved in 50 to 70 parts of hot water; any residue of free sulphur is filtered off, fused with 4 parts of potassium chlorate, 6 parts of sodium carbonate, and 2 parts of sodium chloride, and determined as sulphuric acid. The clear liquid is shaken for a few minutes with cadmium carbonate in a corked flask, and filtered; the precipitated cadmium sulphide is oxidised by fusion with the above-mentioned mixture, and the sulphuric acid found is determined. The sulphur so found was originally present as a polysulphide. The filtrate from precipitated cadmium sulphide may contain sulphuric and thiosulphuric acids. It is divided into two parts: in one part thiosulphuric acid is determined by iodine after addition of sodium bicarbonate; in the other sulphuric acid is estimated according to § 14 or 53, after boiling with hydrochloric acid and filtering from sulphur. If a portion of the original substance be fused with the oxidising mixture already mentioned, and the sulphuric acid be determined and calculated to sulphur, the amount so found should agree with the sum of the free sulphur, and the sulphur existing as polysulphide, as thiosulphate, and as sulphate. Any slight excess may be set down as due to small quantities of higher thionic acids.

From a determination of the sulphur existing as polysulphide, and of the total alkali, it is possible to tell with tolerable accuracy the formula of the polysulphide present (K_2S_2, K_2S_3, K_2S_4, or more probably K_2S_5), provided that one polysulphide only be present. The alkali existing as sulphate, carbonate, and thiosulphate is deducted from the total alkali, and the residue is calculated to that polysulphide whose formula most nearly agrees with the amount of alkali found. This calculation is checked by a determination of the sulphur existing as polysulphide.

The alkali existing as sulphate and as thiosulphate is calculated from the determination of these acids. The total alkali is determined by heating the original substance in an open crucible with a small quantity of ammonium nitrate, or with ammonium sulphate, until the whole of the free sulphur is driven off, and the alkali is converted into sulphate.[1]

Carbonic acid is estimated by adding potassium dichromate to the aqueous solution of the substance, acidifying with sulphuric or nitric (not hydrochloric) acid, and determining according to § 13.

Another method, which is quickly carried out, consists in digesting the finely-powdered substance with strong alcohol, whereby the sulphides only are dissolved. The alkalies may then be determined in the filtrate as sulphates after evaporating to dryness.

§ 81.

Bleaching Salts (Sodium, Calcium, and Magnesium Hypochlorites).

The technical analysis of a bleaching salt may seek to determine the amount of chlorine obtainable by saturating a solution of the salt with hydrochloric acid; or the amount of chlorine really existing as Cl_2O (ClO), *i.e.*, the bleaching effect of the solution.

If no oxyacid of chlorine other than hypochlorous be present, one determination gives an answer to both questions, 1 equivalent of Cl_2O being equal in bleaching effect to 2 equivalents of Cl.

In order to determine the amount of available chlorine, the solution is mixed with an excess of potassium iodide, after acidifying with hydrochloric acid, and the amount of iodine liberated is determined by means of thiosulphate solution, after addition of sodium bicarbonate.

1 equivalent of iodine = 1 equivalent of chlorine.

---

[1] Potassium salts are generally alone present in liver of sulphur; if soda is also present, it is determined along with potash in the residual sulphate; and the equivalent of potash is substituted for that of soda, as directed in § 58.

This method may generally be adopted for the valuation of bleaching liquors; 10 grams or so of bleaching powder are rubbed in a mortar with water, transferred to a ½-litre flask, which is made up to the mark with water, and 50 to 100 cb.c. of the turbid liquid are treated as above described.

In the event of chloric acid being present, Pennot's method is to be recommended for determining the amount of available chlorine. The bleaching liquid is saturated with sodium bicarbonate, and a deci-normal solution of arsenious oxide in sodium bicarbonate is run in from a burette until a drop of the liquid ceases to give a blue colour when spotted on filter-paper soaked in potassium iodide and starch paste.

$$198\ As_2O_3 = 142\ Cl\ (99\ AsO_3 = 71\ Cl).$$

Arsenious oxide does not reduce chloric acid in alkaline solution.

The ferrous sulphate method, described in § 25, gives very good results when chloric acid is absent.

The amount of available chlorine is sometimes stated, on the Continent, in degrees, which express the number of cb.c. of chlorine gas obtainable from 1 gram of the bleaching powder. As 1 cb.c. chlorine weighs 3·177 m.gm., 1 cb.c. of a solution of 4·436 grams As_2O_3 (4·436 grams AsO_3), in 1000 cb.c. of water containing sodium bicarbonate, will correspond to 1 chlorometric degree.

§ 82.

Gypsum.

Water is determined by noting the loss sustained on heating to incipient redness. The dry residue is boiled for a few minutes with a measured volume of normal potassium carbonate solution; the liquid, when cold, is made up to a certain volume, and sulphuric acid is determined in an aliquot portion according to § 17. If it be desired to determine calcium, which is generally the case in analyses of natural gypsum inasmuch as this mineral often contains carbonate and silicate of calcium, the precipitate obtained by boiling with potassium carbonate is dissolved in hydrochloric acid, and the calcium is precipitated by means of ammonium oxalate, and determined by § 21. Or the precipitate may be dissolved in a measured volume of normal hydrochloric acid, and the solution titrated as directed in § 8.

Other bases (iron, aluminium, magnesium), if present, may be determined, after fusion with soda, by the general methods detailed in § 65.

§ 83.

Boiler Crusts.

The main constituents of boiler crusts are gypsum and calcium carbonate. The former is determined by boiling the finely-powdered substance with normal potassium carbonate solution, and determining sulphuric acid in a portion of the filtrate, according to § 17, or, better, § 53.

Calcium is determined in the precipitate by the method given in the preceding paragraph.

The amount of calcium carbonate may be determined by washing the finely-powdered substance with hot water containing potassium chloride until the washings cease to render barium chloride solution turbid; the calcium carbonate in the residue, which is now free from gypsum, may be then alkalimetrically estimated.[1] If the crust contain much gypsum and little calcium carbonate, it is better to make an estimation of carbonic acid, and to calculate the calcium carbonate therefrom.

Boiler crusts also contain common salt, magnesium sulphate and other magnesium salts, and ferric oxide. It may be sometimes necessary to determine the amount of magnesia. This may be done by dissolving in hydrochloric acid, removing the lime by precipitation as oxalate, precipitating the magnesia in the filtrate as magnesium-ammonium phosphate, and determining according to § 52.

---

[1] The residue may contain alumina, sand, &c.; these substances may be dried and weighed as matter insoluble in hydrochloric acid.

Lime and magnesia may also be simultaneously precipitated and determined by § 65.

Alkalies may be determined by adding ammonium carbonate to the aqueous solution, filtering, and evaporating the filtrate to dryness.[1]

§ 84.

Bone Ash.

The composition of bone ash varies according to the method of manufacture employed. That made from fresh bones is much richer in fat and organic matter generally, than that prepared from weathered bones, &c. Water is determined by noting the loss suffered on heating to 100° or 120°; fat and other organic matters are found by heating the dry residue along with a fragment of ammonium nitrate until it is white.[2] The loss represents organic matter.

The ignited residue mainly consists of phosphates of calcium and magnesium, with sand and traces of iron; it is gently warmed with dilute hydrochloric acid, the sand is collected, and phosphoric acid is determined in the filtrate by mixing with sodium acetate solution containing free acetic acid, and running the liquid into a measured volume of standardised uranium test-solution, as directed in § 50.

The presence of iron renders this process rather inexact; in such a case the precipitate which appears on adding sodium acetate is filtered off, ignited and weighed, and one-half of the weight so obtained is set down as phosphoric acid.

Calcium may be determined by dissolving the bone ash in dilute hydrochloric acid, filtering, and precipitating with oxalic acid, followed by addition of sodium acetate.

---

[1] Concerning the formation of boiler crusts, compare the paragraph on water analysis.

[2] The ammonium nitrate used is prepared by cautiously heating the crystallised salt until it fuses; the salt must leave no residue when volatilised on platinum; it must contain no acid other than nitric.

The precipitated calcium oxalate, after washing until the washings cease to precipitate calcium acetate solution, is dissolved in hydrochloric acid, and the oxalic acid is determined by titration with permanganate (§ 21).

The amount of calcium existing as carbonate may be calculated from the results of a carbonic acid determination (§ 13).

Nitrogen is determined in the form of ammonia by burning with soda lime (§ 11).

Fat may be determined by treating a dried portion repeatedly with hot ether, and drying the residue at 120°; the difference represents fat. The sum of fat, water, and fixed residue deducted from the original weight represents the organic matter other than fat.

§ 85.

Bone Char.

The chief constituents of bone char are carbon, phosphoric and carbonic acids, lime, magnesia, iron oxide, sand, and organic matter. Traces of sulphuric and hydrochloric acids, and of alkalies, are also generally to be detected.

For the purposes of the sugar-refiner, an estimation of the amount of calcium carbonate in a sample of bone char is of paramount importance. This estimation is most readily and quickly accomplished by Scheibler's apparatus, a description of which is to be found in most works on general analysis.

For general purposes the following scheme of analysis may be adopted: Water is determined by drying at 100°; the residue is warmed with dilute hydrochloric acid, the insoluble matter is dried, weighed, ignited along with a fragment of ammonium nitrate, and again weighed; the difference between the two weighings represents organic matter and carbon. Lime, iron oxide, phosphoric acid, and magnesia are determined in the filtrate by the methods described in the preceding paragraph. Carbonic acid may be determined by § 13, and from this calcium carbonate may be calculated. From a knowledge of the amount of calcium carbonate present, the sugar-refiner determines the quantity of hydrochloric acid which he must add to the char in order to remove this salt without dissolving the phosphate of calcium.

Bone char frequently contains sulphides of calcium and iron; the total quantity of sulphur present in a sample of bone char may be determined by fusing with equal parts of soda and nitre, and boiling the fused mass with water, when the whole of the sulphur goes into solution as sulphuric acid. The solution also contains phosphoric acid; this is removed by precipitation with magnesia mixture; the filtrate is rendered slightly acid, mixed with calcium chloride, made alkaline with ammonia, and the sulphuric acid is determined according to § 53. Or, the char may be boiled with potassium carbonate, and the sulphuric acid determined in the filtrate. Another portion is acidified with hydrochloric acid, and the sulphuretted hydrogen evolved is determined by passing into ferric chloride and titrating the ferrous salt with permanganate.

§ 86.

Phosphorite, Coprolite, and Superphosphates.

Phosphorite and coprolite are naturally-occurring phosphates; superphosphate is produced artificially from these minerals. The estimation of phosphoric is the main object in the technical analysis of these substances. In *phosphorite* this acid chiefly exists as a calcium salt, partly also in the form of iron and aluminium salts. The finely-powdered mineral is heated with hydrochloric acid; the greater part of the acid is removed by evaporation in a porcelain dish. When the liquid has become thick, and of the consistence of syrup, it is diluted and filtered from the insoluble silica, which is washed with hot water containing hydrochloric acid. The slightly-acid filtrate is mixed with an excess of sodium acetate, whereby the iron and aluminium are precipitated as phosphates. If the filtrate is coloured red, it still contains iron; in this case it must be boiled and again filtered from precipitated iron phosphate. The phosphoric acid, existing in the filtrate as calcium phosphate, is then determined by titration with uranium solution, according to § 50 (inverted method). The precipitate containing iron and aluminium phosphate, after being washed with exceedingly dilute acetic acid, is dissolved in hydrochloric acid, reduced by means of sodium sulphite, the iron and aluminium precipitated by addition of potash and a few drops of sodium silicate solution, the filtrate acidified with hydrochloric acid, saturated with sodium acetate, and the phosphoric acid determined by titration with uranium solution.

The total quantity of phosphoric acid, as also that combined with iron and aluminium, is ascertained by this method. The lime may be determined, if desired, by precipitation as oxalate, after removing phosphoric acid and iron oxide.

The phosphoric acid in *coprolites* may be determined by the same method. In order to remove organic matter it is advisable to heat the mineral in a porcelain crucible along with three times its own weight of a mixture of equal parts of dry soda and nitre before evaporating with hydrochloric acid. Coprolites generally contain much less iron than is found in phosphorite.

Many processes have been proposed for determining the total quantity of phosphoric acid in phosphorite by a simple experiment; the most accurate is that in which the acid is precipitated by adding ammonium molybdate to the acidified solution. This process is, however, somewhat tedious, and is not therefore generally employed by the technical chemist.[1]

By adopting the following process the phosphoric acid and lime may be both determined by one precipitation: The solution of phosphorite in hydrochloric acid is mixed

---

[1] "It has been proposed by Macagno to reduce the precipitated ammonium phospho-molybdate by means of zinc and acid, and to titrate the solution so obtained with standard permanganate. The test experiments show a maximum error of 0·5 per cent of the phosphoric acid present."—*Tr.*

with oxalic acid, a little tartaric acid is added, followed by addition of excess of ammonia to the warm liquid. The whole of the lime is thus precipitated as oxalate, while iron and aluminium remain in solution. A quantity of "magnesia mixture" sufficient to precipitate the whole of the phosphoric acid is then added without previous filtration. The precipitate is collected, washed with warm ammoniacal water until the washings are free from oxalic acid, and dissolved in hydrochloric acid. The liquid is made up to a determinate volume (200 cb.c., for instance), and divided into two equal portions. From one half oxalic acid is removed by addition of chlorine water or sodium hypochlorite, and phosphoric acid is determined therein by § 50 (inverted method). The other half is titrated with permanganate, and from the oxalic acid found the amount of lime is calculated. This method is especially to be recommended when the phosphoric acid determination is the main object of the analysis, and when iron and aluminium are present in small quantities only. If much iron be present, it becomes necessary to add a large quantity of tartaric acid, and the precipitation of phosphoric acid by means of magnesia mixture is not then complete.

In *superphosphates* the greater part of the phosphoric acid is contained as a soluble phosphate. A weighed quantity is rubbed in a mortar with cold water, the solution is filtered,[1] the filtrate is transferred to a litre flask, which is filled to the mark with water, and an aliquot portion is withdrawn; an excess of sodium acetate is added, any precipitate of iron or aluminium phosphate which may form is filtered off and treated as already directed, and the filtrate is titrated against standard uranium solution. If it be desired to estimate the phosphoric acid remaining in the insoluble portion of the superphosphate, the process described under phosphorite is applicable.

The so-called "reduced phosphates" may be determined, according to Fresenius, by digesting the washed residue

---

[1] Some chemists wash the residue with *hot* water.—*Tr.*

for half an hour with ammonium citrate, filtering, and precipitating with magnesia mixture.[1]

§ 87.

Commercial Alums and Aluminium Salts.

The alums which are of commercial importance are those of potash, ammonia, iron, and chromium.

In an alum analysis, determinations of the sesquioxides (of aluminium, iron, chromium), of the sulphuric acid, and of the alkalies, are required. It is sometimes also necessary to estimate impurities—for instance, oxide of iron in potash alum.

Sulphuric acid is determined by dissolving a weighed quantity of the alum in hot water, acidifying with hydrochloric acid, and precipitating by addition of strontium nitrate and alcohol, as directed in § 14, or the process detailed in § 53, *c*, may be adopted. In a second portion alumina may be determined by the process given in § 51.

Potash may be determined by precipitating the sesquioxides by means of ammonium sulphide, from a solution in hot water, washing, dissolving the precipitate in hydrochloric acid, diluting, reprecipitating with ammonium sulphide, and filtering. The two filtrates are then mixed, the liquid is acidified with sulphuric acid, boiled until the sulphur has all separated, filtered, and evaporated to dryness in a weighed platinum dish; the residue is ignited and weighed as potassium sulphate.

Or the solution of the alum is acidified with acetic acid, the aluminium is precipitated by addition of ammonium phosphate, the liquid is filtered, and made up to 300 cb.c.; the phosphoric acid is removed from 100 cb.c. by adding ferric acetate to the boiling liquid, and the potassium is precipitated in the filtrate as tartrate, according to § 12. In this process the aluminium is obtained, free from alkali, in the form of phosphate.

---

[1] The general opinion among analytical chemists seems to be that this process, as indeed all processes for determining "reduced phosphates," is altogether fallacious.—*Tr.*

The general method detailed in § 65 for the estimation of alkalies is very applicable in the analysis of alums. In carrying out this process the alum is dissolved in hot water, an excess of baryta water (free from alkali) is added, carbon dioxide is passed through the liquid, and, after filtration, potash is determined according to § 8. I have convinced myself by experiment that the carbonate of barium, after washing with water, retains none of the alkali. Ammonia may be determined in an alum by boiling with potash, and proceeding according to § 11.

Iron and chromium alums are analysed by processes similar to those just described; iron is reduced by means of zinc in sulphuric acid solution, and determined according to § 19. Chromium is determined by precipitation as barium chromate, according to § 26 or 27, after fusing the dry alum with sodium carbonate and potassium chlorate, or after boiling the solution with potash and bromine.

The foregoing processes are applicable to the analyses of burned alums. Of the other aluminium salts occurring in commerce, the most important are the sulphate and the acetate.

The determination of alumina is the main point in the analysis of these salts; in the case of the former salt the estimation of free sulphuric acid is also of importance. A solution of commercial sulphate of alumina in hot water contains the whole of the alumina and sulphuric acid; if there be any residue insoluble in water, its weight may be determined, but, generally speaking, it is not necessary to analyse it, at any rate not quantitatively.

Alumina is determined by § 51, attention being paid to the directions there given in the event of considerable quantities of iron being present. The total amount of sulphuric acid is determined by § 53. If no sulphates other than sulphate of aluminium be present, it is only necessary to calculate the aluminium found to sulphate—Al_23SO_4 ($Al_2O_33SO_3$)—and to deduct the amount of sulphuric acid required from the total acid found, in order to obtain the amount of free sulphuric acid. In the event of other sulphates being present, the process may be modified as follows:[1] The aluminium sulphate is converted into potash alum by adding half as much pure potassium sulphate as the weight of the substance taken, dissolving the whole in water, and evaporating to 20 or 30 cb.c. A volume of alcohol equal to twice the volume of the liquid is now added, and after standing for one hour the liquid is filtered from the precipitated potash alum. The free acid is determined in the filtrate by titration with half-normal ammonia.

A solution of acetate of alumina is sometimes met with in commerce. The alumina in such a solution may be determined according to § 51.

Some samples of acetate of alumina contain only acetates of aluminium and of potassium; other samples contain also sulphate of potassium. The latter precipitate a basic double sulphate rich in aluminium.

It becomes therefore generally necessary to determine sulphuric acid in samples of commercial acetate of alumina. Inasmuch as the liquid is prepared from potash alum by decomposing with lead acetate, it will contain one equivalent of potash (K_2O) for each equivalent of alumina (Al_2O_3); the amount of the latter being determined, it is therefore possible to calculate that of the former. If the amount of sulphuric acid be also determined it is easy to calculate whether this is more than sufficient to combine with the whole of the potash; if it is, the liquid contains aluminium sulphate in addition to potassium sulphate—*i.e.*, it contains undecomposed alum; if it is not, potassium sulphate only is present in addition to aluminium acetate.

The sulphuric acid determination is best effected by adding hydrochloric acid, strontium chloride, and an equal volume of alcohol to the solution. The precipitated strontium sulphate, after washing with alcohol, is titrated according to § 14 or 53. Acetic acid may be separated by distillation, after addition of sulphuric acid, and determined by direct titration in the distillate.

The iron present may be determined by the iodometric

---

[1] The sulphates generally present in commercial sulphate of alumina are those of magnesium, potassium, and calcium.

process of § 38; or the liquid may be mixed with tartaric acid, ammonia added in excess, and the iron precipitated as sulphide by addition of ammonium sulphide. The precipitate, after washing, may be dissolved in sulphuric acid, the sulphuretted hydrogen removed by boiling, and the iron (after reduction of any traces of ferric salt) determined by permanganate.

§ 88.

Chrome Iron Ore.

The main constituents of this mineral are chromium oxide and ferrous oxide, with a little alumina and magnesia. A technical analysis generally seeks to determine the quantities of chromium and iron. About 1 gram of the very finely-powdered mineral is mixed with 8 parts of fused borax in a platinum crucible, which is then heated to full redness for half an hour, the contents of the crucible being shaken up from time to time. Dry potassium or sodium carbonate is then gradually added until the mass ceases to effervesce; from time to time small quantities of potassium chlorate are added, and the heating is continued until the mass fuses quietly and is of a yellow colour throughout. After cooling, the chromate of potassium is dissolved in hot water, the solution is mixed with a measured volume of standardised ferrous sulphate solution, and the residual ferrous salt is determined by titration with permanganate (§ 26). If the presence of undecomposed potassium chlorate (or hypochlorite) be suspected in the liquid obtained by treating the fused mass with hot water, it is better to precipitate the chromic acid by addition of barium chloride or lead acetate, and to proceed according to § 27.

Iron may be determined by dissolving the fused residue, insoluble in water, in sulphuric acid, reducing ferric to ferrous salt by means of zinc, and titrating with permanganate. If necessary, the magnesia may also be determined in this residue by dissolving in hydrochloric acid, adding tartaric acid and excess of ammonia, and precipitating by addition of ammonium phosphate (§ 52).

§ 89.

Commercially-important Chromates.

Certain chromates are employed as colour-materials; the most important are the chromates of potassium, lead, and copper. The method for estimating chromic acid in the two former salts has been already described (§§ 26 and 27).

In the case of the copper salt, a finely-powdered and weighed quantity is boiled with caustic potash until the residue is black, the liquid is filtered, and after washing the residue with hot water, is acidified with sulphuric acid, and chromic acid is determined according to § 26.

Copper may be determined by dissolving the black residue in hydrochloric acid, and precipitating as cuprous oxide by means of grape-sugar after addition of potash and tartaric acid (§ 22).

Lead may be determined in lead chromate by digesting with sulphuric acid and dilute alcohol at a gentle heat, filtering, washing with dilute alcohol until a drop of the washings ceases to leave a green residue when evaporated on platinum foil, decomposing the lead sulphate by means of potassium carbonate, and determining the lead carbonate, after careful washing with hot water, in accordance with § 8.

Potassium is most easily determined in the chromates of this metal by precipitating the chromic acid as lead chromate, filtering, removing the lead by addition of sulphuretted hydrogen, and precipitating the potassium as tartrate (§ 12). Or the salt may be dissolved in water, the chromium precipitated by ammonia after reduction by means of hydrochloric acid and alcohol, the filtrate evaporated to dryness in a platinum dish, and the residue ignited and weighed as potassium chloride.

Potassium chromates usually contain small quantities of sulphuric acid, which is best determined by precipitation and weighing as barium sulphate in the acidified solution. Or a measured quantity of standardised barium chloride solution may be added to the solution of the chromate containing a little nitric acid, followed by addition of excess of ammonia. The amount of chromic acid in the precipitate which forms is then determined, and is calculated to barium chromate; by deducting the amount of barium so used from the total barium chloride added a residue is obtained representing barium combined with sulphuric acid, and from this the amount of the acid itself is readily deduced.

§ 90.

Manganese Estimation.

The value of a sample of manganese ore is dependent upon the quantity of available oxygen which it contains. The amount of oxygen yielded by manganese ores when heated is not always the same as that obtained by the action of acids and reducing agents upon the same ores. By the quantity of available oxygen is generally understood the amount of oxygen contained in the ore over and above that required to form manganous oxide (MnO). For the determination of this available oxygen the method described in § 23 may be adopted. Inasmuch, however, as many manganese ores contain oxides of manganese other than the peroxide, accompanied with oxides of iron, aluminium, &c., and also varying quantities of moisture, it is necessary that the estimation of available oxygen should be preceded by certain preliminary determinations.

In the analysis of manganese ores great care must be taken to obtain a fair average sample of the whole quantity. At least 100 grams should be reduced to tolerably fine powder in an agate mortar, and 10 grams of this quantity should be again more finely powdered, and placed in a well-stoppered tube. A weighed portion is dried at 100° for 6 to 8 hours, or at 120° for an hour and a half; the whole of the hygroscopic moisture is thus driven off, unaccompanied by any of the water of hydration. The process of § 23 may then be carried out with another portion of the ore. The reduction by means of ferrous sulphate is most readily performed in a flask fitted with a cork and exit tube which dips beneath the surface of boiled water. On withdrawing the source of heat from underneath the flask, the water rushes back.

Pyrolusite often contains manganese sesquioxide (Mn_2O_3) in addition to peroxide (MnO_2). In order to determine the quantities of each oxide, an estimation of the total amount of manganese is necessary. In the absence of manganous oxide (MnO), this may be effected by the method of Mohr. The available oxygen is determined in a portion of the sample. Another portion is heated to redness for fifteen minutes or so in a platinum crucible; the whole of the manganese is thus converted into manganoso-manganic oxide (Mn_3O_4). By titrating the ignited residue with ferrous sulphate, the amount of manganese may be found.

$$Mn_3O_4 + 2FeSO_4 + 4H_2SO_4 = 3MnSO_4 + Fe_2 3SO_4 + 4H_2O.$$

2 equivalents of ferrous converted into ferric sulphate correspond to 3 equivalents of manganous oxide (MnO). The amount of oxygen required to convert the whole of the manganous oxide into sesquioxide is then found (this is done by multiplying the manganous oxide by $\frac{8}{71}$), and this is deducted from the total available oxygen as previously determined. The residue is noted; the quantity of manganese sesquioxide (Mn_2O_3) which this residue is capable of transforming into peroxide (MnO_2) is calculated; the sesquioxide thus found is deducted from the total sesquioxide already determined; the difference represents the quantity of sesquioxide in the sample.

It is often necessary to determine the amount of chlorine which is liberated by the action of a sample of manganese ore upon hydrochloric acid. For this purpose Mohr's apparatus (Fig. 14) is employed. The sample is placed in the small balloon along with an excess of strong pure hydrochloric acid; the exit-tube is somewhat narrowed at the orifice, and is from 320 to 340 millims. in length and from 25 to 30 millims. in width. The large test-tube, into which the exit-tube passes, contains a solution of potassium iodide. The liquid in the flask is boiled so long as chlorine is evolved; after cooling, the tube containing the potassium iodide is disconnected, the contents are washed into a flask (the exit-tube being also washed), and the free iodine is determined by titration with sodium thiosulphate. In order to determine whether the whole of the chlorine has been obtained, a fresh quantity of potassium iodide may be placed in the large test-tube, the apparatus may be arranged as before, and the heating continued.

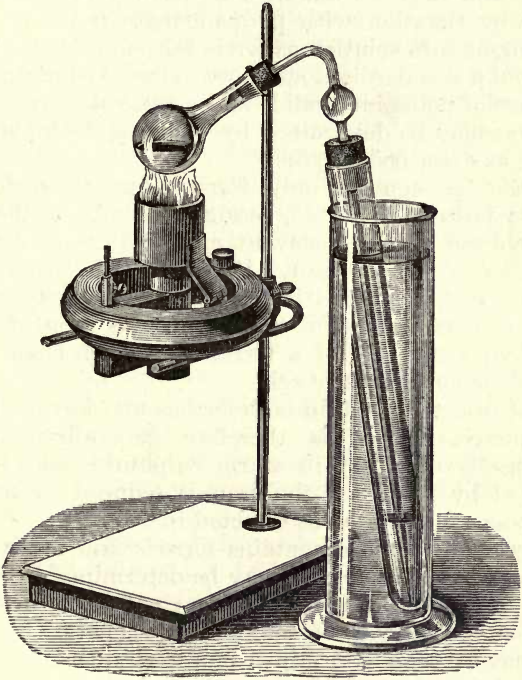

Fig. 14.

The method described in § 38 may also be adopted for the determination of the amount of available chlorine; but Mohr's method, as just described, is to be preferred.

§ 91.

Analysis of Iron Ores.

The examination of an iron ore generally consists in the determination of iron, alumina, and phosphoric acid.

The iron may be obtained as ferrous salt, and determined by titration with permanganate (§ 19), or it may be brought into solution as ferric salt, and determined by means of a standardised stannous chloride solution in the presence of potassium iodide and a little starch; or, lastly, the iron may be determined by warming with potassium iodide, as described in § 38.

If the ore contain only ferric salts, the iodometric method is to be preferred, because it admits of the use of hydrochloric acid as a solvent, and does not necessitate a reduction of the iron salt. If ferrous and ferric salts are both present, I prefer titration with permanganate, inasmuch as it is easier to obtain a pure solution of ferrous salt, than a solution of a ferric salt which shall be free from chlorine and nitric acid.

Most iron ores contain both ferrous and ferric salts; the oxydimetric method is therefore generally employed. The ore is dissolved in warm sulphuric acid, silica is removed by filtration, the iron is reduced by means of pure zinc, and titrated as directed in § 19.

Magnetic iron ore contains ferrous and ferric oxides. The amount of the former may be determined by dissolving a weighed quantity in warm sulphuric acid, with addition of crystals of sodium bicarbonate. The total iron may be then determined in a fresh quantity, and the ferric oxide calculated from the two results.

Hœmatite usually contains ferric oxide, water, and gangue. The water is determined by heating a portion in a bulb of hard glass in a current of air which has been dried by means of calcium chloride. The loss represents water. The residue in the bulb may then be heated in hydrogen, the iron so obtained dissolved in sulphuric acid, and determined by titration with permanganate. If the sample contain phosphoric acid, carbonic acid,

&c., it is better to adopt the method to be described for the analysis of brown iron ores.

Brown iron ore should be dried in an exsiccator for a considerable time before analysis. Water is determined in the sample by heating a weighed portion in a tube containing lead carbonate, and connected with a weighed calcium chloride tube. The portion of the tube nearest to the closed end should contain only lead carbonate, the central part the same salt mixed with the sample, and the anterior part a layer of lead carbonate alone. The heating is carried out in a gas furnace; heat is first applied to the part of the tube nearest the orifice.[1] If carbonic acid be absent, water may be determined by noting the loss of weight which the sample suffers when ignited.

5 grams of the sample, dried in an exsiccator, are evaporated to dryness with hydrochloric acid; the silica is collected and weighed. In a portion of the filtrate iron is determined by § 38; in another portion phosphoric acid is determined by § 50, after separation from iron and alumina by § 57. Sulphuric acid, if present, is determined by saturating a considerable portion of the solution with sodium acetate, boiling, filtering, and proceeding, after acidification, according to § 53.

Alumina, after separation from iron and phosphoric acid by § 57, is determined in accordance with § 51; it may also be determined by § 65.

Lime and magnesia, if present, may be separated and determined as described in § 65.

Manganese may be determined as described in the preceding paragraph, after conversion into manganoso-manganic oxide (Mn_3O_4), by strongly heating a portion of the ore. If organic matter be present, the sample should be heated gently, then moistened with nitric acid and heated again; reduction of the iron oxide is thus avoided.

Bog iron ore is analysed by the method just described for the brown ores. Organic matter and water may be determined by gently heating a portion in an open platinum crucible and noting the loss.

---

[1] The lead carbonate is prepared by heating a quantity of the pure salt to incipient decomposition, and cooling in an exsiccator.

The total iron in *spathic iron ore* is determined by permanganate, after solution in dilute sulphuric acid. Another larger portion of the solution is made slightly alkaline by addition of ammonia, saturated with sulphuretted hydrogen, acidified with a considerable quantity of acetic acid and boiled; the manganese remains in solution, while most of the iron is precipitated. The manganese is precipitated in the filtrate by addition of sodium hypochlorite, and determined as already described (compare § 65).

Lime and magnesia are best determined in spathic ores by dissolving a portion of the ore in hydrochloric acid, removing iron and manganese by addition of ammonia and ammonium sulphide, and proceeding according to § 65.

Carbonic acid is determined by § 13.

§ 92.

Iron Pyrites.

Iron pyrites is used in the manufacture of oil of vitriol, of green vitriol, and of sulphur. It usually contains, in addition to ferric sulphide, sulphides of copper, arsenic, and antimony, and frequently also sulphides of zinc and manganese. For technical purposes, determinations of iron and of sulphur are usually sufficient.

A weighed portion of the finely-powdered substance is fused in a porcelain crucible with 4 parts of a mixture—in equal proportions—of sodium carbonate and potassium nitrate; the fused mass is dissolved in very dilute nitric or hydrochloric acid. Iron is precipitated by boiling the solution with an excess of potassium carbonate, the precipitated hydrate is dissolved in sulphuric acid, and the iron is determined by means of permanganate. The filtrate is acidified with hydrochloric acid, the carbonic acid is expelled by boiling, the liquid is rendered alkaline by addition of ammonia, and sulphuric acid is determined by § 53. The amount of sulphur in pyrites, and in many other natural blendes and sulphides, may be readily determined by fusing with a mixture of 6 parts potassium chlorate, 4 parts sodium carbonate, and 2 parts common salt. If the amount of normal hydrochloric acid required to neutralise the sodium carbonate employed has been determined, and if the quantity of sodium carbonate employed has been carefully weighed, it is only necessary to dissolve the fused mass in water, and to titrate with standard hydrochloric acid in order to determine the amount of sulphur.

Suppose that the quantity of sodium carbonate used required 70 cb.c. normal hydrochloric acid for neutralisation, and suppose that 32 cb.c. were required after fusion, the equivalent of 38 cb.c. hydrochloric acid in sulphuric acid, $= 38 \times 49 = 1862$ m.gm. H_2SO_4, was formed in the process of fusion, the amount of sulphur in the sample was therefore $\frac{16 \times 1862}{49} = 608$ m.gm. (In old notation we have $38 \times 40 = 1520$ m.gm. SO_3, and $\frac{16 \times 1520}{40} = 608$ m.gm. sulphur.) For 1 gram of pyrites about 4 grams of sodium carbonate should be employed. The solution of the fused mass may be advantageously made up to a given volume, and an aliquot portion withdrawn for the titration. The same may be done with the preliminary titration of the sodium carbonate employed.

If arsenic be present in any quantity, the sulphuric acid must be removed from the acidified solution by addition of barium chloride (§ 14), and determined directly. If but little arsenic be present, the sulphuric acid may be directly titrated by § 53, with addition of calcium chloride to precipitate arsenic acid.

The whole of the sulphur contained in pyrites is not obtained either in the manufacture of sulphur or of sulphuric acid.

§ 93.

Calamine.

Calamine is composed principally of zinc carbonate, but generally contains, in addition, oxides of cadmium, lead, iron, calcium, manganese, &c., along with silica.

Water is determined by heating a finely-powdered portion of the mineral to 100° until it ceases to lose weight. The dry substance is then dissolved in dilute hydrochloric acid in a beaker covered with a watch-glass; the beaker is warmed until the residue of silica appears white. The liquid is saturated with sulphuretted hydrogen (cadmium may be determined in the precipitate by § 65), and filtered; the filtrate is saturated with sodium acetate, and the zinc is precipitated as sulphide by passing sulphuretted hydrogen into the liquid. The sulphide of zinc is washed and treated as directed in § 30.

The other constituents of calamine may be determined, if necessary, by processes which have been already detailed.

§ 94.

Zinc Ore.

The zinc may be determined in this ore by the process described in the foregoing paragraph. It is necessary, however, to evaporate down with strong hydrochloric acid; the ore is a silicate of zinc.

§ 95.

Zinc Blende.

If it be desired to determine zinc only, the finely-powdered mineral may be digested with strong nitric acid, filtered, the filtrate boiled down with hydrochloric acid, diluted and saturated with sulphuretted hydrogen. The remainder of the process is the same as that described in § 93.

Sulphur and zinc may be determined in one portion of the mineral by fusing with 4 parts of a mixture of sodium carbonate and nitre in equal proportions, boiling the fused mass in water, and proceeding as described in § 92. The residue insoluble in water may be dissolved in hydrochloric acid, and the zinc determined in the solution.

§ 96.

Galena.

Galena sometimes contains silver.

8 to 10 grams of the mineral in fine powder are heated in a flask with nitric acid free from chlorine, and the liquid is evaporated to dryness. If any dark-coloured specks remain, the process is repeated. The mass is then covered with dilute sulphuric acid, the residue is collected and washed with water containing sulphuric acid; silver is determined in the filtrate by § 47. The residue is transferred to a beaker, and boiled for five or ten minutes with a concentrated solution of sodium carbonate, whereby sulphate is converted into carbonate of lead. The carbonate is collected, washed, and determined according to § 8; or it is dissolved in nitric acid,[1] the solution is saturated with sodium acetate, and the lead is determined by § 27.

Instead of converting the sulphate of lead into carbonate, it may be dissolved in excess of ammonium acetate or tartrate; the lead may be then precipitated by addition of potassium chromate, and determined by § 27.

Or the general separation method of §§ 64 and 65 may be adopted, with digestion after addition of ammonium acetate and potassium dichromate.

Galenas which contain very little silver are fused in a Hessian crucible with 4 parts of soda and ½ part of nitre. The regulus thus produced is dissolved in nitric acid, the lead is precipitated by addition of sulphuric acid, and the silver is determined in the filtrate.

§ 97.

Copper Ores.

The ores of copper may be divided into two classes—*oxides* and *sulphides*. The former contain protoxide or

---

[1] If the lead does not completely dissolve, either the boiling with sodium carbonate has not been sufficiently prolonged, or the precipitate has not been washed completely.

peroxide of copper, associated with varying quantities of different acids; the latter not unfrequently contain sulphide of arsenic and other metallic sulphides along with copper sulphide. The most important ores of copper belonging to the first class are *red copper ore* (cuprous oxide), and *malachite* and *azurite* (basic carbonates).

Of those ores which contain sulphide of copper, the most common are *copper glance* (cuprous sulphide), *copper pyrites* (cuprous sulphide with ferrous sulphide), and *fahl ore* (containing sulphides of antimony and arsenic, and frequently of many other metals).

Determination of the copper is the main point in the technical analysis of these minerals. This may be effected in the case of those ores which contain the copper as oxide, by warming a portion of the finely-powdered mineral with tolerably strong hydrochloric acid until it is thoroughly decomposed, filtering from silica if necessary, nearly neutralising with sodium carbonate, boiling with sodium sulphite until the iron is reduced to ferrous chloride, and precipitating the copper as sulphocyanide by addition of potassium sulphocyanide.

The precipitate, after being washed until the washings cease to colour potassium ferricyanide solution blue, is removed from the filter and boiled with caustic alkali; the precipitated cuprous oxide is collected and washed; the copper is then determined according to § 22.

Or the following process may be adopted. The mineral is dissolved in sulphuric acid—lead sulphate is removed by filtration, if necessary,—the solution is partially neutralised by addition of ammonia, stannous chloride containing ammonium chloride is added until a drop of the liquid ceases to give a red colour with an acidified solution of potassium sulphocyanide, and the copper is precipitated as cuprous iodide by addition of potassium iodide. After complete washing, the precipitate is boiled with an excess of ferrous sulphate until the whole of the iodine is expelled; the copper is then determined by means of permanganate (§ 22).

If lead be absent, the mineral may be dissolved in hydrochloric instead of sulphuric acid. If silver be present, it is advisable to dissolve in sulphuric acid, with addition of a little hydrochloric; to warm this residue with nitric acid, to add excess of ammonia, and after filtration to precipitate the silver by addition of sulphuretted hydrogen, and to proceed as directed in § 47.

Copper may be determined in those minerals in which it exists in the form of sulphide, by fusing one part of the finely-powdered substance with 5 parts of potassium chlorate, 4 parts of sodium carbonate, and 3 parts of sodium chloride in a porcelain crucible, boiling the fused mass with water (sulphuric acid may be determined in the solution), dissolving the residue in hydrochloric acid, and after removing lead by addition of sodium sulphate, precipitating the copper as cuprous iodide or sulphocyanide. Silver, if present, will be found in that portion of the fused mass which was insoluble in hydrochloric acid; it may be determined by treating this residue with nitric acid, ammonia, &c., as already directed. The process of fusion occupies about ten minutes; care must be taken to mix the materials of the flux in the proportions stated above.

§ 98.

Tin Ore.

The mineral, after being finely powdered, is heated to fusion in a covered porcelain crucible, with six times its own weight of a mixture of equal parts of dehydrated sodium carbonate and flowers of sulphur. Fusion is continued until the whole of the free sulphur is burned away; the mass is then dissolved in hot water. The liquid, after filtration, contains the whole of the tin in the form of sodium sulphostannate: it is boiled with addition of bromine or sodium hypochlorite, in order to oxidise the greater part of the sulphur, mixed with a little ammonium sulphide, and acidified with hydrochloric acid.

The precipitated stannic sulphide, mixed with free sulphur, is collected and washed, first with sal-ammoniac solution, then with carbon disulphide; when the disulphide has evaporated, the precipitate is dissolved in ferric chloride solution, and the tin is determined in accordance with § 30. If the tin ore should contain estimable quantities of arsenic and antimony, the method of separation described in § 63 must be adopted.

§ 99.

Cinnabar.

Determination of mercury only is required in the technical analysis of cinnabar. The mineral is dissolved by warming with concentrated hydrochloric acid, with addition from time to time of small quantities of potassium chlorate. Or the ore may be brought into solution by heating it with excess of concentrated caustic potash solution and bromine water for some time, and then acidifying with hydrochloric acid. The solution is heated with addition of sodium sulphite until the smell of sulphur dioxide is apparent, ferrous sulphate solution is added, the liquid is saturated with caustic soda, and again acidified, after a few minutes, by addition of sulphuric acid; the whole of the mercury remains undissolved as mercurous bromide or chloride. The residue is washed with water containing a little sulphuric acid, until it is perfectly white, and the mercury is determined iodometrically by the process of § 40.

Appendix to § 99.

J. B. Hannay has described a very accurate and easy method of determining mercury volumetrically.[1] The cinnabar is dissolved in aqua regia, the solution is diluted, filtered if necessary from undissolved sulphur, neutralised by addition of caustic potash, and mixed with a few drops of ammonia. A standardised solution of potassium cyanide is then run in until the precipitate is completely dissolved. In order to determine the exact point of solution of the last trace of precipitate, light is caused to pass into the liquid through a bulb filled with water, and placed close to the vessel in which the operation is carried out. So long as the smallest particle of solid matter is suspended in the liquid, the path of the rays can be traced through the vessel; the instant that the last particle of solid is dissolved, the lines of light in the liquid disappear. The cyanide solution is standardised against pure mercuric chloride.—*Tr.*

---

[1] *Chem. Soc. J.* (2), xi. 565.

§ 100.

Estimation of Arsenic and Antimony in Minerals.

Arsenic and antimony very frequently occur in the natural metallic sulphides, especially in fahl ore, pyrites, lead glance, zinc blende, &c.

The same elements form the principal constituents of certain minerals, such as kupfer nickel, speiss cobalt, &c.

Antimony appears to accompany arsenic only in sulphur-containing minerals. The method for determining arsenic and antimony in those minerals in which they occur differs somewhat from that already described in §§ 35 and 36.

The mineral is finely powdered, and decomposed by means of fuming nitric acid added in small successive portions, or by treating with excess of caustic potash along with bromine water. The former method is specially applicable when the mineral contains but little arsenic; it is more easy to oxidise the sulphur completely by the second method.

The whole of the sulphides of the metals of the fifth and sixth groups may be decomposed by treatment with caustic potash and bromine or chlorine; the more negative the metal, the more quickly is the action accomplished.

The decomposed mineral is brought into solution by addition of a mixture of hydrochloric and tartaric acids; the liquid is filtered, if necessary, from lead and silver chlorides, boiled with sodium sulphite in order to reduce the arsenic to arsenious oxide, and saturated with sulphuretted hydrogen gas.

Arsenic and antimony are thus precipitated as sulphides along with the metals of the fifth and sixth groups.

The precipitate is allowed to settle, the supernatant liquid is decanted, and the residue is warmed with concentrated hydrochloric acid.

Everything is thus dissolved excepting the sulphides of arsenic and copper. The arsenious sulphide is dissolved in ammonium carbonate, and the solution is treated as directed in § 63.

Antimony may be separated from those metals which accompany it in the solution in hydrochloric acid, and determined according to § 63.

If the alkaline liquid be made strongly acid by means of hydrochloric acid, the arsenic reduced to arsenious oxide by sodium sulphite, and the liquid be rapidly saturated, at 50° to 60° with sulphuretted hydrogen, a precipitate is obtained containing the whole of the arsenic, but free from antimony (lead, cadmium, &c.). The precipitate may then be treated with ammonium carbonate, &c.

In the estimation of arsenic in minerals containing much copper, it is advisable to precipitate the copper as sulphocyanide, after reducing with sodium sulphite, before passing sulphuretted hydrogen into the liquid.

The other metals in arsenical minerals may be separated and determined by the general method of § 65. The mineral is dissolved in concentrated nitric acid (silica, alumina, &c., are filtered off), the solution is boiled down with hydrochloric acid, diluted. and saturated with sulphuretted hydrogen. The precipitate is treated with ammonium sulphide, &c.

§ 101.

Estimation of Bismuth.—*Tr.*

In § 27 a method for determining bismuth has been described, based upon the facts that neutral bismuth solutions are precipitated by addition of potassium chromate or dichromate, and that the chromate of bismuth so produced, when brought into contact with a ferrous salt, converts it into ferric salt.

The translator has shown[1] that the final point in the precipitation of bismuth by means of potassium dichromate may be determined by bringing a drop of the supernatant liquid into contact with a drop of silver nitrate solution spotted upon a white slab.

The bismuth may be separated from other metals by the general method of § 65.

---

[1] *Chem. Soc. J.*, vol. I., 1876, p. 483, and vol. I., 1877, p. 658.

A solution of potassium dichromate is prepared by dissolving 5 grams or so of the recrystallised salt in 1000 cb.c. of water. A quantity of pure bismuthous oxide (Bi_2O_3) is dissolved in the minimum quantity of nitric acid, and sodium acetate is added in quantity sufficient to dissolve the precipitate which first forms. A large excess of the acetate is to be avoided. The solution is made up to a known volume, an aliquot portion is heated to boiling, and the potassium dichromate solution is run in from a burette in successive small quantities. The liquid is boiled for one or two minutes after each addition of dichromate: the precipitate is allowed to settle, and a drop of the supernatant liquid is brought on to a white slab, and is there mixed with a drop of neutral silver nitrate solution. The production of a faint pink colour shows that a sufficient quantity of dichromate has been added. From the mean result of several determinations the value of the dichromate, in terms of bismuth or of bismuthous oxide, is deduced.

In using the standardised dichromate solution the same process is followed. The bismuth is precipitated as oxychloride or as mixed oxychloride and other salts, the precipitate is dissolved in the smallest possible quantity of nitric acid, sodium acetate is added, and the dichromate is run in until precipitation is complete.

A better process than the foregoing for the estimation of bismuth has been lately devised by the translator.

Bismuth is completely precipitated from solutions containing free acetic acid by means of sodium phosphate. The precipitate has the composition expressed by the formula $BiPO_4$. The solution containing bismuth, which must be free from hydrochloric or sulphuric acid, is mixed with a considerable excess of sodium acetate, the liquid is heated to boiling, and a measured volume (excess) of standardised sodium phosphate solution is run in. After boiling for a few moments, the liquid is filtered into a measuring flask, the precipitate is well washed with hot water, the contents of the flask are made up to the mark, and phosphoric acid is determined in an aliquot portion according to the inverted uranium process of § 50.

The sodium phosphate solution used may be of any convenient strength, provided the relation between it and the standard uranium liquid be determined. A $\frac{1}{20}$-normal phosphate solution (35·8 grams to 1000 cb.c.) is convenient. 1 cb.c. of such a solution precipitates 21·0 m.gm. of bismuth. It is preferable to employ sodium phosphate rather than microcosmic salt as precipitant. The titration with uranium may be carried out without filtration from precipitated bismuth phosphate, but the method recommended above gives rather more accurate results.

If bismuth be separated from other metals by the method given in the table, pp. 168, 169, the precipitate must be dissolved in nitric acid and boiled down repeatedly, with addition of the same acid, until all traces of hydrochloric acid are removed, before precipitating with sodium phosphate.

§ 102.

Analysis of Alloys.

a. *Copper-Zinc Alloys* (*Brass, Tombac, &c.*).

The alloy, hammered or rolled into a thin sheet, is dissolved by warming with moderately concentrated nitric acid. If a residue (stannic oxide) remain, it is filtered off. The solution is mixed with sal-ammoniac, and saturated with ammonia, in order to precipitate lead and iron. After filtration, the liquid is divided into two portions. In one portion copper is determined by the process of § 22. The other portion is saturated with sulphuretted hydrogen and filtered; the filtrate is mixed with an excess of sodium acetate, and again saturated with sulphuretted hydrogen. The precipitated zinc sulphide is treated according to § 30.

Or § 65 may be followed, the copper being precipitated as sulphocyanide, and the zinc as sulphide in the filtrate.

b. *Copper-Tin Alloys (Bronze, Gun Metal, Bell Metal).*

The alloy is warmed with tolerably concentrated nitric acid. The greater part of the copper goes into solution, while the tin remains as stannic oxide. The residue is digested for some hours with sodium polysulphide, or with liver of sulphur to which a small quantity of flowers of sulphur has been added; the solution containing the whole of the tin is filtered; the residue is washed with a dilute solution of sodium sulphide, and dissolved in nitric acid; the liquid so obtained is added to the original solution of the alloy in nitric acid, and the copper is determined by § 22. The solution containing the tin as sulphostannate is acidified with hydrochloric acid, the stannic sulphide is collected, washed with sal-ammoniac solution, and treated in accordance with § 30.

Another and easier process consists in dissolving the alloy in hydrochloric acid with addition of potassium chlorate, adding an equal bulk of hydrochloric acid diluted with 5 parts of water, boiling, and precipitating the copper as sulphide by passing in sulphuretted hydrogen; filtering, neutralising the free acid in the filtrate by addition of ammonia, and precipitating the tin with sulphuretted hydrogen.

Or the solution of the alloy may be neutralised with ammonia and saturated with yellow ammonium sulphide, whereby the copper is precipitated while the tin remains in solution.

c. *Copper-Zinc-Nickel Alloys (Nickelsilver, &c.).*

The alloy is dissolved in nitric acid, the solution is partially neutralised with ammonia, warmed, and saturated with sulphuretted hydrogen. The precipitate is dissolved in nitric acid, or in hydrochloric acid with addition of bromine or potassium chlorate, and copper is determined in the solution by § 22. The filtrate from the precipitated copper sulphide is mixed with a large excess of sodium acetate, and zinc is precipitated by means of sulphuretted hydrogen (§ 30). If the precipitated sulphide be dark-coloured, it must be redissolved in hydrochloric acid with addition of a few drops of nitric acid, and the zinc again precipitated, after addition of sodium acetate. The nickel, which now alone remains in solution, is determined according to § 24.

The general process of § 65 may be advantageously followed in the analysis of nickel silver, the copper being precipitated as sulphocyanide.

d. *Copper-Silver Alloys* (*Silverplate and Silver Coins*).

The solution of the alloy in nitric acid free from chlorine is diluted and mixed with hydrochloric acid, whereby the silver is thrown down as chloride. Gentle warming and repeated shaking of the liquid promote the separation of the precipitate. After filtration, copper is determined by § 22. The precipitate is dissolved in ammonia, the silver converted into sulphide by addition of ammonium sulphide, &c., as directed in § 47. If it be desired to determine the silver only, the method described towards the end of § 47 is applicable.

e. *Lead-Antimony Alloys* (*Type Metal*).

The alloy is dissolved by warming with a mixture of tolerably concentrated nitric acid and tartaric acid. The solution is somewhat diluted and mixed with sulphuric acid, whereby the greater part of the lead is precipitated. The filtrate from precipitated lead sulphate is nearly neutralised with ammonia, and warmed with addition of yellow ammonium sulphide. The whole of the antimony goes into solution, while the lead which has not been precipitated as sulphate remains undissolved in the form of sulphide.

After filtration and washing the residue with ammonium sulphide, the liquid is acidulated with hydrochloric acid; the precipitated antimony sulphide is collected, washed, and dissolved in hydrochloric acid; the antimony is determined by the iodometric process of § 35. The residual lead sulphide is warmed with concentrated nitric acid, a few drops of sulphuric acid are added, and the sulphate of lead so formed is added to the main quantity of that salt previously obtained. The sulphate is boiled with potassium carbonate, the liquid is filtered, the residue dissolved in a measured quantity of normal hydrochloric acid, and the lead is determined alkalimetrically after § 8.

The following simpler process may be employed when the accurate determination of the lead is not a matter of paramount importance.

The solution of the alloy obtained as already described is warmed in a basin with a little sodium sulphite until the smell of sulphur dioxide can no longer be perceived. Sulphuric acid is added, the liquid is filtered from lead sulphate, saturated with sodium bicarbonate, and titrated with $\frac{1}{10}$-normal iodine. From the results the amount of antimony is calculated. This process gives good results if care be taken to boil off the sulphur dioxide completely. If the antimony contain arsenic, the results are rather low.

f. *Silver-Gold Alloys.*

The alloy is fused in a porcelain crucible, with three times its own weight of metallic lead. The regulus is slightly hammered out and warmed with nitric acid of sp. gravity 1·2, free from chlorine. So soon as the action ceases the liquid is decanted, and the residue is carefully washed and heated to boiling with concentrated sulphuric acid. Any lead in the nitric acid solution is precipitated by addition of sulphuric acid, and silver is determined in the filtrate, after adding the sulphuric acid solution of the regulus, by the process of § 47.

The gold which remains after treatment with hot sulphuric acid is washed, dried, and weighed.

g. *Platinum Alloys.*

I will describe a method for estimating platinum only in alloys containing the metals of the fourth and fifth groups. The alloy, after being divided by hammering or by filing, is fused with four times its own weight of potassium bisulphate; the metals of groups four and five are thus converted into sulphates, which are dissolved by washing the fused mass with hot water. If lead be present, the wash water must contain ammonium tartrate. The residual platinum is collected, dried, and weighed.

This method may also be applied for the separation of gold from other metals. In order to separate gold and platinum from arsenic, antimony, and tin, the alloy is heated to redness in a stream of chlorine. The three latter metals are thus removed as chlorides, while gold and platinum remain. Or the alloy may be dissolved in aqua regia, and the gold precipitated by addition of oxalic acid, after partial neutralisation of the free acid by means of sodium carbonate (not by potash or ammonia). The oxalic acid in the filtrate is destroyed by addition of chlorine water, the liquid is evaporated and mixed with sal-ammoniac and alcohol, the precipitated platinic ammonium chloride is collected, washed, and ignited; the platinum so obtained is weighed.

Alloys of gold and platinum may be analysed by the last-mentioned process.

§ 103.

Estimation of the more important Impurities in the commoner Metals.

The metals very generally contain small quantities of impurities, consisting of foreign metals and also of sulphides, phosphides, carbides, &c.

The impurities may be classed as *metallic* and *non-metallic*. The metallic impurities of the commoner metals often comprise traces of a very great number of elementary substances.

An outline of the processes for estimating the commoner of these impurities, that is, those which occur in relatively large quantities, can alone be given here. The non-metallic impurities are for the most part removed in the form of hydrides when the metal is treated with hydrochloric or sulphuric acid; the metallic impurities, on the other hand, either remain undissolved or pass into solution along with the metal itself. Arsenic and antimony must be classed, for analytical purposes, among the non-metallic impurities.

Hydrochloric or nitric acid is employed as a solvent on account of the readiness with which the metals, as a rule, dissolve in these acids. The former acid is employed in the examination of zinc, iron, and tin, whereby the more important metallic impurities are also obtained in solution. Manganese, which is an important impurity in specimens of iron, may be thus dissolved, and may then be determined by the process described in the latter part of § 90. Lead often accompanies tin and zinc; the greater part of the lead remains undissolved when the metal is treated with hydrochloric acid; the residue may be dissolved in nitric acid, and the lead determined as chromate or sulphate. The traces of lead which are found in the hydrochloric acid solution of the zinc or tin may be separated from the former metal by addition of potassium chromate, and from the latter by addition of sulphuric acid and alcohol.

As the metals of the copper group are for the most part insoluble, or with difficulty soluble, in hydrochloric acid, we employ nitric acid as a solvent for these metals. Any residue insoluble in nitric may be dissolved in nitro-hydrochloric acid. Most of the metals in solution may be directly precipitated and determined in the form of chlorides or sulphates. Tin may be separated, by means of ammonium sulphide, from all metals of the fourth and fifth groups; it may then be precipitated as sulphide, and, in absence of antimony, directly determined by § 30. Generally speaking, the processes detailed in the preceding paragraph for the analysis of alloys are applicable in the examination of the metals for metallic impurities.

In the search for non-metallic impurities, such solvents must be employed as shall cause no evolution of hydrogen, otherwise the non-metals present might be wholly or partly removed as gases. Aqueous solutions of iodine and bromine present us with such solvents. Almost all metals, except silver and lead, pass into solution when gently warmed for some time with bromine water. The non-metals (including arsenic and antimony), with the exception of carbon and silicon, are also dissolved by these reagents. Carbon may be determined in iron by dissolving the latter in water containing iodine, and washing and drying the residue. As silica usually accompanies the carbon, it is well to burn the dried and weighed residue in a stream of oxygen, and to determine the carbon from the loss. By dissolving a second quantity of the iron in sulphuric acid, a residue is obtained representing the uncombined carbon *plus* silica; this may be also weighed and burned in oxygen. The difference between the two carbon determinations represents combined carbon.

The other non-metals are oxidised and dissolved by bromine or iodine water. Sulphur is the most difficult to oxidise of the common non-metallic substances. It is generally more easy to determine sulphur, when accompanying metals of the fourth and fifth groups, by expulsion as sulphuretted hydrogen (by addition of sulphuric acid), absorption by an ammoniacal solution of zinc sulphate, and subsequent determination as zinc sulphide (§ 30).

After the non-metals have been brought into solution by the use of bromine water, the greater part of the bromine is removed by boiling, or, better, by distillation, and the various acids are determined in the residual liquid. Sulphuric acid may be directly precipitated and determined by means of barium chloride.

Arsenic and antimony, in presence of tin and phosphoric acid, must be obtained in the form of sulpho-salts by digestion with yellow ammonium sulphide; the solution must then be acidulated with hydrochloric acid, and the sulphides of arsenic and antimony separated from tin by § 63. The filtrate contains phosphoric acid, which may be determined directly by uranium solution (§ 50) after addition of sodium acetate.

VOLUMETRIC ANALYSIS OF A FEW ORGANIC SUBSTANCES OF TECHNICAL IMPORTANCE, AND OF WATER.

§ 104.

Examination of Vinegar.

The acidity of vinegar or of commercial acetic acid is determined by neutralising with ½-normal ammonia solution.

1 cb.c. ½-normal ammonia = 30 m.gm. acetic acid, $C_2H_4O_2$ ($C_4H_4O_4$).

If the vinegar be itself coloured, turmeric or blue litmus paper may be employed as an indicator, the ammonia being run in until the turmeric shows a brown, or the litmus a blue colour, when brought into contact with a drop of the liquid.

Acetic acid may be determined in acetates by distilling in a current of steam, after addition of phosphoric acid, and determining the acidity of the distillate. (See also § 21.)

The determination of admixed mineral acids, especially of sulphuric acid, presents no special difficulties.

Examination for aldehyde by titrating with standardised permanganate gives good qualitative, but not quantitative, results. The results of such an examination enable a judgment to be formed as to the purity of a sample of vinegar. Any aldehyde present can only be accurately determined by distilling the neutralised vinegar.[1]

NOTE.

Keiffer's solution is useful in determining the acidity of coloured vinegars. It is prepared by adding ammonia to a solution of copper sulphate until the greenish-blue precipitate which is at first formed is almost entirely dis-

---

[1] Witz recommends methyl-aniline-violet as an indicator when mineral acids are present. I have not found the indications sharp enough for quantitative use.

solved, and filtering. The value of the liquid, in terms of acid, is determined by running standard acid into a measured volume of this liquid until a permanent turbidity is produced.

In examining vinegar the standardised liquid is run from a burette into a measured volume of the sample until a permanent turbidity ensues.

The acid in vinegar may also be determined by adding a known weight of pure finely-powdered marble, boiling, filtering, washing, dissolving the residual marble in normal hydrochloric acid, and determining the excess of acid by $\frac{1}{2}$-normal ammonia. The difference between the amount of marble added and that remaining undissolved represents that which has been acted upon by the acid in the vinegar. (5 parts of marble dissolved = 6 parts of acetic acid.)

In the *Analyst* for August, 1876, a method for detecting and estimating free mineral acids in vinegar is published (Hehner). Vinegar always contains potassium and sodium salts of tartaric, acetic, and other acids. Sulphuric or hydrochloric acid, if added, will decompose equivalent quantities of these salts; any mineral acid *existing in the vinegar in the free state* will cause the ash to have a neutral or acid reaction. So long as the ash of vinegar shows an alkaline reaction, free mineral acid cannot be present in the sample. The alkalinity of the ash is diminished in exact proportion to the amount of mineral acid added to the vinegar. On this fact the quantitative process is based. A measured volume—say 50 cb.c.—of the sample is mixed with 25 cb.c. of deci-normal soda solution, the liquid is evaporated to dryness, and the ash is incinerated at the lowest possible temperature. 25 cb.c. of deci-normal acid are added, the liquid is boiled to expel carbon dioxide, and filtered; after washing the residue, the filtrate is titrated with deci-normal soda. The amount of soda used gives the free mineral acid in the vinegar (1 cb.c. deci-normal soda = 4·9 m.gm. H_2SO_4). If the vinegar contain more than 0·2 per cent of free mineral acid, a larger quantity of soda than 25 cb.c. must be added.—*Tr.*

§ 105.

Tartaric Acid and Cream of Tartar.

Tartaric acid and acid tartrates are readily and accurately determined, in the absence of other acids, by titration with standard alkali.

1 cb.c. $\frac{1}{2}$-normal ammonia = 37·5 m.gm. crystallised tartaric acid. (Same for old notation.)

Normal potash or $\frac{1}{2}$-normal ammonia solution may be employed. The process is carried out as directed in § 16. If a precipitate of potassium bitartrate should form during the titration, the liquid must be more strongly heated.

Tartaric acid may be determined in cream of tartar by dissolving the salt in hot water, colouring with litmus, and titrating with alkali,—best with normal soda. (1 equivalent soda = 150 parts crystallised tartaric acid, in the titration of tartar: same for old notation.)

Crude tartar often contains chalk, which is not altogether dissolved by hot water; the presence of this substance does not interfere with the titration, inasmuch as calcium bitartrate is decomposed by alkalies analagously with potassium bitartrate. The presence of acid salts in crude tartar, however, renders an estimation of the total acidity impossible by the ordinary method. In such a case it is best to determine the total tartaric acid by the process described in § 71.

Crude tartar often contains colouring matter, which imparts a red tint to the aqueous solution of the substance. So soon as the acid is neutralised, the colour changes to green. Litmus need therefore scarcely be used in the titration of coloured samples of tartar. Turmeric paper may be employed as an indicator.

Lime may be determined in crude tartar by dissolving in hydrochloric acid, adding excess of ammonium oxalate and ammonia, boiling, collecting the precipitated calcium oxalate, and determining its amount, after washing, by the process of § 21.

§ 106.

Examination of Urine.

Urine contains many substances: of these the most important are urea, common salt, and phosphoric acid, and, in certain diseased states of the organism, grape-sugar.

1. *Chlorine* (chiefly present in combination with sodium) cannot be determined by the ordinary process with standard silver nitrate solution. The presence of organic matter and of phosphoric acid renders the determination of the final point of the reaction uncertain. Liebig's method, based upon the difference in behaviour of urea towards mercuric chloride and towards other mercuric salts, is generally employed for determining chlorine in urine.

A solution of approximately neutral mercuric nitrate is prepared by dissolving a weighed quantity of pure sublimed mercuric chloride in water, precipitating with potash, collecting and washing the precipitate, dissolving it in a small quantity of nitric acid free from chlorine, evaporating to a syrup, and making up to a definite volume (Dragendorff).

The liquid is standardised as follows: 20 cb.c. of a standard solution of sodium chloride is mixed in a flask with 3 cb.c. of a solution of urea containing 3 to 4 grams urea per 100 cb.c. The mercuric nitrate solution is run in from a burette until a slight permanent precipitate is obtained; from the results, the value of 1 cb.c. of the solution is calculated in terms of chlorine.[1]

The method of using the standard mercuric nitrate solution, for the estimation of chlorine in urine, will be apparent.

---

[1] This reaction depends upon the fact that mercuric salts, with the exception of the chloride, form a white precipitate with urea. The sodium chloride present in the above experiment reacts upon the mercuric nitrate to form mercuric chloride, and it is only when the whole of the chlorine has been thus consumed that the mercuric nitrate is able to produce a permanent white precipitate by acting upon the urea.

2. *Urea* may be determined in urine by Liebig's process, which consists in removing phosphoric acid by shaking a measured volume of the sample with baryta water, filtering, removing dissolved baryta by passing carbon dioxide into the filtrate, filtering a second time, running in standard mercuric nitrate solution until a slight permanent precipitate is obtained, noting the amount of mercuric nitrate employed, and again running in the same solution until precipitation of urea is complete. The final point of the reaction is determined by bringing a drop of the supernatant liquid on to a watch-glass, and adding a drop of sodium carbonate solution (free from chloride); the production of a reddish colour shows that the whole of the urea has been precipitated. If a red colour is not produced, the contents of the watch-glass are washed into the flask, and the addition of mercuric nitrate solution is continued.

The mercuric nitrate must of course have been previously standardised against a solution of urea of known strength (4 grams of urea in 100 cb.c. of water is a convenient test solution). The number of cubic centimetres of mercuric nitrate solution added in order to produce a permanent precipitate in the urine is deducted from the total volume of liquid employed; the difference is calculated to urea.[1]

3. *Phosphoric acid* is estimated in urine by precipitation with ammoniacal magnesium chloride solution containing ammonium chloride, collection of the precipitate after twelve hours, and determination according to § 50.

4. *Sugar* may be determined in urine by the use of an alkaline solution of copper tartrate. 5 grams of pure copper sulphate are dissolved in 30 cb.c. of hot water, 25 grams of pure Rochelle salts are added, followed by the addition of caustic soda until a strongly alkaline, deep-blue liquid is obtained. This liquid must remain unchanged on boiling.

A measured quantity (50 cb.c.) of the urine under examination is added to a portion of the prepared liquid, and the whole is boiled until the precipitate which is

---

[1] See note at end of this paragraph.

produced is of a bright red colour. The precipitate is collected, washed, and brought into a solution of ferric sulphate; the copper is determined by § 22.

$$\left.\begin{array}{r}\text{Cuprous oxide found} \times 0{\cdot}504\\ \text{or Metallic iron found} \times 0{\cdot}643\end{array}\right\} = \text{grape sugar.}$$

If the urine contain much uric acid, it is advisable to add basic lead acetate, and to filter before adding the alkaline copper solution.

Note on Estimation of Urea in Urine.

Urea may be very accurately and readily determined by decomposing by means of sodium hypobromite and measuring the nitrogen set free. Of the various arrangements proposed, that of Dupré[1] is perhaps the simplest. It consists of a burette inverted in a tall cylinder of water, and connected by a side tube with a bottle containing sodium hypobromite and a small test-tube in which is placed 5 cb.c. of the urine under examination. The bottle is closed with a caoutchouc cork; a piece of caoutchouc tubing connects it with the inverted burette. The proper quantity of hypobromite solution is prepared by pouring 23 cb.c. of caustic soda (1 to 2·5 of water) into a stoppered cylinder in which has been placed a sealed tube of thin glass containing 2·2 cb.c. of bromine, and shaking the cylinder until the thin tube is broken. In using the apparatus the bottle containing the hypobromite is inclined so as to allow the urine to come into contact with the liquid; the bottle is briskly agitated for a few minutes and then placed in cold water; after a little time the levels of the water inside and outside the burette are made equal, the volume of gas is read off, and the temperature is observed. The amount of nitrogen evolved is found to be 91 per cent of the urea present. The burette may be graduated so as directly to give readings of the percentage of urea. 36·70 cb.c. of moist nitrogen, at the ordinary temperature and pressure, may be taken as equal to 0·1 gram of urea; or if 5 cb.c. of urine be always employed, then 36·7 cb.c. of nitrogen is equal to 2 per cent of urea.—*Tr.*

---

[1] *Chem. Soc. J.*, vol. I., 1877, p. 534.

§ 107.

Estimation of Sugar.

Sugar, as we have seen in the preceding paragraph, may be determined by the use of an alkaline copper solution. 10 cb.c. of this solution should be equal to not more than 0·1 gram grape sugar; the sugar solution should not contain more than 0·5 per cent sugar. By attending to these details very trustworthy results are obtainable.

The copper solution (10 cb.c. = 0·1 gram grape sugar) is prepared by dissolving 69·278 grams recrystallised copper sulphate in 400 or 450 cb.c. of water containing a few drops of sulphuric acid, adding 200 grams of pure tartaric acid, followed by addition of such a quantity of concentrated caustic soda solution as serves to form a clear blue liquid, and making up to 1000 cb.c. with water. The solution is preserved in a dark place in a glass-stoppered bottle; it must remain perfectly clear when boiled. In order to test this liquid a solution of inverted sugar is prepared by dissolving 0·95 grams of pure cane sugar, dried at 100°, in about 150 cb.c. of water, adding ten drops of tolerably concentrated hydrochloric acid, heating to 70° or 80° for half an hour (replacing the water which evaporates), *nearly neutralising* with sodium carbonate, and diluting to exactly 200 cb.c. 1 cb.c. now contains 5 m.gm. of grape sugar. 10 or 20 cb.c. of the prepared copper solution are warmed along with 40 to 50 cb.c. of dilute caustic soda, in a beaker, to 80° or 90°, and the sugar solution is carefully run in from a burette until the whole of the copper is thrown down in the form of cuprous oxide. The final point of the precipitation is determined by running a drop of the sugar solution on to the surface of the liquid in the beaker (after the precipitate has settled) by the use of a narrow slip of glass, or, better, of porcelain, about 6 m.m. in width, and noticing whether a yellowish cloud forms behind the slip of glass or porcelain. If the copper solution be of correct strength, 20 cb.c. should be reduced by 40 cb.c. of the prepared sugar solution.

In examining sugar syrup the same method of procedure is to be employed. The syrup, diluted at least fifty times, is warmed on a water-bath for half an hour, after addition of 10 or 15 drops of pure hydrochloric acid; the liquid is then diluted so that 1 cb.c. may contain not more than 5 m.gm. grape sugar, and titrated against standardised copper solution.

$$\text{Grape sugar} \times \frac{19}{20} = \text{cane sugar.}$$

In the event of the syrup containing both cane and grape sugar, the diluted liquid is to be titrated against standardised copper sulphate solution, whereby the grape sugar is determined. (Cane sugar does not affect the copper solution.) Another portion is to be warmed with acid and again titrated against the copper solution; the total sugar is thus obtained. The grape sugar present as such is deducted from the total, and the residue is calculated to cane sugar.

Deeply-coloured syrups may be treated with basic lead acetate, and filtered, before inverting by means of acid.

§ 108.

Guano.

Water is determined by drying about 2 grams in an exsiccator over sulphuric acid. In 1 gram of the dried substance nitrogen is determined by combustion with soda lime as directed in § 11. 1 gram of the dried guano is fused with an equal weight of nitre and 2 grams of calcined sodium and potassium carbonates. The fused mass is dissolved out with hydrochloric acid (filtered if necessary), the liquid is partially neutralised by addition of ammonia, and precipitated with excess of sodium acetate. In the filtrate frcm this precipitate phosphoric acid is determined by the inverted method of § 50. The precipitate produced on adding sodium acetate may be dissolved in hydrochloric acid, the iron reduced by means of sodium sulphite, the solution saturated with potash and filtered, the filtrate acidified, and the phosphoric acid determined by § 50.

§ 109.

Tannic Acid.

Hamer has shown that the specific gravity of a solution containing tannic acid before, and after, the removal of the tannic acid, is proportional to the amount of the acid originally present. In order to determine tannic acid in such vegetable substances as gall nuts, oak bark, &c., a solution is prepared by digesting the finely-powdered substance with eight or ten times its weight of hot water, filtering, and washing. The specific gravity of the clear liquid is then determined, preferably by means of the specific-gravity bottle. Another portion of the liquid is digested with about one-third of its own weight of powdered hide[1] and filtered. The specific gravity of the filtrate is determined. The amount of tannic acid corresponding to the gravity before and after the treatment with hide is found from the accompanying table; the less is deducted from the greater amount; the difference represents the percentage of tannic acid present in the solution examined.

Specific Gravity.	Percentage of Tannic Acid.	Specific Gravity.	Percentage of Tannic Acid.	Specific Gravity.	Percentage of Tannic Acid.
1·0004	0·1	1·0072	1·8	1·0140	3·5
1·0008	0·2	1·0076	1·9	1·0144	3·6
1·0012	0·3	1·0080	2·0	1·0148	3·7
1·0016	0·4	1·0084	2·1	1·0152	3·8
1·0020	0·5	1·0088	2·2	1·0156	3·9
1·0024	0·6	1·0092	2·3	1·0160	4·0
1·0028	0·7	1·0096	2·4	1·0164	4·1
1·0032	0·8	1·0100	2·5	1·0168	4·2
1·0036	0·9	1·0104	2·6	1·0172	4·3
1·0040	1·0	1·0108	2·7	1·0176	4·4
1·0044	1·1	1·0112	2·8	1·0180	4·5
1·0048	1·2	1·0116	2·9	1·0184	4·6
1·0052	1·3	1·0120	3·0	1·0188	4·7
1·0056	1·4	1·0124	3·1	1·0192	4·8
1·0060	1·5	1·0128	3·2	1·0196	4·9
1·0064	1·6	1·0132	3·3	1·0200	5·0
1·0068	1·7	1·0136	3·4		

---

[1] The powdered hide is prepared by rasping untanned hide with a file; it is to be moistened with water, and pressed before use.

NOTE ON ESTIMATION OF TANNIC ACID.

The foregoing method for the estimation of tannic acid cannot be considered a satisfactory one. Of the many processes which have been proposed, that of Löwenthal[1] appears to yield the most accurate results. For carrying out this process the following standard liquids are required:—

A dilute solution—preferably $\frac{1}{20}$-normal—of potassium permanganate.

A solution of 5 grams of pure "precipitated indigo" in 1000 cb.c. of water.

A solution of 25 grams of strong glue, swollen by cold water, and subsequently dissolved by heating in 1000 cb.c. of water; the liquid is saturated with pure salt.

A saturated solution of pure salt containing 25 cb.c. of sulphuric acid or 50 cb.c. of hydrochloric acid (1 to 3 of water) per litre.

A quantity of the tanning material (about 10 grams if sumach or valonia, about 20 grams if bark) is repeatedly boiled with water, the liquid is allowed to cool, and is made up to 1000 cb.c. 10 cb.c. are diluted to 600 or 700 cb.c., 25 cb.c. of the indigo solution and 10 cb.c. of dilute sulphuric acid (1 to 3 of water) are added, and permanganate is run in until the colour of the liquid changes to a clear yellow. The amount of permanganate used is noted. 10 cb.c. of the dilute sulphuric acid and 25 cb.c. of the indigo solution are then treated in an exactly similar manner *without* the addition of the tannin solution. The difference between the two quantities of permanganate used represents the amount consumed in the oxidation of the total astringent substances in 10 cb.c. of the liquid under examination.

In order to obtain reliable results the amount of permanganate used in the first titration should not exceed one and a half times the quantity used in the second. If this proportion be exceeded, it is better to make a fresh trial, using a larger quantity of indigo solution.

100 cb.c. of the tannin solution are now mixed with 50 cb.c. of the solution of glue containing common salt, the mixture is well stirred, 100 cb.c. of the solution of salt containing acid are added, and after standing four or five hours the whole is filtered. The tannin is thus completely precipitated. An aliquot portion of the clear filtrate is titrated with permanganate; the amount of permanganate formerly found to be used by the acid and indigo alone is deducted; the residue represents permanganate consumed in the oxidation of gallic acid and other astringent substances other than tannin present in the liquid under examination.

According to Neubauer, 1 cb.c. of $\frac{1}{20}$-normal permanganate is equal to 2·078 m.gm. of gallo-tannic acid; or, according to Oser, to 3·118 m.gm. of oak-bark tannin. It is perhaps better, however, meanwhile to consider the results as comparative only.—*Tr.*

---

[1] *Zeitsch. Anal. Chem.* 1877, p. 33.

§ 110.

Examination of Water.[1]

In the examination of a water which is to be used in steam boilers it becomes very important to have a method for estimating the amount of "crust" which will be formed in the boiler by the evaporation of a given quantity of water.

Gypsum is chiefly concerned in the formation of hard boiler crusts; chalk, unless associated with silica in the water, is generally precipitated in a more pulverulent form. By determining the amount of gypsum, we have therefore a measure of the crust-producing power of the water. Gypsum may be determined by § 53. An estimation of lime should also be carried out, so that there may be no doubt that the sulphuric acid really exists in the form of calcium sulphate. It will generally be necessary to concentrate the water before making these determinations; if a precipitate form during concentration, it may be removed by filtration.

The water in a steam boiler is under a pressure of about four atmospheres; 1000 parts of such water are capable of dissolving about 1 part of gypsum ($CaSO_4.2H_2O$). This result has been obtained by direct experiment. A water containing 1 part, or more than 1 part, of gypsum per 1000 parts, is not fit for technical use. A water containing 0·5 parts of gypsum per 1000 parts may be evaporated in the boiler until its volume is reduced to one-half before it begins to deposit gypsum; or the *evaporation-value* of such a water equals 50 per cent. A water containing 0·25 parts of gypsum per 1000 parts may be boiled down to three-fourths of its original volume without danger of formation of boiler-crust; the evaporation-value in this case amounts to 75 per cent.

---

[1] In this paragraph I have given the main points of Dr. Fleischer's observations on water: these observations relate almost exclusively to water which is to be used for technical purposes. The greater part of those pages which deal with the examination of potable waters has been added by me.—*Tr.*

Generally, if G represent the amount of gypsum ($CaSO_4.2H_2O$) in centigrams, per litre of water, the evaporation-value, = V, will be found from the equation $V = 100 - G$.

The application of this formula enables the manufacturer to determine to what extent he may carry the evaporation of the water with which his boilers are supplied, without danger of boiler-crust formation. When the limit of evaporation has been reached, the boiling should be stopped and the water run off.

In the examination of a water which is to be used for technical purposes, it is customary to determine "temporary" and "permanent" hardness by the use of a standardised soap solution. Pettenkofer recommends the determination of free carbonic acid by titrating 500 cb.c. of the sample with $\frac{1}{10}$-normal caustic baryta solution until a red-brown colour is produced on turmeric paper, the collection of the precipitate so formed, solution in hydrochloric acid, and determination of lime by § 21. The lime being calculated to carbonate represents the "temporary hardness." The "total hardness," *i.e.*, total quantity of lime and magnesia, may be determined by evaporating 500 cb.c. of the sample to the bulk of about 100 cb.c., adding a few drops of hydrochloric acid and an excess of ammonium oxalate, followed by addition of a few drops of tartaric acid—if iron be present—saturation with ammonia, and addition of microcosmic salt. Lime and magnesia are then determined in the precipitate (§ 65) after collection and washing.

Alkalies may be determined in water by evaporating a considerable volume to dryness, adding a little sulphuric acid, again evaporating nearly to dryness, dissolving in a little water, adding baryta water, saturating with carbon dioxide, boiling, filtering, evaporating the filtrate with a little hydrochloric acid and excess of platinum tetrachloride nearly to dryness, washing, first with platinum tetrachloride and then with alcohol, drying and igniting the residue, and determining the potassium chloride by means of standard silver solution, as directed in § 47. By evaporating the filtrate to dryness, igniting the residue, and titrating with silver solution, the soda may be determined.

Silica may be determined in water by evaporating a considerable quantity nearly to dryness, adding ammonium carbonate, filtering, evaporating the residue to dryness after addition of hydrochloric acid, again adding a little hydrochloric acid, and again evaporating to dryness, moistening with water acidulated with hydrochloric acid, collecting the residue and weighing it, after washing, drying, and igniting.

Sulphuretted hydrogen may be determined by titration with iodine (§ 34).

Potable Waters.[1]

In the examination of a potable water we generally seek to determine (1) the total solid matter in solution; (2) the amount of organic matter; and (3) the amount of poisonous metals, supposing the presence of such metals to have been proved.

Total solid matter is determined by evaporating a measured quantity—preferably 70 cb.c—of the sample to dryness in a weighed platinum basin by means of steam, and weighing the residue. The weight, stated in m.gms., of the residue from 70 cb.c. gives, without calculation, grains of solid matter per gallon.

For the measurement of organic matter we have recourse to indirect methods. We measure substances which are the products of the natural decomposition of organic matter, and we attempt to decompose the organic matter actually present as such in the water, and measure the products of this decomposition.

The method of Frankland and Armstrong professes, it is true, to directly measure the organic carbon and nitrogen present in water. A description of this method, which cannot be said to have met with general acceptance among chemists, would be altogether beyond the range of the present work.

---

[1] I do not profess to give more than an outline of the methods of water analysis. This must be filled up by reference to a standard work on the subject.—*Tr.*

Of the products of the natural decomposition of organic matter in water, the most important are nitrates and nitrites, chlorine, and ammonia or ammonium salts.

Nitrates may be determined by evaporating 1 litre of water with addition of a little sodium carbonate, dissolving the residue in a little distilled water, and applying the process of § 39. A portion of the same liquid in which nitric acid is determined may be acidulated with sulphuric acid and distilled. Nitrous acid may then be estimated in the distillate in accordance with § 31. Other methods for determining nitrates and nitrites are often employed; the principle of these generally consists in reducing the nitrates, &c., to ammonia by such reagents as aluminium, zinc and iron, copper and zinc, &c., and determining the ammonia produced either by the ordinary alkalimetric method or by Nesslerising (see next page).

Chlorine may be determined by the process of § 47; it is advisable, however, to employ a more dilute silver solution. If 4·79 grams of pure fused silver nitrate be dissolved in 1 litre of water, a solution is obtained, 1 cb.c. of which will precipitate 1 m.gm. of chlorine. If 70 cb.c. of the water under examination be used, the number of cubic centimetres of silver solution employed gives directly grains of chlorine per gallon.

Ammonia salts may be determined by distilling 500 cb.c. of the sample after addition of a little pure sodium carbonate, and estimating the ammonia in the distillate. The most accurate method of measuring small quantities of ammonia is that called Nesslerising. This process consists in adding Nessler's reagent to a quantity of pure distilled water containing a known quantity of ammonia, and comparing the depth of colour so produced with that formed by adding the same amount of the reagent to an equal volume of the distillate from the water under examination.

Nessler's reagent is a solution of mercuric iodide in potassium iodide rendered strongly alkaline with potash or soda; it is prepared by dissolving 3 parts of potassium iodide and 1 part of mercuric chloride in about 22 parts of hot water, adding a solution of mercuric chloride until a very slight permanent precipitate is produced, then adding about 4½ parts of solid caustic potash or 3½ of soda, diluting slightly, and adding a few drops of a saturated solution of mercuric chloride. After settling, the clear, slightly yellow liquid is run off into well-stoppered bottles, which should be kept nearly filled with the liquid.

For the process of Nesslerising, a standard solution of ammonia is required. This is prepared by dissolving 3·15 grams of sublimed sal-ammoniac in 1 litre of water, and diluting a portion with ninety-nine times its own volume of distilled water *free from ammonia.* 1 cb.c. of this standard contains 0·01 m.gm. ammonia (NH_3).

The process of Nesslerising is conducted by running 50 cb.c. of distilled water, *free from ammonia,* into a cylinder of white glass placed alongside of an exactly similar cylinder containing 50 cb.c. of the distillate from the water under examination, running into the former a measured volume of the standard ammonia solution, adding to each a small quantity of the Nessler's reagent by the aid of a little pipette, stirring up the contents of the cylinders by means of thin glass tubes having small bulbs blown on their lower extremities, and comparing the depths of colour by looking through the columns of liquid, a white slab or piece of paper being placed beneath the cylinders. If the two colours do not agree in depth, a fresh standard, containing more or less ammonia than the first, must be prepared. The Nessler solution must be added *after* the addition of the standard ammonia. Distillation of the sample is continued until the distillate is free from ammonia.

Having determined those substances which are products of the natural decomposition of organic matter in water, we now proceed to decompose, by artificial means, the organic matter still present in the water, and to measure the products of this decomposition.

The method very generally adopted consists in boiling the residue in the retort with an alkaline solution of permanganate of potassium, whereby the organic matter suffers partial decomposition, and ammonia is evolved.

The alkaline permanganate solution is prepared by dissolving 1 part of crystallised potassium permanganate and 25 parts of solid potash in 125 parts of water, boiling for some time, and setting aside in a stoppered bottle. 50 cb.c. of this solution are required for each analysis, half a litre of water being used. The details of the estimation of ammonia have been already given. The distillation is continued, after addition of permanganate, until the distillate is free from ammonia, the latter being determined in each 50 cb.c. of distillate.

Of the poisonous metals which may be present in potable waters, copper and lead are the more common. They may be detected by the brown colour produced on acidulating 100 cb.c. of the water with a few drops of acetic acid, and adding a little sulphuretted hydrogen water. If no colour is produced, a larger quantity of the water should be evaporated, to the bulk of 100 cb.c. or so, and again tested by addition of sulphuretted hydrogen.

Small quantities of copper may be determined by adding a little ammonium nitrate solution and a few drops of a dilute solution of potassium ferrocyanide to a measured volume of the sample. The depth of colour produced is imitated in an equal bulk of pure water by adding ammonium nitrate solution, a few drops of ferrocyanide, and standard copper solution from a burette. The process is essentially the same as that described under Nesslerising; it is not necessary, however, to make a fresh standard for each trial. The copper solution (unlike the ammonia) may be added *after* the ferrocyanide. The water must be neutral. The standard copper solution should be of a strength such that 1 cb.c. = 0·1 mg.m. copper; it may be readily prepared by dissolving 0·393 gram of recrystallised copper sulphate in 1 litre of water. Iron, if present in the water, is removed by evaporating to a small bulk after addition of a few drops of nitric acid, adding a slight excess of ammonia, filtering, dissolving the precipitate in nitric acid, again boiling down, and precipitating with ammonia; the two filtrates are mixed, excess of ammonia is removed by boiling, and copper is determined in the liquid. The presence of small quantities of lead does not interfere with this method of determining copper; one part of the latter metal may be estimated in 2½ million parts of water.[1]

Small quantities of lead (in absence of copper) may be accurately determined by adding a few drops of sulphuretted hydrogen water to a measured volume (50 or 100 cb.c.) of the sample, and imitating the depth of colour produced by adding a standard lead solution to an equal bulk of pure water, with which a few drops of sulphuretted hydrogen water have been mixed. The water should be neutral, or but very faintly acid. The standard lead solution is prepared by dissolving 0·166 grams of recrystallised lead acetate in 1 litre of water; 1 cb.c. = 0·1 m.gm. lead. 1 part of lead may be determined in 2½ million parts of water.[2]

It is sometimes necessary to determine small quantities of iron in potable waters. This may be done by adding to a measured quantity of the water about 1 cb.c. of dilute sulphuric acid, followed by addition of a dilute solution of permanganate of potassium until a permanent faint pink colour is produced, and making up to 1 litre. 50 or 100 cb.c. of the water thus prepared are placed in a cylinder, 5 cb.c. of dilute nitric acid and a few drops of potassium ferrocyanide solution are added. The depth of colour is imitated in a second cylinder containing an equal bulk of pure water, a few drops of ferrocyanide solution, and 5 cb.c. of dilute nitric acid, by running in a prepared and standardised iron solution from a burette. The iron solution is prepared by dissolving 0·7 gram pure ferrous-ammonium sulphate in a little water, adding 1 cb.c. of dilute sulphuric acid, oxidising the iron by addition of permanganate, and making up to 1 litre. 1 cb.c. of this solution = 0·1 m.gm. iron.

1 part of iron may be estimated by this process in 13 million parts of water.[3]

With regard to the interpretation to be put upon the

---

[1] Carnelley, *Proc. Manch. Lit. and Phil. Soc.*, XV., 24.

[2] Pattison Muir, *Proc. Manch. Lit. and Phil. Soc.*, XV., 31.

[3] Carnelley, *Mem. Manch. Lit. and Phil. Soc.*, 1874-75, p. 346.

results of water analyses by the "ammonia method," it would be quite beyond the scope of this book to enter into details. Suffice it to say that the investigations of Wanklyn Chapman and Smith, and others, appear to justify the conclusion that a good potable water should not show more than 0·08 parts "free" and 0·10 parts "albumenoid" ammonia per million. If these numbers are exceeded, the water must be at least suspected. Chlorine is never found in any quantity in pure water, except under peculiar conditions of the soil. The presence of this element in amounts exceeding 1 or 1½ grains per gallon points to contamination, generally to animal contamination. If it be known that the water is derived from a soil rich in chlorides, this conclusion is of course invalidated.

Nitrates generally point to the previous existence of organic matter. The causes which determine the presence and quantity of nitrates are, however, so complicated that no very safe conclusion concerning organic contamination can be deduced from an estimation of nitrates alone. This remark indeed applies to each of the individual determinations in an analysis of water. The results must be taken as a whole.

The ammonia process appears to be exceedingly useful in measuring, comparatively, the quantities of decomposing organic matter in water. When we attempt to measure organic matter which has not begun to decompose, or organic matter (such as peaty matter) which only undergoes decomposition with difficulty, the process cannot be relied upon. Of course it is decompos*ing* organic matter which is especially harmful.

APPENDIX.

TABLE I.

Atomic Weights and Symbols of the Elements.[1]

Name.	Symbol.	Atomic Weight.		Name.	Symbol.	Atomic Weight.	
		New.	Old.			New.	Old.
Aluminium,	Al	27·26	13·7	Mercury,	Hg	200	100
Antimony,	Sb	122·3	122·3	Molybdenum,	Mo	96	48
Arsenic,	As	75	75	Nickel,	Ni	58·8	29·4
Barium,	Ba	137	68·5	Nitrogen,	N	14·04	14
Bismuth,	Bi	210	208	Osmium,	Os	199	99·6
Boron,	B	11	11	Oxygen,	O	15·96	8
Bromine,	Br	79·95	80	Palladium,	Pd	106·5	53·3
Cadmium,	Cd	152	56	Phosphorus,	P	31	31
Caesium,	Cs	133	133	Platinum,	Pt	197	98·7
Calcium,	Ca	40	20	Potassium,	K	39·13	39·1
Carbon,	C	12	6	Rhodium,	Rh	104·4	52·2
Cerium,	Ce	138	46	Rubidium,	Rb	85·4	85·4
Chlorine,	Cl	35·46	35·5	Ruthenium,	Ru	104·4	52·2
Chromium,	Cr	52·2	26·1	Selenium,	Se	79·5	39·7
Cobalt,	Co	58·8	29·4	Silver,	Ag	107·97	107·97
Copper,	Cu	63·2	31·7	Silicon,	Si	28	14
Didymium,	D	145	47·5	Sodium,	Na	23·04	23
Erbium,	E	112		Strontium,	Sr	87·5	43·8
Fluorine,	F	19	19	Sulphur,	S	32·07	16
Gallium,	G	?	?	Tantalum,	Ta	182	182
Gold,	Au	197	197	Tellurium,	Te	128	64
Hydrogen,	H	1	1	Thallium,	Tl	203·64	204
Indium,	In	113·4	35·9	Thorium,	Th	115·7	57·86
Iodine,	I	126·85	127	Tin,	Sn	118	59
Iridium,	Ir	197	99	Titanium,	Ti	50	25
Iron,	Fe	56	28	Tungsten,	W	184	92
Lanthanum,	La	139	46·4	Uranium,	U	240	60
Lead,	Pb	206·92	104	Vanadium,	V	51·4	68·6
Lithium,	Li	7·02	7	Yttrium,	Y	61·7	30·6
Magnesium,	Mg	24	12	Zinc,	Zn	65·2	32·5
Manganese,	Mn	54·2	27·5	Zirconium,	Zr	89·6	44·8

---

[1] In this table I have placed the old atomic weights as used by Dr. Fleischer alongside of the new weights.—*Tr.*

TABLE II.

THE CONSTANT FACTOR (ϕ) FOR CALCULATING THE AMOUNTS OF TWO SUBSTANCES FROM THE RESULTS OF INDIRECT ANALYSIS.

Determined. (Weight = G).	Sought.	Found by Titration. (Weight = g).	ϕ	$(G - g)\ \phi$ =	Remarks on the Methods of Analysis opposite Table.
KCl and NaCl	K	NaCl	2·42857	K	I.
Do.	KCl	Do.	4·63354	KCl	
Do.	K_2O (KO)	Do.	2·92546	K_2O (KO)	
K_2SO_4 and Na_2SO_4	K	Na_2SO_4 ($NaOSO_3$)	2·42857	K	II.
($KOSO_3$ and $NaOSO_3$)	K_2O (KO)	Do.	2·92546	K_2O (KO)	
Do.	K_2SO_4 ($KOSO_3$)	Do.	5·40993	K_2SO_4 ($KOSO_3$)	
Do.	K_2CO_3 ($KOCO_2$)	Do.	4·29192	K_2CO_3 ($KOCO_2$)	
K_2CO_3 and Na_2CO_3 ($KOCO_2$ and $NaOCO_2$)	K_2CO_3	Na_2CO_3 ($NaOCO_2$)	4·29192	K_2CO_3	III.
$BaCO_3$ and $CaCO_3$ ($BaOCO_2$ and $CaOCO_2$)	Ba	$CaCO_3$ ($CaOCO_2$)	1·41237	Ba	
Do.	BaO	Do.	1·57731	BaO	
Do.	$BaCO_3$ ($BaOCO_2$)	Do.	2·03092	$BaCO_3$ ($BaOCO_2$)	
Do.	$BaSO_4$ ($BaOSO_3$)	Do.	2·40206	$BaSO_4$ ($BaOSO_3$)	
$SrCO_3$ and $CaCO_3$ ($SrOCO_2$ and $CaOCO_2$)	Sr	$CaCO_3$	1·84033	Sr	
Do.	SrO	Do.	2·17647	SrO	
Do.	$SrCO_3$ ($SrOCO_2$)	Do.	3·10084	$SrCO_3$ ($SrOCO_2$)	
Do.	$SrSO_4$ ($SrOSO_3$)	Do.	3·85714	$SrSO_4$ ($SrOSO_3$)	
$SrSO_4$ and $CaSO_4$ ($SrOSO_3$ and $CaOSO_3$)	Sr	$CaSO_4$ ($CaOSO_3$)	1·84033	Sr	IV.
AgCl and AgBr	Br	AgCl	1·79775	Br	V.

Remarks on the Methods of Analysis (Table II).

I. The substance is titrated with silver nitrate; the amount used is calculated to NaCl.

II. The dehydrated salt is boiled with caustic baryta, filtered, and titrated with normal hydrochloric acid. By multiplying the acid used by half the equivalent of Na_2SO_4 ($NaOSO_3$) (the whole equivalent if old notation be employed), the amount of sodium sulphate corresponding with the alkali present is found.

III. The same factors serve for calculating K, K_2O (KO), KCl, and K_2SO_4 ($KOSO_3$), as for the chlorides and sulphates.

IV. The salts are transformed into carbonates by the use of K_2CO_3 ($KOCO_2$); the amount of normal acid required for neutralisation is determined. The factors are the same as those used for the carbonates.

V. Iodine is determined in an aliquot portion by means of ferric chloride. The chlorine, bromine, and iodine are precipitated with a measured volume of silver solution, the excess of silver in the filtrate being determined. As the iodine has been determined, the amount of silver corresponding with AgI, AgBr, and AgCl is known. The silver required to combine with iodine is deducted from the total silver, and the residue is calculated to AgCl. This is deducted from the weight of AgCl + AgBr (obtained by deducting AgI from the total weight), and the residue is multiplied by ϕ in order to find Br.

This table shows the remarkable fact that the factor required for calculating a certain compound from the weight of two bases, is the same whatever these 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.

TABLE III.

PERCENTAGES OF SULPHURIC ACID (H_2SO_4) IN AQUEOUS ACID OF VARYING GRAVITY.

(Bineau, Otto. Temp. = 15°).

Spec. Gravity.	Per Cent.	Spec. Gravity.	Per Cent.	Spec. Gravity.	Per Cent.
1·8426	100	1·568	66	1·239	32
1·8420	99	1·557	65	1·231	31
1·8406	98	1·545	64	1·223	30
1·8400	97	1·534	63	1·215	29
1·8384	96	1·523	62	1·2066	28
1·8376	95	1·512	61	1·198	27
1·8356	94	1·501	60	1·196	26
1·834	93	1·490	59	1·182	25
1·831	92	1·480	58	1·174	24
1·827	91	1·469	57	1·167	23
1·822	90	1·4586	56	1·159	22
1·816	89	1·448	55	1·1516	21
1·809	88	1·438	54	1·144	20
1·802	87	1·428	53	1·136	19
1·794	86	1·418	52	1·129	18
1·786	85	1·408	51	1·121	17
1·777	84	1·398	50	1·1136	16
1·767	83	1·3886	49	1·106	15
1·756	82	1·379	48	1·098	14
1·745	81	1·370	47	1·091	13
1·734	80	1·361	46	1·083	12
1·722	79	1·351	45	1·0756	11
1·710	78	1·342	44	1·068	10
1·698	77	1·333	43	1·061	9
1·686	76	1·324	42	1·0536	8
1·675	75	1·315	41	1·0464	7
1·663	74	1·306	40	1·039	6
1·651	73	1·2976	39	1·032	5
1·639	72	1·289	38	1·0256	4
1·627	71	1·281	37	1·019	3
1·615	70	1·272	36	1·013	2
1·604	69	1·264	35	1·0064	1
1·592	68	1·256	34		
1·580	67	1·2476	33		

TABLE IV.

Percentages of Real Nitric Acid (HNO_3) in Aqueous Acid of Varying Gravity.

(Kolb, *Ann. Ch. Phys.*, (4), 136).

The numbers marked *a* are results of direct observation ; the others are obtained by interpolation.

HNO_3.	Specific Gravity.		HNO_3.	Specific Gravity.	
Per Cent.	At 0°.	At 15°.	Per Cent.	At 0°.	At 15°.
100·00	1·559	1·530	58·88	1·387	1·366
99·84*a*	1·559*a*	1·530*a*	58·00	1·382	1·363
99·72*a*	1·558*a*	1·530*a*	57·00	1·376	1·358
99·52*a*	1·557*a*	1·529*a*	56·10*a*	1·371*a*	1·353*a*
97·89*a*	1·551*a*	1·523*a*	55·00	1·365	1·346
97·00	1·548	1·520	54·00	1·359	1·341
96·00	1·544	1·516	53·81	1·358	1·339
95·27*a*	1·542*a*	1·514*a*	53·00	1·353	1·335
94·00	1·537	1·509	52·33*a*	1·349*a*	1·331*a*
93·01*a*	1·533*a*	1·506*a*	50·99*a*	1·341*a*	1·323*a*
92·00	1·529	1·503	49·97	1·334	1·317
91·00	1·526	1·499	49·00	1·328	1·312
90·00	1·522	1·495	48·00	1·321	1·304
89·56*a*	1·521*a*	1·494*a*	47·18*a*	1·315*a*	1·298*a*
88·00	1·514	1·488	46·64	1·312	1·295
87·45*a*	1·513*a*	1·486*a*	45·00	1·300	1·284
86·17*a*	1·507*a*	1·482	43·53*a*	1·291*a*	1·274*a*
85·00	1·503	1·478	42·00	1·280	1·264
84·00	1·499	1·474	41·00	1·274	1·257
83·00	1·495	1·470	40·00	1·267	1·251
82·00	1·492	1·467	39·00	1·260	1·244
80·96*a*	1·488*a*	1·463*a*	37·95*a*	1·253*a*	1·237*a*
80·00	1·484	1·460	36·00	1·240	1·225
79·00	1·481	1·456	35·00	1·234	1·218
77·66	1·476	1·451	33·86*a*	1·226*a*	1·211*a*
76·00	1·469	1·445	32·00	1·214	1·198
75·00	1·465	1·442	31·00	1·207	1·192
74·01*a*	1·462*a*	1·438*a*	30·00	1·200	1·185
73·00	1·457	1·435	29·00	1·194	1·179
72·39*a*	1·455*a*	1·432*a*	28·00	1·187*a*	1·172*a*
71·24*a*	1·450*a*	1·429*a*	27·00	1·180*a*	1·166
69·69	1·444	1·423	25·71*a*	1·171*a*	1·157*a*
69·20*a*	1·441*a*	1·419*a*	23·00	1·153	1·138
68·00	1·435	1·414	20·00	1·132	1·120
67·00	1·430	1·410	17·47*a*	1·115*a*	1·105*a*
66·00	1·425	1·405	15·00	1·099	1·089
65·07*a*	1·420*a*	1·400*a*	13·00	1·085	1·077
64·00	1·415	1·395	11·41*a*	1·075*a*	1·067*a*
63·59	1·413	1·393	7·22*a*	1·050*a*	1·045*a*
62·00	1·404	1·386	4·00	1·026	1·022
61·21*a*	1·400*a*	1·381*a*	2·00	1·013	1·010
60·00	1·393	1·374	0·00	1·000	0·999
59·59	1·391*a*	1·372*a*			

TABLE V.

PERCENTAGES OF REAL HYDROCHLORIC ACID (HCl) IN AQUEOUS ACID OF VARYING GRAVITY.

(Ure. Temp. 15°).

Sp. Gravity.	Per Cent.	Sp. Gravity.	Per Cent.	Sp. Gravity.	Per Cent.
1·2000	40·777	1·1328	26·913	1·0637	13·049
1·1982	40·369	1·1308	26·505	1·0617	12·641
1·1964	39·961	1·1287	26·098	1·0597	12·233
1·1946	39·554	1·1267	25·690	1·0577	11·825
1·1928	39·146	1·1247	25·282	1·0557	11·418
1·1910	38·738	1·1226	24·874	1·0537	11·010
1·1893	38·330	1·1206	24·466	1·0517	10·602
1·1875	37·923	1·1185	24·058	1·0497	10·194
1·1857	37·516	1·1164	23·650	1·0477	9·786
1·1846	37·108	1·1143	23·242	1·0457	9·379
1·1822	36·700	1·1123	22·834	1·0437	8·971
1·1802	36·292	1·1102	22·426	1·0417	8·563
1·1782	35·884	1·1082	22·019	1·0397	8·155
1·1762	35·476	1·1061	21·611	1·0377	7·747
1·1741	35·068	1·1041	21·203	1·0357	7·340
1·1721	34·660	1·1020	20·796	1·0337	6·932
1·1701	34·252	1·1000	20·388	1·0318	6·524
1·1681	33·845	1·0980	19·980	1·0298	6·116
1·1661	33·437	1·0960	19·572	1·0279	5·709
1·1641	33·029	1·0939	19·165	1·0259	5·301
1·1620	32·621	1·0919	18·757	1·0239	4·893
1·1599	32·213	1·0899	18·349	1·0220	4·486
1·1578	31·805	1·0879	17·941	1·0200	4·078
1·1575	31·308	1·0859	17·534	1·0180	3·670
1·1537	30·990	1·0838	17·126	1·0160	3·262
1·1515	30·582	1·0818	16·718	1·0140	2·854
1·1494	30·174	1·0798	16·310	1·0120	2·447
1·1473	29·767	1·0778	15·902	1·0100	2·039
1·1452	29·359	1·0758	15·494	1·0080	1·631
1·1431	28·951	1·0738	15·087	1·0060	1·124
1·1410	28·544	1·0718	14·679	1·0040	0·816
1·1389	28·136	1·0697	14·271	1·0020	0·408
1·1369	27·728	1·0677	13·863		
1·1349	27·321	1·0657	13·456		

TABLE VI.

PERCENTAGES OF AMMONIA (NH_3) IN AQUEOUS SOLUTIONS OF THE GAS OF VARYING GRAVITY.

Sp. Gravity.	Per Cent.	Sp. Gravity.	Per Cent.	Sp. Gravity.	Per Cent.
0·9517	12·000	0·9602	9·750	0·9692	7·375
0·9521	11·875	0·9607	9·625	0·9697	7·250
0·9526	11·750	0·9612	9·500	0·9702	7·125
0·9531	11·625	0·9616	9·375	0·9707	7·000
0·9536	11·500	0·9621	9·250	0·9711	6·875
0·9540	11·375	0·9626	9·125	0·9716	6·750
0·9545	11·250	0·9631	9·000	0·9721	6·625
0·9550	11·125	0·9636	8·875	0·9726	6·500
0·9555	11·000	0·9641	8·750	0·9730	6·375
0·9556	10·950	0·9645	8·625	0·9735	6·250
0·9559	10·875	0·9650	8·500	0·9745	6·000
0·9564	10·750	0·9654	8·375	0·9749	5·875
0·9569	10·625	0·9659	8·250	0·9754	5·750
0·9574	10·500	0·9664	8·125	0·9759	5·625
0·9578	10·375	0·9669	8·000	0·9764	5·500
0·9583	10·250	0·9673	7·875	0·9768	5·375
0·9588	10·125	0·9678	7·750	0·9773	5·250
0·9593	10·000	0·9683	7·625	0·9778	5·125
0·9597	9·875	0·9688	7·500	0·9783	5·000

TABLE VII.

Percentages of Potash (K_2O) in Aqueous Solutions of Varying Gravity.

(Tünnermann. 15°).

Sp. Gravity.	Per Cent.	Sp. Gravity.	Per Cent.	Sp. Gravity.	Per Cent.
1·3300	28·290	1·1979	18·671	1·0819	8·487
1·3131	27·158	1·1839	17·540	1·0703	7·355
1·2966	26·027	1·1702	16·408	1·0589	6·224
1·2805	24·895	1·1568	15·277	1·0478	5·002
1·2648	23·764	1·1437	14·145	1·0369	3·961
1·2493	22·632	1·1308	13·013	1·0260	2·829
1·2342	21·500	1·1182	11·882	1·0153	1·697
1·2268	20·935	1·1059	10·750	1·0050	0·5658
1·2122	19·803	1·0938	9·619		

TABLE VIII.

Percentages of Soda (Na_2O) in Aqueous Solutions of Varying Gravity.

(Tünnermann).

Sp. Gravity.	Per Cent.	Sp. Gravity.	Per Cent.	Sp. Gravity.	Per Cent.
1·4385	30·220	1·2912	19·945	1·1428	9·670
1·4193	29·616	1·2843	19·341	1·1330	9·066
1·4101	29·011	1·2775	18·730	1·1233	8·462
1·4011	28·407	1·2708	18·132	1·1137	7·857
1·3923	27·802	1·2642	17·528	1·1042	7·253
1.3836	27·200	1·2578	16·923	1·0948	6·648
1·3751	26·594	1·2515	16·379	1·0855	6·044
1·3668	25·989	1·2453	15·774	1·0768	5·440
1·3586	25·385	1·2392	15·110	1·0675	4·835
1·3505	24·780	1·2280	14·500	1·0587	4·231
1·3426	24·176	1·2178	13·901	1·0500	3·626
1·3349	23·572	1·2008	13·297	1·0414	3·022
1·3273	22·967	1·1948	12·692	1·0330	2·418
1·3198	22·363	1·1841	12·088	1·0246	1·813
1·3143	21·894	1·1734	11·484	1·0163	1·209
1·3125	21·758	1·1630	10·879	1·0081	0·604
1·3053	21·654	1·1528	10·275	1·0040	0·302
1·2982	20·550				

TABLE IX.

BEAUME'S HYDROMETER.

A. For Liquids heavier than Water.

B°.	Sp. Grav.	B°.	Sp. Grav.	B°.	Sp. Grav.	B°.	Sp. Grav.
0	1·000	20	1·152	39	1·345	58	1·617
1	1·007	21	1·160	40	1·357	59	1·634
2	1·013	22	1·169	41	1·369	60	1·652
3	1·020	23	1·178	42	1·382	61	1·670
4	1·027	24	1·188	43	1·397	62	1·689
5	1·034	25	1·197	44	1·407	63	1·708
6	1·041	26	1·206	45	1·421	64	1·727
7	1·048	27	1·216	46	1·434	65	1·747
8	1·056	28	1·226	47	1·448	66	1·767
9	1·063	29	1·236	48	1·462	67	1·788
10	1·070	30	1·246	49	1·476	68	1·809
11	1·078	31	1·256	50	1·490	69	1·831
12	1·086	32	1·267	51	1·505	70	1·854
13	1·094	33	1·277	52	1·520	71	1·877
14	1·101	34	1·288	53	1·535	72	1·900
15	1·109	35	1·299	54	1·551	73	1·924
16	1·118	36	1·310	55	1·567	74	1·949
17	1·126	37	1·322	56	1·583	75	1·974
18	1·134	38	1·333	57	1·600	76	2·000
19	1·143						

B. For Liquids lighter than Water.

B°	Sp. Grav.	B°.	Sp. Grav.	B°.	Sp. Grav.	B°.	Sp. Grav.
10	1·000	23	0·918	36	0·849	49	0·789
11	0·993	24	0·913	37	0·844	50	0·785
12	0·986	25	0·907	38	0·839	51	0·781
13	0·980	26	0·901	39	0·834	52	0·777
14	0·973	27	0·896	40	0·830	53	0·773
15	0·967	28	0·890	41	0·825	54	0·768
16	0·960	29	0·885	42	0·820	55	0·764
17	0·954	30	0·880	43	0·816	56	0·760
18	0·948	31	8·874	44	0·811	57	0·757
19	0·942	32	0·869	45	0·807	58	0·753
20	0·936	33	0·864	46	0·802	59	0·749
21	0·930	34	0·859	47	0·798	60	0·745
22	0·924	35	0·854	48	0·794		

TABLE X.

Relation between English and Metric Weights and Measures.

1. *Measures of Weight.*

Milligram . . . . . = 0·01543235 troy grains.
Centigram . . . . . = 0·1543235 ,,
Decigram . . . . . = 1·543235 ,,
Gram . . . . . . = 15·43235 ,,
Do. . . . . . . = 0·643 pennyweight.
Do. . . . . . . = 0·03216 oz. troy.
Do. . . . . . . = 0·03527 oz. avoirdupois.
Kilogram . . . . . = 2·6803 lbs. troy.
Do. . . . . . . = 2·20462 lbs. avoirdupois.
Metric ton (1000 kilos.) . . = 2204·62 ,,

2. *Measures of Length.*

Millimetre . . . . = 0·03937 inches.
Centimetre . . . . = 0·3937 ,,
Decimetre . . . . = 3·937 ,,
Metre . . . . = 39·37 ,,
Do. . . . . = 3·2809 feet.
Do. . . . . = 1·0937 yards.

Inch = 2·53995 centimetres; foot = 3·04794 decimetres; yard = 0·91438 metres; mile = 1609·32 metres.

Scale.

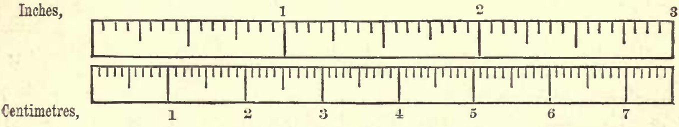

TABLE XI.

To convert degrees Fahrenheit into degrees Centigrade and vice versâ.

$$(C^\circ \times 1{\cdot}8) + 32 = F^\circ.$$
$$(F^\circ - 32) \div 1{\cdot}8 = C^\circ.$$

TABLE XII.

To convert degrees of Twaddell's Hydrometer into Specific Gravity.

(Degrees Twaddell × 5) + 1000 = sp. gravity.
(Sp. gravity − 1000) ÷ 5 = degrees Twaddell.

TABLE XIII.

For use in calculating the results of Oxydimetric and Iodometric Analyses, in which the Substance to be determined is not directly found.

CONTRACTIONS.

o = iron oxidised from ferrous to ferric salt; *r* = iron reduced from ferric to ferrous salt; *f* = free, or set free; *a* = available.

Sought.	Form in which Estimated.	Titration gave the Equivalent Amount of	Calculation Formula.	Reference t Text.
FeO	Fe_2Cl_4 (FeCl)	Fe	Fe × $\frac{9}{7}$ = FeO	§ 19
Fe_2O_3	Fe_2Cl_4	Fe	Fe × $\frac{10}{7}$ = Fe_2O_3	19
$H_2C_2O_42H_2O$ (C_2O_32HO)	$H_2C_2O_4.2H_2O$ (C_2O_33HO)	Fe	Fe × $\frac{9}{8}$ = $H_2C_2O_42H_2O$ (C_2O_33HO)	20
CaO	CaC_2O_4 ($CaOC_2O_3$)	Fe	Fe × $\frac{1}{2}$ = CaO	21
a.O	MnO_2	*o*.Fe	*o*.Fe × $\frac{1}{7}$ = *a*.O	23
Mn	MnO_2	*o*.Fe	*o*.Fe × 0·491 = Mn	23
Co	Co_2O_3	*o*.Fe	*o*.Fe × $\frac{2{\cdot}1}{2}$ = Co	24
Ni	Ni_2O_3	*o*.Fe	*o*.Fe × $\frac{2{\cdot}1}{2}$ = Ni	24
Pb	$PbCrO_4$ ($PbOCrO_3$)	*o*.Fe	*o*.Fe × 1·232 = Pb	27
Bi	$Bi_2O_32CrO_3$ (BiO_32CrO_3)	*o*.Fe	*o*.Fe × 1·25 = Bi	27
BaO	$BaCrO_4$ ($BaOCrO_3$)	*o*.Fe	*o*.Fe × 0·91 = BaO	27
CrO_3	CrO_3	*o*.Fe	*o*.Fe × 0·596 = CrO_3	26
f.Cl	Cl	*o*.Fe	*o*.Fe × 0·6339 = *f*.Cl	25
Cu	Cu_2O	*r*.Fe	*r*.Fe × 1·133 = Cu	22
Cu	Cu_2I	*r*.Fe	*r*.Fe × 0·566 = Cu	22
Sn	$SnCl_2$ (SnCl)	*r*.Fe	*r*.Fe × 1·053 = Sn	29
Sn	SnS_2	*r*.Fe	*r*.Fe × 0·527 = Sn	30
Cd	CdS	*r*.Fe	*r*.Fe × 1 = Cd	30
Zn	ZnS	*r*.Fe	*r*.Fe × 0·581 = Zn	30
Fe	Fe_2O_3	*f*.I	*f*.I × 0.441 = Fe	38
HNO_3 (NO_5)	*o*.Fe	*f*.I	*f*.I × 0·1653 = HNO_3 *f*.I × 0·1417 = NO_5	39
f.Cl	*f*.Cl	*f*.I	*f*.I × 0·28 = *f*.Cl	41
f.Br	*f*.Br	*f*.I	*f*.I × 0·63 = *f*.Br	41
Hg	Hg_2Cl_2 (Hg_2Cl)	combd. I	combd. I × 1·5748 = Hg	40

TABLE XIV.

GENERAL VIEW OF THE FORM IN WHICH THE MOST IMPORTANT METALS, NON-METALS, AND ACIDS ARE DETERMINED, AND OF THE METHODS OF DETERMINATION EMPLOYED.

a = Alkalimetric and Acidimetric methods; i = Iodometric; o = Oxydimetric; p = Precipitation; and w = Gravimetric methods.

Element.	Form in which Determined.	Method of Determination.	Pages.	Element.	Form in which Determined.	Method of Determination.	Pages.
Al	$AlPO_4$	*p.*	117	Au	Au	*w.*	160
Sb	Sb_2O_3	*i.*	93	I	$I.HIO.HIO_3$.	*i.*	103, 104, 106
As	As_2O_3	*i.*	94		$HI.Cu_2I$	*a, o* and *i.*	97, 98
Ba	$BaO.BaCO_3$	*a.*	40, 44	Fe	$FeSO_4$ or Fe_2Cl_4.	*o.*	69
Ba	$BaCrO_4$	*o.*	81		Fe_23SO_4 or Fe_2Cl_6	*i.*	97
Ba	$BaSO_4$	*p.*	127	Mg	$MgO.Mg(NH_4)PO_4$	*a, p.*	119
B	$Mg_3(BO_3)_2$	*w, a.*	174	Mn	$MnO_2.Mn_3O_4$	*o.*	75
Bi	$Bi_2O_32CrO_3$	*o.*	81	Mn	$Mn(NH_4)PO_4$	*p.*	119
Bi	$Bi_2O_32CrO_3$	*p.*	230	Hg	Hg_2Cl_2	*i.*	101
Bi	$BiPO_4$	*p.*	231	Mo	MoO_3	*o.*	87
Br	$Br.HBrO_3$	*i.*	103	Ni	Ni_2O_3	*o.*	77
Br	HBr. AgBr	*a, w.*	106	N	NH_4HO	*a.*	45
C	$C.H_2C_2O_4.\ \overline{T}.\overline{Cit}.$	*w, o, a.*	60, 71, 238	N	$HNO_2.HNO_3$	*o, a* and *i.*	44, 86, 100
Cd	CdS	*o.*	84	P	H_3PO_4	*p.*	115
Ca	$CaCO_3.CaSO_4$	*a.*	40, 44	Pt	Pt	*w.*	160
Ca	CaC_2O_4	*o.*	71	S	$H_2S.H_2S_2O_3.H_2SO_3$	*i.*	90, 92, 184
Ca	$CaSO_4$	*p.*	127	S	H_2SO_4	*a* and *p.*	57, 120
Cl	$Cl.HClO.HClO_3$.	*o* and *i.*	79, 103, 114	Ag	AgCl	*i* and *p.*	105, 111
	$HCl.AgCl.Hg_2Cl_2$	*a, p, i.*	102, 111	Si	SiO_2	*w.*	142
Co	Co_2O_3	*o.*	77	Sr	$SrO.SrCO_3.SrSO_4$	*a.*	40, 44
Cu	Cu_2O	*o.*	73	Ti	TiO_2	*o.*	87
Cu	Cu_2I	*o* and *i.*	73, 74	Sn	$SnCl_2$	*o* and *i.*	83, 94
Cr	CrO_3	*o.*	80	Sn	SnS_2	*o.*	84
F	$CaF_2.K_2SiF_6$	*w, a.*	54, 176	Zn	ZnS	*o.*	84

NOTE ON FILTRATION.

After the paragraph on filtration (p. 27) was in type, a very simple and efficacious little piece of apparatus for securing rapid filtration was devised by Mr. E. V. Miller, a student in the laboratory of this college. Mr. Miller has been good enough to allow me to introduce a description of his apparatus in this place.

The apparatus (see fig. 15) consists of a piece of glass tubing about 200 m.m. or so in length and 20 m.m. in diameter, drawn out at one end to an orifice perhaps one-fourth of the original diameter of the tube. The narrowed end of the tube connects, by caoutchouc and glass tubing, with a caoutchouc cork, which is fitted tightly into the flask destined to receive the filtrate. The funnel which is to contain the precipitate passes through a second hole in this cork. The funnel is furnished with a platinum cone pierced over its entire surface with a multitude of small holes made by a needle. The outer and wider end of the piece of tubing is closed with a good-fitting cork, through which passes a rod bearing, on its inner extremity, a cork which is made to fit air-tight within the tube. This latter condition is readily fulfilled by covering the cork with woollen threads which are moistened from time to time. The wide tube may very conveniently be adjusted along the filter-stand by means of wire or string; the whole arrangement is then very handy

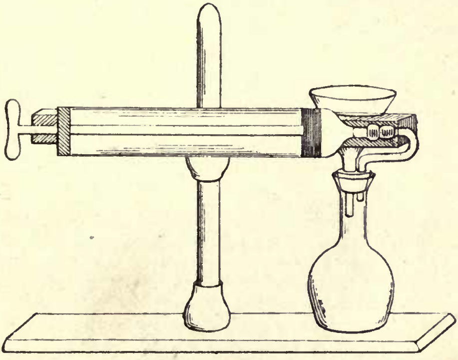

Fig. 15.

and readily transportable. The funnel having been filled with the liquid to be filtered, the piston in the wide tube is drawn back as far as possible, the air is thus rarefied in the flask, and the liquid quickly rushes through the filter; when the whole of the liquid has passed into the flask the cork is momentarily withdrawn from the flask, the piston is pushed back, the cork is again inserted, and the piston is again drawn back; this process is repeated until the whole of the liquid has been filtered.

Mr. Miller has made several attempts towards adapting a valve to the apparatus, but he finds that withdrawing the cork is the readiest and surest method for accomplishing the desired object. The platinum cone is essential; a double paper filter is not sufficient to withstand the pressure to which it is subjected.—*Tr.*

INDEX.

PRINTED BY ROBERT MACLEHOSE, GLASGOW.