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The Theory of Quantitative Analysis and its Practical Application

The Theory of Quantitative Analysis

and its Practical Application

By

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LONDON

GEORGE ROUTLEDGE & SONS, LTD.

BROADWAY HOUSE: 68–74 CARTER LANE, E.C.

1925

Printed in Great Britain by Stephen Austin & Sons, Ltd., Hertford

PREFACE

IN all chemical investigations analysis plays a fundamental part, and sooner or later accurate quantitative determinations of some element or group of elements have to be made. In fact, every branch of chemistry is dependent upon good analytical work, although this is sometimes not appreciated as fully as it should be.

It is quite true that analytical methods have in the main been developed empirically, but they are based on the same laws that hold sway in other branches of chemistry. In most cases, now that theoretical knowledge has advanced sufficiently, it is possible to interpret the operations of quantitative analysis in terms of the general chemical laws, and to develop new methods, if need be, by their help, instead of empirically. This treatment benefits physical chemistry since it illustrates the laws which obtain therein, and on the other hand a proper understanding of the physico-chemical foundations of chemical analysis should make it easier to meet the numerous difficulties which constantly occur in the course of analytical work. It should also help to check the hasty publication of analytical processes which too often turn out to be unsatisfactory because theoretically unsound.

On this new basis Analytical and Physical Chemistry are seen in their true perspective as two interwoven parts of one great subject—Chemistry. Ostwald, in his *Scientific Foundations of Analytical Chemistry* (Leipzig, 1894), was the pioneer in this treatment of the subject, which has made great headway of recent years.[1] It is the present author's experience, however, that practice and theory require to be combined more intimately than is done even now. It has been his aim to illustrate every theoretical point by examples which it is hoped are representative of the best methods and the most important quantitative

[1] Special mention must be made of Böttger's *Qualitative Analyse vom Standpunkte der Ionenlehre*, Leipzig, 1908 (2nd edition), and of Stieglitz's *The Elements of Qualitative Chemical Analysis*, New York, 1911.

estimations in Analytical Chemistry. The plan has been to begin with the estimation which seemed to involve the smallest number of theoretical points and to lead up from that to more complex cases. The order of the estimations resulting from this system is naturally different from that usually adopted, but there appears to be no disadvantage in this. No attempt has been made to write a complete treatise on Quantitative Analysis, but rather to consider most of the physico-chemical principles at the basis of all analytical operations. To illustrate each point processes have been chosen which are either of practical importance or else particularly well adapted for purposes of illustration. Gravimetric and volumetric methods only are considered. As the aim has been to illustrate and discuss the physico-chemical basis of analysis rather than the more purely chemical aspect, separations have been included only so far as seemed necessary for this purpose. The more purely physical methods of analysis such as electrolytic, electrometric, colorimetric, polarimetric, refractrometric, etc., lie outside the scope of the book. Some of these are applicable only under very special circumstances, for others special treatises are available (e.g. Classen: *Quantitative Analyse durch Elektrolyse*; G. and H. Krüss: *Kolorimetrie und Quantitative Spektralanalyse*) and to these and the recent literature the reader is referred.

Nearly all existing textbooks on Quantitative Analysis suffer from one peculiarity. However precise the details which may be given for carrying out an estimation, there is nearly always some essential figure lacking. Frequently it is found that, while the quantities of reagents to be used, or the volumes of solutions to be operated upon, are most carefully mentioned, no indication is given of the approximate amount of the substance being estimated to which these particulars are intended to refer. It will only be by chance that a student following such directions will work under the best conditions. In the present book an effort has been made to avoid this type of error and to give precise working details in all cases where such are needed. The reasons for these details are discussed in the theoretical sections.

The book is not intended for beginners but for those who already possess some knowledge of Analytical and Physical Chemistry, and the author hopes that it will prove interesting and helpful even to experienced analytical chemists.

It is assumed that all who use the book will be familiar with the Ionic Theory and have a working knowledge of the Law of Mass Action. Constant use of both will be made. As solubility plays such an important part in gravimetric analysis a special effort has been made to consider the factors which determine solubility, and to show the essential similarity between the forces which lead to solution in a solvent and ordinary chemical forces. Modern research tends to show that eventually the same forces are concerned in holding together a crystal and the constituents of a solution whether the latter is crystalloidal or colloidal. The old distinction between chemical and physical forces tends to disappear. Solution of a crystal in a solvent and the behaviour of colloidal solutions must be regarded as due to an interplay of chemical forces. Some questions have therefore been dealt with at considerable length on account of their bearing on such problems rather than because of their intrinsic importance for quantitative analysis itself. It is hoped that the reader's interest in wider physico-chemical problems may be roused in this way through the analytical work, and that the numerous references given will be of assistance in studying special subjects more fully. These references serve to indicate the help derived by the author from many books and journals. In addition, he desires to thank Mr. P. E. Turner for reading much of the original manuscript and offering many useful criticisms.

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November, 1924.

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CHAPTER I

INTRODUCTORY

QUANTITATIVE analysis, which aims at the estimation of the various constituents present in any given substance, can be divided into two sections, namely, Gravimetric Analysis and Volumetric Analysis. Broadly speaking, one can say that in the former the constituent to be estimated is converted into some suitable compound of known composition, which is subsequently carefully weighed, or the constituent may be separated and weighed as such. In the latter one determines the exact volume of a solution of known composition which is required to complete some definite chemical reaction with the constituent to be estimated. In Gas Analysis, which is really a special branch of Volumetric Analysis, what is usually determined is the decrease of volume after the gas which is being estimated has been absorbed by a suitable solvent.

To obtain accurate results in quantitative work it is necessary to pay great attention to the manipulation. As the reader is assumed to be acquainted with the general methods, only a few details will be mentioned to which, in the author's experience, too little attention is often paid.

For quantitative work it is nearly always best to use lipped beakers, as otherwise there is danger of liquid running down the outside of the beaker when it is poured out. Unnecessarily large beakers should be avoided. On transference of liquid from one vessel to another, the liquid should always be poured down a glass rod: otherwise, even with lipped beakers, some will run down the outside. All glass rods and glass tubes used in quantitative work should be of a suitable size and length, and should have their ends rounded off in the blowpipe flame. If this is not done, there

is a danger of fragments of glass breaking off and getting into precipitates. Sharp-ended rods and tubes are liable to lead to scratching and possible cracking of beakers.

Great attention should, of course, be paid to cleanliness. Beakers and other vessels should be clean not only inside, but outside also. The working bench, filter stands, etc., should be kept as clean as possible. Beakers, funnels, etc., containing solutions or precipitates, should be kept covered in order to exclude dirt, a precaution especially necessary in towns.

The bunsen burner is a simple piece of apparatus which is often misused. When it is employed to ignite a precipitate or to boil a liquid, it is advisable to commence with a small flame. In this way one avoids cracking vessels by the sudden expansion due to too rapid heating, and minimizes the danger of spurting, which may occur, for instance, on heating a moist precipitate too suddenly. The air supply of the burner should always be so regulated that there is just not a tiny luminous point to the flame. The danger of "striking back" is then reduced to a minimum. This is especially important if a flame is to be left burning over night. Vigorous boiling of solutions during quantitative work should, as a rule, be avoided; it is nearly always unnecessary and often harmful, for there is always danger of loss by spurting even when the vessel is covered with a clock glass. When a considerable volume of liquid has to be concentrated by evaporation, this is often best done in an uncovered beaker over a flame the size of which is so regulated that the solution just does not boil. Under these conditions the evaporation proceeds quite rapidly. If the evaporation is to be taken to dryness, it should be carried out (or at any rate completed) on the water bath in a porcelain dish. A beaker is not very suitable for evaporations on the water bath, since it cannot be heated so well as a dish, and the evaporation is much slower in consequence.

Care should be used to take a suitable weight of the substance for analysis. In the case of gravimetric estimations, sufficient should be taken initially to yield 0·1 to 0·3 gram of the compound which has finally to be weighed.

Of course, this may not always be possible if the substance being estimated is present only in small amount.

What has to be borne in mind is that working with too large amounts is as bad as working with too small amounts. The latter practice is bad chiefly because the errors of weighing may then be considerable, but, further, it necessitates very much greater care, since the loss of a drop of solution, etc., may cause a very large error. Now, although working with large quantities reduces any errors due to weighing, the bulky precipitates obtained are much more difficult to wash, and this tends to make the results obtained too high. In addition, large precipitates take much longer to filter, and so the analysis becomes more tedious. One has to try and strike a happy mean, and with a good balance, sensitive to one- or two-tenths of a milligram with ordinary small loads, the quantities given above are most suitable both from the point of view of the rapidity of the analysis and the accuracy of the results obtained.

In the majority of cases one has some idea of the approximate composition of the substance which is being analysed, and one weighs out an amount for analysis accordingly. In other cases, it is often well to make a rough preliminary estimation before proceeding to the exact analysis. This may save much subsequent trouble.

Great attention should be paid to the bulk of liquid used in an analysis. The appropriate volume to use must vary from case to case and can be satisfactorily learned only by experience. It is a mistake to work with too dilute solutions since the filtering of large volumes prolongs the analytical process. Then again many precipitates have an appreciable solubility, and any errors caused by this will naturally be magnified by the presence of a large quantity of liquid. For this reason also it is a mistake to wash precipitates with an excessive quantity of water.

It is just as wrong to work with too concentrated solutions, for many precipitates separate in a very finely divided form in such cases, and are difficult to filter. Quantitative separations also are very often unsatisfactory in strong solutions.

During an analysis in which several estimations have to be made, the bulk of liquid will gradually increase owing to the water used in washing the various precipitates. When the amount of solution becomes inconveniently great it should be concentrated by evaporation before proceeding further.

Perhaps the most important of all points upon which good analytical work depends is the careful regulation of the amounts of the various reagents used. These amounts should be just a little more than sufficient to bring about the desired reaction. A *slight* excess of the reagent is nearly always adequate, whilst a large excess is often harmful. There are a few cases in which reagents have to be used in large quantity, but they are quite exceptional and will always be specially mentioned.

The amounts of acids and alkalies used for neutralization, acidification, etc., should be very carefully regulated. The success of many precipitations, especially of sulphides, depends in large measure on the careful adjustment of the acidity. The presence of a large amount of acid is harmful in the majority of cases. When a metal or salt has to be dissolved in acid, the minimum amount of the latter should be used, and it is often well to remove the excess by evaporation before proceeding with the analysis.

Although the proper regulation of the amounts of reagents is in great measure a result of the analytical skill resulting from experience, a great deal can be done to further it by having the various reagents made up to certain definite strengths, which should be indicated on the labels. These indications naturally need to be only approximate. In the case of acids and alkalies they can be noted in terms of normality, as indeed can strengths of other reagents also. In many cases, however, it is more convenient to indicate on the label the amount of the reagent which should be used for precipitating a given quantity of the substance in the estimation or separation of which it is used. Thus, for example: Ammonium oxalate solution is employed practically only in the separation or estimation of calcium. A solution saturated at the ordinary temperature is the most

convenient, and 10 c.c. of this is more than sufficient to precipitate 0·1 gram of CaO. On the label should accordingly be written " Use 10 c.c. for every 0·1 gram CaO ".

If preferred, all solutions can be made up to some common equivalent strength, say twice normal, but, on the whole, this is not so satisfactory, as some of the solutions will probably be inconveniently strong and others inconveniently weak.

A slight sediment often forms after a time in the reagent bottles, but by taking out the solutions in pipettes, disturbance of the sediment may be avoided.

The filtration and washing of precipitates are important operations worthy of more consideration than is generally given them. According to the nature of the precipitate and the treatment to which it is to be subjected, the filtration is carried out either on an ordinary filter paper or through a Gooch crucible.

For precipitates which filter readily, and which are to be ignited before weighing, an ordinary filter paper is nearly always most convenient, except in cases where the precipitate is likely to be reduced by the carbon of the filter paper during the ignition. Even in many such cases, however, an ordinary filter can be used if the paper is ignited apart from the bulk of the precipitate, and the ash treated suitably to counteract the effects of the reduction. The filter papers must be either ashless or such as yield known amounts of ash. The size and nature of the paper must be chosen according to the amount and state of division of the precipitate to be filtered. The finer a precipitate the closer the grain of the paper must be. The paper should be folded so as to fit the funnel properly, since the rate of filtration depends largely on this factor.

The last traces of precipitate are sometimes difficult to transfer to the filter. If they stick to the beaker they can be loosened by the aid of a small piece of india-rubber tubing passed over the end of a glass rod. Then by holding the vessel at a suitable inclination over the filter the remains of the precipitate can be rinsed into it by means of a jet from the wash bottle. The aperture of the jet should be

of such a size as to deliver not too coarse nor too fine a stream of water.

As regards the actual washing of the precipitate there are several points to bear in mind. In many cases the washing is done with pure water, and where this is not so the fact will be specially mentioned. If a precipitate is not appreciably soluble in hot water, this latter should be used as it filters more rapidly. During the washing care should be taken that the precipitate is rinsed down to the apex of the filter paper, so that it can be separated the more easily for the subsequent ignition. Attention should also be paid to the washing of the extreme rim of the paper, which is otherwise liable to escape thorough washing. This is best carried out by allowing water to fall vertically on to the rim from the wash bottle jet (or a pipette) drop by drop. With a little practice this is easily done, and avoids any tendency there may be for the precipitate to creep over the filter paper on to the funnel. This will probably happen if a full jet of water is directed on to the rim of the paper.

It is better to wash the precipitate with several successive small quantities of water than with a few large quantities. A simple mathematical calculation shows that the same amount of soluble matter can be removed in that way with the employment of less water. This is desirable both on the score of economy of time and of minimizing any error due to solubility of the precipitate. After each addition of wash water the filter should be allowed to drain completely before a fresh addition is made. The washing must always be continued either until a few drops of the wash liquor caught separately and evaporated to dryness leave no visible residue, or until they give no reaction when suitably tested for the substance which has to be removed by washing.

When thoroughly washed the precipitate is dried either in the water or steam oven, and then, in the majority of cases, is ignited before weighing. In some cases (e.g. HgS, CdS) where the precipitate is volatile, or would be oxidized or otherwise decomposed, such ignition is out of the question. The precipitate can then be heated only to a sufficiently high temperature to dry it thoroughly without causing

other complications. A temperature of 100° is that most commonly employed for this purpose, though sometimes a higher temperature (110°, 150°, etc.) may be needed. The particular conditions suitable for each case will be specially mentioned. In such cases a Gooch crucible should be used, and of course should be weighed before the filtration after being dried under the same conditions as those to be subsequently used for the precipitate.

Gooch crucibles can be used in many other cases, and it is possible to ignite them gently. In the author's opinion, however, a Gooch crucible is not to be recommended as a rule in cases where the filtrate is required for a subsequent estimation owing to the awkward rinsing out of the filter flask which is required. Precipitates can be weighed on ordinary filter papers if they can be dried at a temperature not above 100°; higher temperatures are not permissible owing to charring of the paper. The filter paper in such cases must be dried to constant weight at the same temperature before use. Weighed filter papers require more care than a Gooch crucible, but will give very good results. The paper on removal from the oven should be at once placed in a well-stoppered weighing bottle, and should be weighed in that after being left to cool for a sufficient time in the balance case. The weighing bottle should not be put in the oven.

Precipitates are ignited before weighing in order to burn off the filter paper, to completely dry the solid, and in many cases to drive off combined water, ammonia, sulphur, etc. In some exceptional cases (MnS, ZnS, e.g.) the ignition has to be carried out in an atmosphere of inert gas, such as hydrogen, to prevent oxidation.

In most cases it is best to burn the filter paper apart from the precipitate. After thoroughly drying the latter in the water oven, the previously weighed crucible in which the ignition is to be carried out is placed on a clean sheet of glazed paper, and the dry precipitate scraped into it as completely as possible with the help of a clean dry knife or spatula. The filter paper is then folded up to a narrow strip so that the apex of the original cone remains at one end. A corner of the other end is then held in a clean pair of

crucible tongs, and the paper is burned by holding it (over the crucible) in the bunsen flame until all the carbon has disappeared.

If any of the precipitate has crept on to the funnel during the washing, this can be removed by moistening the top of the dried paper with a drop of water and rubbing it round the funnel.

The ash of the paper is allowed to fall into the crucible, into which also any particles which may have fallen on to the glazed paper are carefully brushed. The crucible and contents are then carefully ignited, allowed to cool in the desiccator, and weighed.

In those cases where the precipitate adhering to the filter paper is reduced by the latter during its ignition, the bulk of the precipitate is not put directly into the crucible, but is first placed on the glazed paper. The ash of the filter paper is allowed to fall into the empty crucible, and is suitably treated to counteract the effect of the reduction (see, for instance, the treatment in the case of AgCl). The rest of the precipitate is then brushed off the glazed paper into the crucible and the whole is ignited.

The above method of burning the filter paper is far simpler and better than that usually described in which it is held in a spiral of platinum wire. With the wire there is considerable danger of the small amount of precipitate still on the filter paper, or of its reduction products, coming in contact with the wire and spoiling both it and the estimation. This danger is avoided by holding the filter paper in the tongs by a corner on which there is no precipitate. The tiny unburned corner of the paper can either be thrown away, or dropped into the crucible and burned there, according to the personal view of the operator.

In weighing the ignited precipitates it must be remembered that all solids have to a greater or less extent the property of adsorbing or condensing moisture on their surface. The amount adsorbed depends on the temperature and the pressure of the water vapour present in the air, and to a very great extent on the area of surface exposed. The moisture so retained by bodies which in the ordinary sense are perfectly

dry may be considerable in cases where a large surface is exposed, as with a very fine powder or a large glass vessel. For this reason ignited precipitates are best allowed to cool in the dry air of a desiccator before weighing, and empty crucibles should be ignited and cooled in the same way before being weighed at the commencement of an estimation.

For full details of how to use the chemical balance and how to calibrate a set of weights, the reader is referred to Treadwell's *Quantitative Analysis*, or the other analytical textbooks. It is, however, as well to point out that it is of the utmost importance that the weights should be calibrated when first bought and also at intervals of about two years afterwards, as they slowly get out of adjustment when constantly in use.

It is hardly necessary to remark that since the accuracy of volumetric work depends upon the accuracy of the graduated vessels employed, these should always be carefully calibrated and kept thoroughly clean. It is especially necessary that burettes and pipettes should be free from grease, otherwise they do not deliver correctly. Materials used as standards must be carefully purified.

It often happens that the solutions intended for volumetric work are insufficiently mixed. The process of diffusion in solution is very slow, and unless great care is taken to mix the solutions by thorough shaking, both before filling the graduated flask up to the mark and afterwards as well, it is very likely that the solution will not be uniform in composition. During the earlier stages of mixing striæ may often be observed in the solution showing the presence of streams of liquid of different concentration from the rest. The refractive index of the solution depends upon its concentration, hence the visibility of these streams even when they are colourless.

When preparing solutions for volumetric work it is to be remembered that in all cases the solution has to be made up to a certain volume, and must not be made by adding that volume of distilled water to the solid. For instance, a normal solution of sodium carbonate is obtained by dissolving $\frac{Na_2CO_3}{2}$ or 53 grams of the solid, in distilled

water and making the solution up to a litre. The solution so obtained will naturally be different fron one made by dissolving 53 grams of sodium carbonate in a litre of distilled water. This latter solution would be a little more dilute than the former because the sodium carbonate occupies a certain amount of space even in the dissolved state—although not so much as in the solid state. But, in any case, the volume occupied by the dissolved solid is considerable, and, if not allowed for, may cause large errors.

It is extremely probable that if two compounds were absolutely indifferent towards each other chemically the volume occupied by a solution of one in the other would be exactly the sum of the volumes of the two constituents in the pure state. In practice, however, this is never so, and in the vast majority of cases there is a contraction observed, though in a few instances the volume of solution is slightly greater than the sum of the volumes of the constituents. It is of course hard to say whether the contraction is due to the solvent or the solute, but it probably arises from residual forces of attraction between the molecules of solvent and solute of the same nature as those considered later in connexion with the hydration of ions and salt molecules in aqueous solution.

In this connexion a recent paper by Hartley and Barrett [1] may be consulted. The contractions on solution of one gram molecule of a number of potassium salts of monobasic acids are given for infinite dilution at 18°. They range mostly from 8 to 12 c.c. That of KIO_3 is exceptionally high, being 21·4 c.c. The paper shows also the effect of varying concentration on the molecular contraction.

[1] *J. Chem. Soc.*, 1923, **123**, 398.

CHAPTER II

DOUBLE DECOMPOSITION

The Solubility Product

THE simplest possible cases in quantitative analysis are those in which a double decomposition occurs with formation of an insoluble compound of the element or radicle to be estimated. The numerous interesting theoretical points which arise in this connexion may be suitably discussed with special reference to the quantitative estimation of barium in one of its soluble compounds.

The Estimation of Barium as Sulphate

An amount of the compound which will yield from 0·2 to 0·4 gram of barium sulphate is accurately weighed out and dissolved in 50–100 c.c. of distilled water, to which one or two c.c. of dilute hydrochloric acid may be added. The solution is heated to boiling, and is precipitated by the addition drop by drop of a small excess of hot dilute sulphuric acid. The beaker with contents is left to stand on the water bath for an hour or two, and the precipitate is then filtered off on a good close-grained filter. The precipitate, after thorough washing with hot water (until the wash waters are no longer acid to litmus paper or give no reaction for sulphate), is ignited and weighed. The ignition in the open crucible over the bunsen should be continued for about ten minutes after all the carbon has burnt off. A small amount of the sulphate is reduced to sulphide by the carbon of the filter paper, but after a short ignition in the air the sulphide is re-oxidized to sulphate.

Mass-Action Law and Solubility

The reaction leading to the precipitation of the barium sulphate is represented by the equation :—

$$BaCl_2 + H_2SO_4 \rightleftarrows BaSO_4 + 2HCl$$

and the reaction, like all chemical reactions, is a "reversible" (or "balanced") one—that is to say, it proceeds only until a condition of equilibrium is established between the four compounds in the above equation. We should then have in agreement with the law of mass action :—

$$\frac{[BaCl_2]\,[H_2SO_4]}{[BaSO_4]\,[HCl]^2} = \text{Constant.}$$

Square brackets denote the equilibrium concentrations of the respective substances in solution in gram mols. per litre.

For any ordinary concentrations of $BaCl_2$ and H_2SO_4 a condition of equilibrium cannot be reached without a precipitate forming owing to the fact that more $BaSO_4$ would be present than the solution could dissolve, for $BaSO_4$ is a very insoluble compound. The solution in contact with the precipitated $BaSO_4$ will fulfil the condition expressed by the above equation, which indicates that the solution will contain not only H_2SO_4 and HCl, but also $BaCl_2$ and $BaSO_4$ (in minute amounts).

Other factors must, however, be considered. If the solution is reasonably dilute only a small part of the above salts will be present in the un-ionized condition. They will be almost completely split up into the ions $H^{\cdot}$, $Ba^{\cdot\cdot}$, Cl', and SO_4'', each undissociated salt being in equilibrium with the ions derived from it, as follows :—

$$\left.\begin{array}{lll} Ba^{\cdot\cdot} + 2Cl' \rightleftarrows BaCl_4 & [Ba^{\cdot\cdot}]\,[Cl']^2 & = K_1\,[BaCl_2] \\ 2H^{\cdot} + SO_4'' \rightleftarrows H_2SO_4 & [H^{\cdot}]^2\,[SO_4''] & = K_2\,[H_2SO_4'] \\ Ba^{\cdot\cdot} + SO_4'' \rightleftarrows BaSO_4 & [Ba^{\cdot\cdot}]\,[SO_4''] & = K_3\,[BaSO_4'] \\ H^{\cdot} + Cl' \rightleftarrows HCl & [H^{\cdot}]\,[Cl'] & = K_4\,[HCl] \end{array}\right\}$$

Each of these equilibria may be represented by the mass-action equation given in brackets where K_1, K_2, K_3, K_4 are the respective equilibrium constants. These facts must be borne in mind, but for our further purpose we need only consider the reaction—

$$Ba^{\cdot\cdot} + SO_4'' \rightleftarrows BaSO_4$$

However much SO_4 or Ba may be present in a solution, a precipitate of $BaSO_4$ will not be obtained unless they are present as ions.

The mass-action equation $[Ba^{\cdot\cdot}]\,[SO_4''] = K_3\,[BaSO_4]$ can be further simplified when solid $BaSO_4$ is present, for

in that case we have a further equilibrium, namely, that between the solid $BaSO_4$ and the un-ionized dissolved $BaSO_4$:—

$$Ba^{\cdot\cdot} + SO_4'' \rightleftarrows BaSO_4 \text{ dissolved} \rightleftarrows BaSO_4 \text{ solid.}$$

The precipitation of $BaSO_4$ can take place only by displacing the equilibrium from left to right, and so long as any solid $BaSO_4$ is present the concentration of the un-ionized dissolved $BaSO_4$ will be automatically kept constant. Hence we may write :—

$[Ba^{\cdot\cdot}][SO_4''] = K_3[BaSO_4] = K$. This constant K is called the "*Solubility Product*", and its significance is that in presence of solid $BaSO_4$ the product of the concentrations of $Ba^{\cdot\cdot}$ and SO_4'' in any aqueous solution must remain constant at any given temperature, however their individual values may vary.

Although the above considerations show that it is impossible to precipitate absolutely all the barium as $BaSO_4$, yet the solubility of the latter is so small as to be generally negligible in practice.

One of the conditions necessary to render a precipitate suitable as a means of separating and estimating an element or radicle is that it should have a small solubility under the conditions of precipitation. A result of this is that the precipitate tends to separate out very quickly, and therefore in a very fine state of division. If it is too fine it may be very difficult to filter on account of the particles passing through the pores of the filter paper.

Increased solubility of fine particles. The majority of compounds are more soluble in hot water than in cold, and in consequence if precipitated hot separate out more slowly and in coarser particles than when precipitated cold. This is clearly advantageous for the subsequent filtration. But the matter is more complex than this, for the particles of the precipitate which separate first come out more quickly than those which separate subsequently (owing to a certain degree of supersaturation being reached before any separation occurs). The precipitate therefore consists of particles of different sizes. Now, a fine particle is more

soluble than a coarse particle[1] of the same substance, so that if the solution in contact with the precipitate under consideration is saturated with respect to the fine particles it will be supersaturated with respect to the others. The fine particles will therefore gradually dissolve, and the coarse ones will become bigger at their expense owing to deposition upon them of fresh substance from solution. Now this process goes on much more quickly the higher the temperature, and this partly accounts for the advantageous results of precipitation from hot solutions.

The precipitate of barium sulphate is crystalline, and the above considerations apply specially to such crystalline precipitates. As a rule the less soluble such a precipitate is, the more necessary it is to precipitate hot and to digest or allow to stand some time before filtration.

The solubility of a compound is influenced in several ways by different factors which are often of great importance in quantitative work. The most important effects are those due to the presence of other salts. These may either diminish or increase the solubility.

Effect of salts yielding a common ion on the solubility. *The solubility of a compound is diminished by the presence of another salt yielding an ion similar to one of those yielded by the compound.* The reason for this will be apparent if we consider, for example, the case of barium sulphate. As already explained above, the solubility of this compound is regulated by the relation

$$Ba^{\cdot\cdot} + SO_4'' \rightleftarrows BaSO_4 \text{ dissolved} \rightleftarrows BaSO_4 \text{ solid}$$

and by the mass-action equation

$$[Ba^{\cdot\cdot}][SO_4''] = K_s[BaSO_4] = K.$$

[1] This has been shown to be true experimentally. It is similar to the higher vapour pressure exerted by small drops of liquid as compared to that of large drops. Hulett (*Z. physikal. Chem.*, 1901, **37**, 385) found that at 25° a solution saturated with respect to $BaSO_4$, the particles of which were 0·0018 mm. in diameter, contained 0·00229 grm. $BaSO_4$ per litre. When the particles of $BaSO_4$ were only 0·0011 mm. in diameter the saturated solution contained 0·00415 grm. $BaSO_4$ per litre. The same author found similar differences in the case of gypsum ($CaSO_4 \cdot 2H_2O$) and mercuric oxide.

Now, it is plain from this that less $BaSO_4$ will dissolve in a solution of Na_2SO_4, say, than in pure water, for the product $[Ba^{\cdot\cdot}][SO_4^{\prime\prime}]$ must remain constant, and since we have increased $[SO_4^{\prime\prime}]$ the other factor $[Ba^{\cdot\cdot}]$ must diminish, and it can only do this by some of the $Ba^{\cdot\cdot}$ ion separating from solution with an equivalent amount of $SO_4^{\prime\prime}$ ion as $BaSO_4$. If the concentration of $SO_4^{\prime\prime}$ ion due to the Na_2SO_4 is moderately large, practically all the $Ba^{\cdot\cdot}$ may be removed from solution and the solubility of the $BaSO_4$ will then be accounted for almost entirely by the undissociated dissolved $BaSO_4$, the amount of which would be very small as we are dealing with very dilute solutions.

From what has been said above it might seem desirable to use a considerable excess of the precipitant. This, however, is not the case, and it can be said that in practically all cases only a small excess of the precipitant should be used. There are several reasons for this. First, the consideration of the effect of the size of particles on the solubility given above shows that the presence of much excess of the precipitant will in the case of very insoluble precipitates like barium sulphate tend to make the precipitate still finer (by causing it to separate more rapidly from solution), and consequently more troublesome to filter.

Secondly, since the excess of precipitant has to be removed by washing the precipitate, it is obvious that little would be gained by adding it initially, and thirdly, excess of precipitant is often injurious in other ways, which will be considered later.

To illustrate quantitatively the effect on the solubility of sparingly soluble salts of other salts yielding a common ion a well-known example may be quoted. The solubility of silver acetate in weak solutions of sodium acetate and of silver nitrate was determined by Nernst.[1] His results for 16° are given in the following tables, in which are also given the necessary data for calculating the solubility product of the silver acetate ; this product, it will be seen, remains sensibly constant. The tables are as given by Stieglitz,[2]

[1] *Z. physikal. Chem.*, 1889, **4**, 372.

[2] *The Elements of Qualitative Chemical Analysis*, 1912, vol. **1**, p. 146.

concentrations being stated as gram molecules (or gram ions) per litre. In column 1 are the concentrations of sodium acetate or silver nitrate; column 2 gives the percentage ionization of the salt at the dilution given; column 3 the amount of silver acetate dissolved; column 4 the percentage ionization of the silver acetate; column 5 the total concentration of the acetate ion; column 6 that of silver ion, while column 7 gives K the solubility product, i.e. $[Ag^{\cdot}][CH_3COO']$.

1 Na. acetate	2 %	3 Ag. acetate	4 %	5 $[CH_3COO']$	6 $[Ag^{\cdot}]$	7 K
		0·0603	70·8	0·0427	0·0427	0·00182
0·061	78·6	0·0392	64·5	0·0733	0·0253	0·00185
0·119	75·8	0·0280	59·7	0·1069	0·0167	0·00179
0·230	70·8	0·0208	52·3	0·1736	0·0109	0·00189
$AgNO_3$						
0·061	82·0	0·0417	64·0	0·0267	0·0767	0·00205
0·119	78·4	0·0341	58·6	0·0200	0·1133	0·00227
0·230	74·0	0·0195	51·7	0·0101	0·1801	0·00182

The quantitative effect of excess of SO_4'' ion on the solubility of $BaSO_4$ may be deduced as follows. The solubility of $BaSO_4$ in water at 19° is 0·0023 gram per litre = 0·00001 gram mol. per litre.[1] On the assumption that in such a dilute solution the salt is ionized to the extent of 98 per cent,[2] the solubility product is found to be $[Ba^{\cdot\cdot}][SO_4'']$ = $(0{\cdot}0000098)^2 = 0{\cdot}000000000096$ or $9{\cdot}6 \times 10^{-11}$. It follows that a solution of barium sulphate in pure water would contain about 0·00134 gram of barium ion per litre. This amount would be left behind in every litre of filtrate from the $BaSO_4$ precipitate if the theoretical amount of H_2SO_4 had been used in its precipitation, on the assumption that the HCl simultaneously formed did not influence the solubility. But owing to the very small value of the solubility product a very slight excess of sulphate will suffice to reduce enormously the amount of barium remaining in solution. Thus an excess of only 0·1 gram, i.e. 0·001 gram mol., of H_2SO_4 per litre would

[1] Holleman, *Z. physikal. Chem.*, 1893, **12**, 125.

[2] The actual figure is not known, but this is a likely value from the known dissociation of salts like KCl in dilute solutions.

increase the concentration of SO_4'' ion about one hundred times, and $BaSO_4$ would be precipitated until the concentration of $Ba^{\cdot\cdot}$ ion had been reduced a hundred times. The loss of $Ba^{\cdot\cdot}$ ion in the filtrate would thus be reduced to about 0·013 milligram per litre (= 0·022 milligram $BaSO_4$). In addition to this, however, there is the small amount of un-ionized $BaSO_4$, the amount of which is unaffected by the excess of SO_4'' ion added. This we have supposed to amount to 2 per cent of the total $BaSO_4$ contained in a saturated solution of $BaSO_4$ in pure water. It would, therefore, amount to about 0·046 milligram per litre. It follows that even with a very insoluble instance like barium sulphate and working under favourable conditions the weight of precipitate obtained may be too low to the extent of nearly 0·1 milligram for every litre of solution, wash liquor, etc. Many precipitates which have to be dealt with are much more soluble than barium sulphate, so the undesirability of using excessive amounts of wash water or working with very dilute solutions is apparent.

In connexion with the above it should be noted that most of the experimental work on the effect of electrolytes on the solubility of sparingly soluble salts has been carried out with compounds yielding two monovalent ions. The case of barium sulphate was not examined experimentally until comparatively recently,[1] and it seems to be more complicated than is indicated in the above discussion. Thus it was found that in sulphuric acid solutions weaker than 0·3N the solubility of barium sulphate was practically the same as in pure water. Only when the acid was stronger than this did it have a marked depressing effect on the solubility. The effect of both $BaCl_2$ and H_2SO_4 in diminishing the solubility of $BaSO_4$ in solutions of other electrolytes such as HNO_3 was shown to be very marked. The peculiar effects noted with dilute H_2SO_4 may be connected with the comparatively small value of the second dissociation constant of H_2SO_4 [2] or, again, it may have something to do with the fact that the $BaSO_4$ used in the investigation was in an excessively fine state of division.

[1] Karaoglanow, *Z. anal. Chem.*, 1917, **56**, 224.

[2] See p. 40.

Somewhat similar results to the above have been obtained with radium sulphate,[1] which has been shown to have the same solubility in pure water as in sulphuric acid solutions of strengths ranging from 0·01N to 50 per cent. There is a marked rise in solubility when the strength of the acid is above 65 per cent.

Effect of salts not yielding a common ion on the solubility.

The solubility of a compound is increased by the presence of another salt yielding no ion in common.

For the discussion of this effect we can consider the result of treating barium sulphate with a solution of ammonium chloride. In the solution in contact with solid $BaSO_4$ we shall have the equilibria

$$Ba^{\cdot\cdot} + SO_4'' \rightleftarrows BaSO_4 \rightleftarrows BaSO_4 \text{ solid}$$
$$NH_4^{\cdot} + Cl' \rightleftarrows NH_4Cl$$

But some of the $Ba^{\cdot\cdot}$ and Cl' ions will unite to form undissociated $BaCl_2$, while some undissociated $(NH_4)_2SO_4$ will be produced in a similar manner, so that there will be two further equilibria to consider, viz. :—

$$Ba^{\cdot\cdot} + 2Cl' \rightleftarrows BaCl_2$$
$$2NH_4^{\cdot} + SO_4'' \rightleftarrows (NH_4)_2SO_4$$

The result of this is that more $BaSO_4$ must dissolve than would dissolve in pure water in order to supply the additional $Ba^{\cdot\cdot}$ and SO_4'' ions required for these two additional equilibria. This effect of neutral salts is small,[2] but it is sometimes utilized, as, for example, in the case under discussion. We have seen that the precipitate of barium sulphate, owing to its extreme insolubility, is liable to give trouble during the filtration, and requires careful handling. Sometimes a gram or two of ammonium chloride is added to the barium solution before adding the sulphuric acid.[3] When

[1] Lind, Underwood and Whittemore, *J. Amer. Chem. Soc.*, 1918, **40**, 465.

[2] The large effect in the opposite direction caused by neutral salts in certain cases is due to more complex causes, which will be considered later.

[3] As a matter of fact, this addition is more commonly made in the converse case—that is to say, when analysing a sulphate—but it is more convenient to discuss the *raison d'être* at this point.

this is done the $BaSO_4$ separates out more slowly and in less finely divided form, owing to the increase in its solubility. This increase, however, is small, and has no appreciable effect on the result. The small amount of hydrochloric acid added acts in the same way. Whether any such addition is required depends upon what salts or acids are already present in the solution.

The effect of substances not yielding an ion in common with a sparingly soluble compound on the solubility of the latter may be illustrated by the following figures for barium sulphate, which refer to a temperature of about 20°.

	Solvent.	Grms. present per 100 c.c. solution.	
	Pure water		$BaSO_4$: 0·00023
Banthisch (*J. pr. Chem.*, 1884, **29**, 54)	Dilute Hydrochloric acid	HCl : 1·82	$BaSO_4$: 0·0067
	,, ,, ,,	HCl : 3·65	$BaSO_4$: 0·0089
	Dilute nitric acid	HNO_3 : 3·15	$BaSO_4$: 0·0070
	,, ,, ,,	HNO_3 : 6·31	$BaSO_4$: 0·0107
Fraps (*Amer. Chem. J.*, 1902, **27**, 288)	$MgCl_2$ solution	$MgCl_2$: 0·1	$BaSO_4$: 0·0030
	,, ,,	$MgCl_2$: 0·25	$BaSO_4$: 0·0030
	,, ,,	$MgCl_2$: 1·00	$BaSO_4$: 0·0033

It must always be remembered that water itself has an effect on the solubility of a salt such as $BaSO_4$ precisely similar to that of any other substance not yielding an ion in common with the salt. Thus with $BaSO_4$ and water the ionic reactions

$$\begin{cases} BaSO_4 \rightleftarrows Ba^{\cdot\cdot} + SO_4'' \\ 2HOH \rightleftarrows 2H^{\cdot} + 2OH' \end{cases}$$

$$\begin{cases} Ba(OH)_2 \rightleftarrows Ba^{\cdot\cdot} + 2OH' \\ H_2SO_4 \rightleftarrows 2H^{\cdot} + SO_4'' \end{cases}$$

which can be written as the summation molecular equation $BaSO_4 + 2HOH \rightleftarrows Ba(OH)_2 + H_2SO_4$, have to be considered. These reactions lead to the formation of a certain small amount of un-ionized $Ba(OH)_2$ and H_2SO_4 so that the solubility of $BaSO_4$ in pure water is actually greater than it would be did no such reaction with the water occur. It follows from this that the calculations previously made of the solubility product of $BaSO_4$, etc., are not quite correct, because no account was taken of any interaction with the water. The true solubility product of $BaSO_4$ would be somewhat lower than that calculated.

This interaction between dissolved substances and water is called "hydrolysis" and will be considered more fully in a later chapter, but, as will be seen from what has just been said, hydrolysis is only a special case of a much more general effect. It may be pointed out that the increased solubility of the sparingly soluble salt caused by interaction with the water or dissolved electrolyte depends essentially on the extent to which the products of the interaction are ionized. The less they are ionized the greater is the increase in solubility, for the increase is due to the un-ionized molecules formed, not to their ions.[1]

The Volumetric Estimation of Chlorides (Bromides and Iodides) by Mohr's Method

In this method a *neutral* solution of the substance being analysed is titrated with a standard solution of silver nitrate in the presence of a small quantity of potassium chromate.

To a suitable amount of the solid (dissolved in a small quantity of distilled water) or solution (carefully neutralized if necessary) [2] contained in a white basin are added 5 drops of a 5 per cent potassium chromate solution for every 50 c.c. of solution. The silver nitrate solution is then run in slowly from the burette, the operator stirring vigorously all the time with a glass rod with flattened head and occasionally crushing up the large clots of silver chloride. As soon as a reddish coloration appears, which persists after stirring for a minute or two, the titration is finished and the amount of chloride is easily calculated from the amount of silver nitrate used.

This method depends upon the fact that the solubility of silver chloride is a good deal smaller than that of silver chromate. As a consequence of this when the silver nitrate is added it is silver chloride which is first precipitated. Silver chromate cannot separate as a permanent solid phase until the concentration of the chlorine ions has been reduced practically to vanishing point. Just where the silver nitrate solution runs into the chloride solution this condition may be present from the very beginning and red silver chromate

[1] Philip, *J. Chem. Soc.*, 1905, **87**, 987.

[2] The neutralization can be effected very conveniently by means of a small excess of pure precipitated calcium carbonate.

will appear for a moment, but will at once disappear on stirring.

A glance at the two mass-action equations :—

$$[Ag^{\cdot}][Cl'] = K_1[AgCl]$$
$$[Ag^{\cdot}]^2[CrO_4''] = K_2[Ag_2CrO_4]$$

will make it clear that if the solution has a high CrO_4'' ion concentration the solubility product of Ag_2CrO_4 might be reached while there were still a considerable number of chlorine ions left in the solution. Hence, only a small amount of potassium chromate should be used. It is also to be noted that after a while the Ag_2CrO_4 formed when the end point is reached sinks and becomes mixed up with the much greater bulk of AgCl and is more or less completely masked. With a little practice, however, there is no difficulty in telling the point.

Some workers prefer to carry out the titration in a conical flask. By suitably shaking this the silver chloride can be prevented from forming large clots ; these are undesirable since they may enclose solution and prevent it reacting with the silver nitrate.

When the end point is reached in this titration it is evident that the two ionic products

$$[Ag^{\cdot}][Cl'] = K_1[AgCl]$$
$$[Ag^{\cdot}]^2[CrO_4''] = K_2[Ag_2CrO_4]$$

will have reached their maximum values, the respective solubility products. Now at 18° solutions saturated with respect to AgCl and Ag_2CrO_4 respectively contain 0·00134 gram (= 0·0000094 gram mol.) AgCl and 0·0252 gram (= 0·00008 gram mol.) Ag_2CrO_4 per litre.

Hence (assuming in both cases complete ionization and no hydrolysis) we have—

$$[Ag^{\cdot}][Cl'] = (9{\cdot}4 \times 10^{-6})^2 = 8{\cdot}84 \times 10^{-11}$$

and[1] $[Ag^{\cdot}]^2[CrO_4''] = (1{\cdot}6 \times 10^{-4})^2\ (8 \times 10^{-5}) = 2{\cdot}05 \times 10^{-12}$

From these two equations by squaring the first and dividing so as to cancel $[Ag^{\cdot}]^2$ we get the ratio—

$$\frac{[Cl']^2}{[CrO_4'']} = \frac{(8{\cdot}84 \times 10^{-11})^2}{2{\cdot}05 \times 10^{-12}} = \frac{1}{2{\cdot}62 \times 10^{8}}$$

[1] As Ag_2CrO_4 yields two $Ag^{\cdot}$ ions for one CrO_4'' ion the $Ag^{\cdot}$ ion concentration is twice that of the CrO_4'' ion.

Now, if 5 drops (= 0·25 c.c.) of 5 per cent K_2CrO_4 solution had been used with 50 c.c. solution in the titration, the CrO_4'' ion concentration would be approximately 0·1494 gram (= 0·00129 gram ion) per litre. It follows at once from the value of the above ratio $\frac{[Cl']^2}{[CrO_4'']}$ that Ag_2CrO_4 will not appear as a permanent precipitate until the chlorine ion concentration [Cl'] has been reduced to $2{\cdot}22 \times 10^{-6}$ gram ion per litre or $7{\cdot}8 \times 10^{-5}$ gram per litre. This is well within the limits of permissible error, and actually a larger error will be caused by the fact that a certain small excess of $AgNO_3$ solution must be added in order that the Ag_2CrO_4 formed may be seen. This error can, however, be allowed for if necessary by finding how much silver solution is required to give the same tint in a similar volume of liquid containing no chloride, but the same amount of chromate as is used in the actual analysis.

The standard silver nitrate solution required for this titration can be made up by direct weighing, but is then liable to be very slightly too weak owing to small inclusions of moisture in the crystals. It is therefore best standardized by titration as above against sodium chloride obtained by saturating with HCl gas a saturated solution of ordinary common salt. The sodium chloride precipitated in this way is drained off on a Büchner funnel and ignited gently to drive off all moisture and HCl.

The precipitation of the sodium chloride by the action of the HCl is partly due to the diminution of its solubility caused by the great increase in the concentration of the chlorine ions (although it is probably in part due also to another effect discussed on page 32). It is not absolutely necessary to pass in HCl gas—mere addition of concentrated hydrochloric acid is sufficient, but in this case the yield of the precipitated sodium chloride is smaller owing to dilution by the water contained in the concentrated hydrochloric acid. The increase of the chlorine ion concentration caused in this way is not sufficient for the solubility products of the salts present as impurities to be reached, so that the sodium chloride precipitated is quite pure.

The following table[1] gives the solubility of NaCl in presence of HCl at 30°:—

HCl grm. mol. per litre	NaCl grm. mol. per litre
0·0	5·400
0·4575	4·932
1·786	3·589
3·052	2·463
5·950	0·630
7·205	0·268

Mohr's method can be used equally well for estimating bromides, or iodides or silver (in which case a standard solution of sodium chloride must be available).

The Estimation of Silver by Volhard's Method

This useful method for estimating silver volumetrically is carried out as follows. From 0·25 to 0·4 gram of a silver alloy (for example) is dissolved in a flask or beaker in nitric acid which is free from chloride. The solution is heated on the water bath to decompose nitrous acid and is then diluted to about 50 c.c. with distilled water. One c.c. of ferric sulphate solution is added and the solution is titrated with an approximately $\frac{N}{10}$ solution of potassium or ammonium thiocyanate which has previously been standardized by Volhard's method against pure silver. The flask should be shaken vigorously during the titration. After all the silver has been precipitated as white insoluble AgCNS the further addition of a drop of thiocyanate solution causes a reddish brown coloration which persists after shaking. This gives the end point of the titration. The solution should be quite cold during the titration and the beaker is held against a white background. The ferric sulphate solution used as indicator in this process is prepared by making a cold saturated solution of ferric alum and adding enough nitric acid to remove any brown colour the solution may have.

[1] Masson, *J. Chem. Soc.*, 1911, **99**, 1136.

Such brown coloration is due to presence of small amounts of colloidal ferric hydroxide or basic ferric salts formed by hydrolysis. Addition of acid throws back the hydrolysis. Volhard's method is liable to give slightly high results for silver possibly owing to the AgCNS precipitate occluding or adsorbing some KCNS. There seems no doubt that the red colour produced when a soluble thiocyanate is added to a ferric salt solution is due to ferric thiocyanate in the non-ionized condition. The CNS' ion is colourless, while the Fe''' ion has a pale yellow colour. $Fe(CNS)_3$ is red and soluble in ether; it can thus be extracted from the solution obtained by adding KCNS to a ferric salt solution. This extraction by ether is of some importance since it supports the view that the colour of the red aqueous solutions is due to un-ionized $Fe(CNS)_3$ and not to a compound ferri-thiocyanate (or its ions) such as $K_3Fe(CNS)_6$. Such complex thiocyanates have been obtained as dark green crystalline solids by Rosenheim and Cohn.[1] They are easily decomposed by water with formation of red solutions. In absolute alcohol they give violet solutions containing a complex anion $Fe(CNS)_6'''$ which, however, is not present in the red aqueous solutions. The formation of dark red $Fe(CNS)_3$ from nearly colourless ions probably indicates some tautomeric change in the non-ionized molecule similar to that which occurs with indicators and which is discussed in Chapter IV. Where no change of structure occurs non-ionized salts appear to have a colour similar to that of their ions. According to Werner a dark red colour is characteristic of fully co-ordinated ferric iron. Lowry[2] considers that ferric thiocyanate has a fully co-ordinated non-electrolytic structure which may be written thus $\left[\mathrm{Fe}\left(\begin{smallmatrix}\diagup\!\!\diagdown\mathrm{N}\\ \diagdown\!\!\diagup\mathrm{C}\end{smallmatrix}\right)_3\right]$, which indicates that the ferric atom is co-ordinated with the nitrogen and sulphur (see Chapter XIII). The formation of $Fe(CNS)_3$ from its ions is by no means complete, a position of equilibrium in the reaction $Fe''' + 3CNS' \rightleftarrows Fe(CNS)_3$ being reached.

[1] *Z. anorg. Chem.*, 1901, **27**, 280.
[2] *J. Chem. Soc.*, 1923, **123**, 830.

The colour of such a solution can in fact be deepened by the addition of either $Fe^{\cdots}$ or of CNS' ions. This is of importance analytically. If the red coloration due to $Fe(CNS)_3$ is being used as a test for ferric ion a considerable amount of soluble thiocyanate should be used. Conversely, as in Volhard's method, where it is desired to detect the slightest excess of thiocyanate, a considerable amount of ferric indicator is required. The red coloration due to $Fe(CNS)_3$ is given in presence of considerable amounts of free nitric acid (or other strong mineral acids), but not in weakly acid or neutral solutions containing much acetate, tartrate, etc., for in such solutions the ferric iron is converted into other forms than ferric ion ($Fe^{\cdots}$). For un-ionized $Fe(CNS)_3$ to be formed $Fe^{\cdots}$ ions must be present. It is important to use the same amount of the ferric indicator when standardizing the thiocyanate solution, as when titrating the silver solution, for the exact position of the end point will be slightly affected by variation in the amount used.

Volumetric Estimation of Chlorides, Bromides, or Iodides by Volhard's Method

Mohr's volumetric method can be applied only in neutral solution, but it is sometimes convenient or necessary to titrate chlorides, bromides, or iodides in acid solution. Volhard's method enables this to be done. Two standard solutions are required, one of silver nitrate and one of potassium or ammonium thiocyanate. These are best made about decinormal. To a known amount of the chloride (bromide or iodide) solution is added a known amount of the standard silver nitrate solution, using rather more than is required to precipitate all the chloride (bromide or iodide). One c.c. of the ferric solution is then added, and the excess of silver is titrated with the standard thiocyanate. The amount of silver nitrate required to precipitate the chloride (bromide or iodide) is thus obtained. No trouble is experienced in the case of bromides or iodides, and the end point is perfectly sharp. With the chlorides, however, there is precipitation of AgCNS to start with, and a momentary coloration as the thiocyanate solution is run in. The colora-

tion disappears on shaking until finally a point is reached where addition of another drop of thiocyanate gives a coloration which seems as though it were going to persist. It also disappears after a short time, and more thiocyanate can be slowly added with precisely the same result and so on, more or less indefinitely. This behaviour is due to the fact that AgCNS (solubility product $1{\cdot}1 \times 10^{-6}$) is about nine times less soluble than AgCl (solubility product $9{\cdot}4 \times 10^{-6}$). In consequence of this the precipitated AgCl which is present reacts slowly with the slight excess of thiocyanate in the supernatant red solution. The AgCl would in this way be practically all converted into AgCNS before a really permanent red coloration was obtained. To meet this difficulty the usual procedure is to filter off (and, of course, wash) the precipitated AgCl before titrating the excess of silver nitrate. If, however, one is prepared for the behaviour above described, it is possible to tell the correct end point pretty accurately without such filtration.

AgBr (solubility product $5{\cdot}8 \times 10^{-7}$) and AgI (solubility product $1{\cdot}6 \times 10^{-8}$) being both much less soluble than AgCNS, there is no such difficulty in the titration of bromides or iodides and filtration is never necessary.

Estimation of Silver by Gay-Lussac's Method

This is undoubtedly the most accurate method of determining silver, but it requires some practice. It is chiefly used for the analysis of silver bullion. A full description of the method will be found in Sutton's *Volumetric Analysis*, 1904, p. 304, or Treadwell's *Textbook of Analytical Chemistry*, 1919, vol. **2**, p. 702. It depends upon the fact that if a sodium chloride solution is added to one of silver nitrate and the mixture shaken vigorously the precipitated silver chloride settles, leaving a clear supernatant liquid. On adding more chloride solution it will be seen whether a further precipitate is produced. If so, the mixture is again shaken and again tested with the chloride solution until no further precipitate is obtained.

To apply this method satisfactorily it is necessary to

determine first the approximate silver content of the alloy in some other way (e.g. by Mohr's or Volhard's method).

Three standard solutions are required :—(1) A pure sodium chloride solution. It is customary for this to be so adjusted that 100 c.c. are exactly equivalent to either 1 or 0·5 gram silver, though this is not necessary. (2) A pure sodium chloride solution exactly one-tenth the strength of solution (1) ; and (3) a solution of pure silver nitrate of exactly the same strength as the weak solution (2) of sodium chloride. These three solutions must be prepared with great care from very carefully purified sodium chloride and metallic silver.

The actual determination of silver in the alloy is carried out as follows :—An amount of the alloy is weighed out which contains slightly more silver than can be precipitated by 100 c.c. of the strong sodium chloride solution (solution 1). The alloy is placed in a 200 c.c. bottle provided with a well-ground stopper, the underside of which has been ground to a point. 5 c.c. of pure nitric acid (1·2 sp. gr.) are added per gram of alloy and the bottle is gently heated on the water or sand bath till the metal has dissolved. Nitrous fumes are blown out of the bottle which is then allowed to cool down to room temperature.

The test bottle is fitted inside a cardboard or tin tube reaching to the stopper in order to protect the precipitated silver chloride from the action of light. 100 c.c. of the strong sodium chloride (solution 1) are then carefully run into the bottle from a calibrated pipette, the moistened stopper is inserted and covered with a piece of black cloth. Bottle and contents are then vigorously shaken till the silver chloride has clotted and the liquid becomes clear. The stopper is then slightly lifted and its point touched against the neck of the bottle to remove most of the adhering liquid, again inserted, and any particles of chloride washed down from the top of the bottle by carefully shaking the clear liquid over them. The bottle is then placed under the burette containing the weak sodium chloride (solution 2) and 0·5 c.c. added. The mixture is shaken, cleared, another 0·5 c.c. put in and the bottle lifted partly out of its case to see

if the precipitate is considerable ; lastly, two or three drops only of the solution are added at a time until no further opacity is produced by the final drop.

The total volume of the weak NaCl (solution 2) needed to reach this point is noted. Call it x. It will be found, however, that if the contents of the bottle are tested with the dilute $AgNO_3$ (solution 3) a further precipitate of AgCl is obtained. The volume of solution 3 that must be added until precipitation ceases is determined. It will be about 1 c.c. Let the value actually found be y c.c. If now the test solution is treated with solution 2 it will be found that there is an apparent excess of silver and y c.c. must be added until no further precipitate is obtained. But then there will again appear to be excess of chloride which will require y c.c. of solution 3 to precipitate it and so on indefinitely.

The correct value of the silver content of the alloy is given by the amount $100 - \left(\frac{x - \frac{y}{2}}{10}\right)$ c.c. of the solution 1, for this volume of solution 1 contains an amount of NaCl exactly equivalent to the silver in the amount of alloy used.

The explanation of the peculiar behaviour described above has been given by Stieglitz.[1]

By addition of the NaCl solution a point is reached where $[Ag^{\cdot}] = [Cl']$ and, at this—the correct end point—exactly sufficient sodium chloride solution will have been added to convert all the silver present into chloride. Further addition of NaCl, however, will still cause precipitation of AgCl by increasing $[Cl']$ and reducing $[Ag^{\cdot}]$ until the latter has become so small that further precipitation cannot be detected. This corresponds to the experimental reading x. On now adding $AgNO_3$ solution a precipitation of AgCl is obtained by increasing $[Ag^{\cdot}]$ and reducing $[Cl']$, and this goes on until visible precipitation ceases because $[Cl']$ has become too small. If y c.c. of $AgNO_3$ are required for this, it is evident that when $\frac{y}{2}$ c.c. had been added the concentrations $[Ag^{\cdot}]$

[1] *The Elements of Qualitative Chemical Analysis*, 1912, vol. 1, p. 150.

and [Cl′] must have been equal and that this would also have been the case at a point $\frac{y}{2}$ c.c. short of the original experimental reading. Hence follows the correct titration value to be used in calculating the silver content of the alloy (see above).

It is worth noting that when the stronger NaCl solution is such that 100 c.c. are equivalent to 1 grm. of silver the value of $\frac{y}{2}$ is about 0·5 c.c. of the weak NaCl solution and hence corresponds to 0·0005 gram of silver. So that the value obtained for the silver content by taking the reading at which further addition of NaCl solution produced no further precipitate would be about 0·05 per cent too high.

This 0·0005 gram silver practically corresponds to the silver in solution in forms ($AgNO_3$, $Ag^{\cdot}$, etc.) other than un-ionized AgCl. Now a saturated solution of AgCl in pure water contains 0·0001 gram silver in 100 c.c., practically all as $Ag^{\cdot}$ ions, and the higher value 0·0005 indicated above is due to the presence of the $NaNO_3$ formed during the titration and to some HNO_3, both of which increase the solubility of the AgCl. It is to be noted that at the stage in the titration where [$Ag^{\cdot}$] is equal to [Cl′] addition of either NaCl, or $AgNO_3$ solution will cause a precipitate of AgCl.

A similar behaviour should be observed with a saturated solution of any salt, but the conditions of solubility, etc., are not always suitable for such observation.

The Anomalies shown by Strong Electrolytes [1]

Up to the present it has been assumed in the theoretical discussions that all salts and acids obeyed the Law of Mass Action. Were this the case, then, owing to the relative simplicity of the mechanism of the precipitations, etc., it would be a comparatively easy matter to predict and employ the theoretically best experimental conditions. But unfortunately for the analytical chemist matters are far less

[1] Bauer, *Ahrens' Sammlung*, 1903, **8**, 466. Drucker, *Ahrens' Sammlung*, 1906, **10**, 1. Lewis, *A System of Physical Chemistry*, 2nd ed., 1918, vol. **1**, pp. 184–6, 224–9; vol. **2**, pp. 189–204.

simple owing to the fact that strong electrolytes do not apparently obey the law of mass action in its simple form. Non-electrolytes and weak acids and weak bases obey the law very exactly in dilute solution—that is to say in solutions less than about 0·1 normal and very often in much more concentrated solutions, though that must not be expected—for it must always be remembered that the law of mass action is based upon the assumption that the " active mass " of a dissolved substance is proportional to its molecular concentration, which holds only for dilute solutions. Now although strong electrolytes do not as a rule obey the law of mass action even in dilute solution, nevertheless, there is good reason for believing that the general trend of events is correctly foretold by the mass action equations. For this reason the latter have been employed in the explanations given up to the present—and, indeed, it would be unnecessary and foolish to forego their use altogether, for they are undoubtedly of great assistance. Indeed, in many analytical cases, as, for instance, in the case of precipitations of sulphides of the heavy metals in which all conditions (dilute solutions, weak acids, weak bases) are favourable the law of mass action is accurately followed.

In the case of a strong electrolyte MX, instead of the expression $\frac{[M^{\cdot}][X']}{[MX]}$ being a constant, its value gradually increases with increase in concentration of the solution. This cannot be fully accounted for in spite of a very large amount of experimental work carried out by numerous investigators. There are reasons for thinking that at infinite dilution solutions of strong electrolytes do obey the law of mass action, but this is not theoretically necessary.

Since strong electrolytes do not obey the law of mass action under ordinary conditions it is clear that the principle of the solubility product cannot apply accurately to them.

In the case of an electrolyte MX yielding two monovalent ions we should have, according to the law of mass action, $\frac{[M^{\cdot}][X']}{[MX]} = \text{constant} = k$. With excess of the solid in equilibrium with the solution [MX] is automatically kept

constant so that the above expression reduces to $[M'][X'] = k[MX] = K$, K being called the solubility product. It is clear that if this solubility expression were strictly correct, it would also follow that [1] :—

(1) The product of the concentration of the ions of a salt present as solid phase has the same value in dilute solutions of other salts as it has when present alone.[2]

(2) The concentration of the un-ionized portion of a salt present as solid phase has the same value in dilute solutions of other salts as it has when present alone.[3]

In cases where the law of mass action is not obeyed it is plain that both of the above statements cannot be correct, and indeed both might be incorrect. The work of Noyes [4] has shown that the first statement is approximately correct in many cases, though usually the ionic product is actually somewhat greater in presence of other salts than in their absence.

Arrhenius [5] showed that the second statement is far from true, the concentration of the un-ionized salt being considerably less in solutions of other salts than in pure water.

It is to be noted that the deviations of the ions from the behaviour deduced from the law of mass action is in the opposite direction to that of the un-ionized portion of the electrolyte. The un-ionized molecules are, moreover, markedly abnormal while the ions are relatively normal. These results are of considerable analytical importance, and show that in the case of the numerous sparingly soluble salts dealt with in gravimetric analysis we can make use of the solubility product expression even though the salts do not obey the law of mass action. Since the ionic product remains practically constant in the presence of the solid salt, the effect of other electrolytes, in small concentrations, on the solubility can be foretold not only qualitatively but almost quantitatively. This follows, in spite of the fact

[1] Noyes and Bray, *J. Amer. Chem. Soc.*, 1911, **33**, 1643.
[2] Nernst, *Z. physikal. Chem.*, 1889, **4**, 379.
[3] Noyes, *Z. physikal. Chem.*, 1890, **6**, 243.
[4] *J. Amer. Chem. Soc.*, 1911, **33**, 1643.
[5] *Z. physikal. Chem.*, 1899, **31**, 224.

that the concentration of the un-ionized part of the salt does not remain constant, because, owing to the sparing solubility of the salts, hardly any is present except in the ionized condition.

Conditions in an aqueous solution of an electrolyte are probably far more complex than is assumed in the simple theory of electrolytic dissociation. The abnormal behaviour of strong electrolytes is perhaps largely due to the fact that far simpler equilibria have been assumed to prevail than is actually the case. There is evidence to show that ions and undissociated molecules are probably hydrated in aqueous solution. The extent of this hydration is uncertain, but it may be responsible to some extent for the anomalous behaviour of strong electrolytes.

The "salting out" effect of strong electrolytes in diminishing the solubility not only of other electrolytes but also of non-electrolytes (e.g. the diminished solubility of chlorine in sodium chloride solutions) is generally regarded as evidence in favour of hydration of the molecules or ions of the added electrolyte. Water thus converted into water of hydration is no longer present as "free" water, and consequently loses its usual solvent power. An example of "salting out" of analytical interest is that referred to on page 22, where pure NaCl was obtained by passing in gaseous HCl or adding strong hydrochloric acid to a saturated solution of NaCl. The precipitation of the NaCl may in part be due to the effect of the chlorine ion common to both electrolytes, but is probably largely due to removal of "free" water by the added HCl.

That complex ions play some part in the anomalous behaviour of strong electrolytes also seems certain.

For a fuller consideration of the very important question of the abnormal behaviour of strong electrolytes the reader is referred to Lewis' *System of Physical Chemistry*.

CHAPTER III

ACIDIMETRY AND ALKALIMETRY

The Theory of Indicators

THE various applications of this most important branch of volumetric analysis depend upon the behaviour of acids on ionization and also upon the behaviour of certain organic compounds which are used as "indicators". The work of Hantzsch and others has shown clearly that these indicators are in reality weakly acid or basic compounds which exist in two differently coloured tautomeric forms. One of these is a neutral [1] body, while the other is capable of yielding an ion of the same colour as itself, and hydrogen or hydroxyl ion, and can enter freely into electrolytic equilibria.

In pure aqueous solution all the above will be in equilibrium with one another. Thus:—$H^{\cdot}$ (or OH') + other ion $\rightleftarrows$ un-ionized acidic (or basic) form $\rightleftarrows$ tautomeric neutral form, or, to take a concrete example, with litmus we should have: $H^{\cdot}$ + (blue litmus ion)$'$ $\rightleftarrows$ blue un-ionized litmus acid $\rightleftarrows$ red neutral form of litmus, regulated by the mass-action equations: [un-ionized blue acid] $= K_1$ [red neutral form]; $[H^{\cdot}]$ [blue ion$'$] $= K_2$ [un-ionized blue acid] $= K_1 K_2$ [red neutral form]. Consider now the effect of adding acid or alkali to a neutral solution of litmus. It is clear that on adding acid the hydrogen ions will combine with the blue anion to form the undissociated blue acid, which will then undergo rearrangement to form the red neutral compound. If, on the other hand, alkali is added, the hydroxyl ions will combine with the hydrogen ions, the place of which

[1] The neutral form may be very slightly ionized. This does not materially affect the general deductions made below. For a complete discussion of the Theory of Indicators see *The Theory and Use of Indicators*, by Prideaux (Constable and Co., London, 1917), where earlier references to the subject are given.

will be taken by fresh ones resulting from the ionization of some of the undissociated blue acid, which will be replaced by the tautomeric change of more of the red form. Thus, on adding acid the colour of the solution will change from blue to red, while additions of alkali will cause the reverse change. The tautomeric change causing the alteration of colour is therefore a function of the $H^{\cdot}$ (or OH') concentration.

The colour of the aqueous solution will clearly depend upon the relative concentrations of the red form, of the blue acid and of the coloured ion, and these concentrations are regulated by the two equilibrium constants K_1 and K_2. It is plain that if K_1 is infinity or unduly large the compound will be of no use as an indicator, for it would signify either that there was no neutral form capable of existence in aqueous solution or that the equilibrium amount was very small. In such a case, therefore, there would be no colour change or only a very obscure one on the addition of acid or alkali. For a satisfactory indicator the constant K_1 should be small.

A second important point is that the colour of the indicator should be deep so that a very small amount will suffice to colour the solution markedly, for it must be remembered that the indicator has to be neutralized as well as the other acid or base present. Naturally, so long as one of the tautomeric forms is coloured that is sufficient, for then there will be a change from coloured to colourless. In addition to showing a striking change of colour, if a compound is to be of any use as an indicator, the tautomeric change from acid (or basic) to neutral form (and vice versa) must take place rapidly. Tautomeric rearrangements may be very slow. Ionic equilibria, so far as is known, are always attained with immeasurably high velocities, so that any sluggishness in the response of the indicator is not likely to be due to the ionic portion of the change. Some of the indicators in use (e.g. cyanin) do under certain conditions take an appreciable time to change colour.

The value of the dissociation constant K_2 of the indicator acid also has a great bearing upon its behaviour and upon the applications to which it can be put. It is clear from the mass-action equations given above that the smaller the

dissociation constant the smaller will be the amount of hydrogen ions required to force back the dissociation of the indicator acid to such an extent that only the colour of the neutral form is visible.

With a suitably small quantity of any given indicator, a certain minute amount of a strong acid would be required to effect the colour change, but more of a weaker acid would be needed, for the effect is entirely due to the hydrogen ions, and a given quantity of a weak acid will contain less of these than will the equivalent amount of a stronger acid. Hence, when an acid is being titrated by an alkali, which for the present we will suppose to be a strong one, so soon as the acid left unneutralized has been reduced to this critical amount further addition of alkali will cause formation of the indicator ion and consequent change of colour.

If the acid is a strong one the amount of alkali required to reach this point will correspond almost exactly to that theoretically required for neutralization. But if the acid is weak considerably less than the theoretical amount of alkali may have been added when the colour change of the indicator occurs, and it may very easily happen that with a weak acid this error would be so large as to make it impossible to titrate the acid. There are in fact many very weak acids which cannot be titrated.

It is also evident that the smaller the dissociation constant of the indicator the weaker the acid which can be titrated by its means without appreciable error.

The apparent dissociation constants of indicators such as are given on page 39 really depend upon both K_1 and K_2, and are equal to their product $K_1 K_2$ (see equations on page 33). It follows, therefore, that if K_1 is small enough the dissociation constant K_2 of the acidic form of the indicator may be quite large—corresponding to a strong acid—while the "apparent" dissociation constant is only small. It is the apparent dissociation constant of the indicator which is important in determining the conditions under which it can be used.

When titrating a base with a strong acid exactly the reverse holds.

In an aqueous solution of a base BOH, to which a few drops of an indicator HIc have been added, we should have the two ionic equilibria :—

$$B^{\cdot} + Ic' \rightleftarrows BIc$$
$$B^{\cdot} + OH' \rightleftarrows BOH$$

On adding a strong acid to this solution the hydrogen ions would unite with the hydroxyl ions to form water until the concentration of hydroxyl was reduced to a value comparable with that of the Ic′ ions. What will then happen will depend upon whether the strength of the acid HIc is a good deal greater than that of the acid HOH or not. If HIc is a sufficiently strong acid all the hydroxyl ions will be converted into un-ionized water before any un-ionized HIc is formed. That is to say un-ionized HIc will form (and the corresponding colour change occur) only after the amount of acid theoretically required to neutralize the base has been added.

If, however, the strength of HIc is comparable to that of water, then the formation of HIc and the resultant colour change will take place before all the hydroxyl ions have disappeared, and consequently before the amount of acid theoretically required to neutralize the base has been added.

Hence, weak bases, such as ammonia, must be titrated in presence of a strongly acidic indicator like methyl orange. Weak acidic indicators like phenolphthalein are useless in such cases, and can be used only with strong bases.

The arguments developed above hold for the case of acidic indicators, which split off a hydrogen ion on ionization. Exactly similar arguments hold for the basic indicators, which split off hydroxyl ions, but they must be reversed so that weak bases must be titrated with weak basic indicators, while weak acids must be titrated in the presence of strong basic indicators.

The majority of indicators in common use are of acidic character, such as methyl orange,[1] litmus, phenolphthalein.

Cyanin and dimethyl-amino-azo-benzene are indicators of a basic nature.

[1] The case of methyl orange is, however, unusually complicated (see Thiel, *Ahrens' Sammlung*, 1911, **16**, 387).

It must, of course, be remembered that in none of the above cases is it a question of any of the ions disappearing absolutely. Their concentration may become infinitely small, but theoretically it never becomes zero.

It is interesting to consider the condition of the solution with respect to the hydrogen and hydroxyl ion concentration at the point of neutrality as determined by the indicator. In pure water the concentration of hydroxyl and hydrogen ions is equal, for one molecule of water can only give one of each :—

$$H^{\cdot} + OH' \rightleftarrows HOH$$

This equilibrium is regulated by the mass-action equation :

$$\frac{[H^{\cdot}][OH']}{[HOH]} = K$$

Since in the case of water itself (or in dilute solutions generally) the value of [HOH] in this expression is sensibly constant, it is customary to combine it with K. In this way we obtain $[H^{\cdot}][OH'] = K[HOH] = K_w$. K_w is best called " the ionic product " of water though it is often referred to as the dissociation constant. In pure water at 20°, $[H^{\cdot}] = [OH'] = 1 \times 10^{-7}$ normal.

As the molecular weight of HOH is 18 the value of [HOH] in pure water is $\frac{1000}{18} = 55.5$. The ionic product, K_w, of water is therefore 55·5 times the true dissociation constant K. (see the values given in the table on page 40).

In any dilute aqueous solution the concentrations of $H^{\cdot}$ and OH' ions must be such that $[H^{\cdot}][OH'] = K_w$. Although the product of the concentrations must be constant it does not follow that the ratio $\frac{[H^{\cdot}]}{[OH']}$ will be equal to unity as it is in pure water. It may be, but this will be very exceptional, and from what has been said above it will be realized that even a solution containing an acid and a base in chemically equivalent amounts will not as a rule show the same concentration of both hydrogen and hydroxyl ions, and consequently although " neutral " in the sense of containing equivalent amounts of acid and base, such solutions are not usually

strictly " neutral " in the sense of being equally concentrated with respect to hydrogen and hydroxyl ions.

What one really does by the use of indicators is to determine the amount of a given acid or alkali which will be sufficient to give a solution with a certain hydrogen ion concentration when added to a given alkali or acid.

Different indicators will correspond to different hydrogen ion concentrations, and the results obtained by their use correspond to stoicheiometrical relationships only when they have been chosen so that they fulfil the conditions discussed above.

The Ionization and the Strength of Acids

The manner and extent to which acids are ionized in aqueous solution depends very largely upon the nature of the acid, the most important regulating factor being the basicity of the latter. The greater number of monobasic inorganic acids are strong acids, that is to say that they are very largely ionized in fairly weak solutions (from 90—50 per cent in $\frac{N}{10}$ solution). There are a few, however, that are very weak, and there are others intermediate between the two extremes. Thus in $\frac{N}{10}$ solution HCl and HNO_3 are 90 per cent ionized, nitrous acid about 5 per cent, and HCN only 0·01 per cent. These differences are due to some inherent property of the molecules, but, broadly speaking, it is found that the higher the electro-affinity of the anion derived from an acid the stronger the acid (see Chapter IV). In the case of polybasic acids matters are far more complicated. It is found that the tendency for the first hydrogen ion to split off is from 100 to 100,000 times as great as the tendency for the second to do the same, while, in cases where it is possible, a third hydrogen ion is split off with far greater difficulty than is the second, and so on. So it often happens that a polybasic acid is a strong acid so far as the first hydrogen is concerned, a weak one as regards the second, and a very weak one as regards the third. This is the case with H_3PO_4. Some polybasic acids are, however, very weak even with regard to the first hydrogen, as for example H_2CO_3 and H_2S.

Organic acids are mostly very weak; one or two, such as trichloracetic, are comparable in strength to the strong inorganic acids; others such as acetic acid are of intermediate strength, but by far the greater number are very weak indeed.

Dissociation Constants of Acidic Indicators and of Acids, and their bearing on Analytical Practice

Let us now briefly consider how the considerations alluded to above affect actual analytical practice.

The dissociation constants of methyl orange, litmus and phenolphthalein are as follows:—

Methyl orange . . .	$4{\cdot}6 \times 10^{-4}$
Litmus	1×10^{-6}
Phenolphthalein . . .	8×10^{-10}

In the following table[1] the dissociation or ionization constants of the commoner acids are given. In the third column are the numerical values (dissociation constants) of the mass-action expressions in the second column. These expressions are given to show clearly to what stage of ionization, in the case of polybasic acids, the dissociation constants refer. Benzoic acid and phenol have been added to the list given by Stieglitz. Strong acids do not obey the law of mass action (see Chapter II), so that in their case the values in brackets are given for purposes of comparison. They are the values of the mass-action expressions for 0·1 molar solutions.

For an acid to be titratable in presence of any given indicator its dissociation constant should be at least ten times that of the indicator. As the dissociation constants of HCl, HBr, HI, HNO_3, H_2SO_4 are so much greater than those of the three indicators given, any one of the latter can be used in the accurate titration of these acids.

The above figures show, however, that methyl orange is a stronger acid than acetic—hence it cannot be used in

[1] Stieglitz, *The Elements of Qualitative Chemical Analysis*, 1912, vol. **1**, p. 104, where full references are given to the original papers on which the table is based.

titrating it. Neither is litmus sufficiently weaker than acetic acid to be quite satisfactory ; phenolphthalein, however, answers all requirements. Litmus or phenolphthalein could be used in the case of benzoic acid and many

Acid	Equilibrium Ratio	Dissociation Constant
Hydrochloric	$[H^+][Cl^-]/[HCl]$	(1)
Hydrobromic	$[H^+][Br^-]/[HBr]$	(1)
Hydriodic	$[H^+][I^-]/[HI]$	(1)
Nitric	$[H^+][NO_3^-]/[HNO_3]$	(1)
Sulphuric	$[H^+][HSO_4^-]/[H_2SO_4]$	(1)
	$[H^+][SO_4^{--}]/[HSO_4^-]$	3×10^{-2}
Chromic	$[H^+][HCrO_4^-]/[H_2CrO_4]$	(1)
	$[H^+][CrO_4^{--}]/[HCrO_4^-]$	6×10^{-7}
Oxalic	$[H^+][HC_2O_4^-]/[H_2C_2O_4]$	$3{\cdot}8 \times 10^{-2}$
	$[H^+][C_2O_4^{--}]/[HC_2O_4^-]$	5×10^{-5}
Phosphoric [1]	$[H^+][H_2PO_4^-]/[H_3PO_4]$	1×10^{-2}
	$[H^+][HPO_4^{--}]/[H_2PO_4^-]$	2×10^{-7}
	$[H^+][PO_4^{---}]/[HPO_4^{--}]$	4×10^{-13}
Benzoic	$[H^+][C_7H_5O_2^-]/[C_7H_6O_2]$	6×10^{-5}
Arsenic	$[H^+][H_2AsO_4^-]/[H_3AsO_4]$	5×10^{-3}
Nitrous	$[H^+][NO_2^-]/[HNO_2]$	5×10^{-4}
Acetic	$[H^+][C_2H_3O_2^-]/[C_2H_4O_2]$	$1{\cdot}8 \times 10^{-5}$
Carbonic	$[H^+][HCO_3^-]/[H_2CO_3]$	3×10^{-7}
	$[H^+][CO_3^{--}]/[HCO_3^-]$	7×10^{-11}
Hydrogen Sulphide	$[H^+][HS^-]/[H_2S]$	9×10^{-8}
	$[H^+][S^{--}]/[HS^-]$	1×10^{-15}
Boric	$[H^+][H_2BO_3^-]/[H_3BO_3]$	7×10^{-10}
Hydrocyanic [2]	$[H^+][CN^-]/[HCN]$	7×10^{-10}
Phenol [2]	$[H^+][C_6H_5O^-]/[C_6H_6O]$	$1{\cdot}3 \times 10^{-10}$
Water	$[H^+][OH^-]/[H_2O]$ at 25°	2×10^{-16}
	at 100°	9×10^{-15}
	$[H^+][OH^-] = K_w$ at 25°	$1{\cdot}2 \times 10^{-14}$
	at 100°	5×10^{-13}

of the stronger organic acids. As a rule, however, it is safer to use phenolphthalein when titrating organic acids, as the majority of these are weaker acids than litmus.

[1] According to Prideaux, *J. Chem. Soc.*, 1911, **99**, 1224, the third dissociation constant of phosphoric acid is 3×10^{-12}.

[2] Walker and Cormack, *J. Chem. Soc.*, 1900, **77**, 5.

It will be seen that boric acid is comparable in strength to phenolphthalein, so that the latter cannot be used as indicator in the titration of the former.[1] There are, it is true, indicators which are considerably weaker acids than even boric acid, and theoretically there should be no difficulty in titrating this and even weaker acids in their presence. The conditions are such, however, that in practice satisfactory results can hardly be obtained in the titration of acids having a smaller dissociation constant than about 1×10^{-10}.[2]

As is well known, sodium carbonate, borax, sodium silicate, or indeed the alkali salts of any acid with dissociation constant less than about 5×10^{-7}, can be titrated with a strong acid such as hydrochloric acid in presence of methyl orange just as though the carbonic, boric, silicic, etc., acids were not present. For the reasons outlined above, solutions of such weak acids as these practically do not affect methyl orange, so that any NaOH added causes the latter to indicate a marked alkaline reaction. Consequently, when methyl orange is added to a solution of the sodium salt of such an acid it shows an alkaline reaction which can be removed only by adding an amount of the strong acid equivalent to the sodium present [3] :—

$$Na_2CO_3 + 2HCl = 2NaCl + H_2CO_3.$$

The weak acid so displaced being without action on the methyl orange, the solution can be titrated as though it contained only NaOH.

Since carbonic acid does affect phenolphthalein it is plain that when weak acids have to be titrated in presence of phenolphthalein a standard alkali must be used which is quite free from carbonate.

[1] A method of getting over this difficulty is considered on page 227.

[2] See Theil, *Ahrens' Sammlung*, 1911, **16**, 318.

[3] This is not strictly accurate in the case of a carbonate, but the effect of the carbonic acid is so slight as hardly to be noticeable if the solutions are stronger than decinormal. If below that strength it is as well to heat the solution being titrated nearly to boiling just before the end is reached, allow to cool, and then finish the titration. About 0·1 c.c. more of decinormal acid will be required if this is done.

The case of polybasic acids must finally be briefly referred to. Since there is a large difference in most cases between the different dissociation constants of polybasic acids (see p. 40), it is sometimes possible to titrate them in several stages by using suitably chosen indicators. Thus when phosphoric acid is titrated with sodium hydroxide in presence of methyl orange only one equivalent of NaOH per molecule of H_3PO_4 is required to cause the indicator to change colour; if the indicator is phenolphthalein two equivalents must be added, while with trinitrobenzene as indicator approximately three equivalents are needed; but, as the third stage of the phosphoric acid ionization is so feeble, this last titration is somewhat uncertain. In the case of sulphuric acid both the ionization stages correspond to such strong acids that it is not possible to separate them, and when titrated with methyl orange, litmus or phenolphthalein two equivalents of NaOH per molecule of H_2SO_4 are required for neutralization in each case.

On referring to the table of acid dissociation constants it will be seen that carbonic acid is stronger than phenolphthalein only so far as its first hydrogen ion is concerned. As regards its second hydrogen ion, carbonic acid is about ten times less acidic than phenolphthalein. For this reason the bicarbonates of the strong alkalies react almost exactly neutral to phenolphthalein. If carbonic acid is titrated with caustic soda or potash in presence of phenolphthalein, the colour change occurs when one equivalent of alkali has been added to one molecule of carbonic acid. Conversely, if a sufficiently dilute solution of Na_2CO_3 or K_2CO_3 is treated with a strong acid in presence of phenolphthalein slowly enough to prevent escape of CO_2 the colour change occurs when one equivalent of acid has been added for each molecule of carbonate. The well-known method for titrating carbonate in presence of caustic alkali depends on this. The solution is first titrated carefully with phenolphthalein as indicator, and the point at which the colour goes is noted, methyl orange is then added, and the addition of acid continued till the solution is neutral to methyl orange.

Dissociation Constants of Basic Indicators and of Bases, and their bearing on Analytical Practice

The two best-known indicators which are weak bases are dimethylamino-azo-benzene and cyanin. Their dissociation constants are :—

Cyanin	$4{\cdot}2 \times 10^{-5}$
Dimethylamino-azo-benzene . .	1×10^{-11}

Much less is known about the dissociation constants of inorganic bases than about dissociation constants of inorganic acids. This is largely because the majority are polyacid and very slightly soluble. The following table [1] contains the values for soluble inorganic bases, while those for aniline, pyridine, and methylamine are included for comparison. As in the case of the table for acids, the bracketed values are not constant, they are the values for $\frac{N}{10}$ solutions. The value for $Ca(OH)_2$ is an estimated one, as it is not sufficiently soluble to give a decinormal solution.

Polyacid bases ionize in steps just as do polybasic acids. The tendency of the first OH to ionize is greater than that of the second, and so on. Comparatively little is known, however, about the separate stages of ionization.

In the case of ammonia, hydrazine, and the three organic bases the dissociation constants are the apparent ones, referred, that is to say, to the total concentration of the base, not merely to that of the actual hydroxide, which is unknown. The true dissociation constants would be much greater.[2]

A glance at the dissociation constants of cyanin and dimethylamino-azo-benzene will show that among basic indicators they occupy much the same position as do litmus and phenolphthalein among the acidic ones. Cyanin is much more basic than dimethylamino-azo-benzene, and can consequently only be used for titrating strong bases (with

[1] Stieglitz, *The Elements of Qualitative Chemical Analysis*, 1912, vol. **1**, p. 106.

[2] See Chapter VI.

Base	Equilibrium Ratio	Dissociation Constant
Potassium hydroxide	$[K^{\cdot}][OH^{'}]/[KOH]$	(1)
Sodium hydroxide	$[Na^{\cdot}][OH^{'}]/[NaOH]$	(1)
Barium hydroxide	$[Ba^{\cdot\cdot}][OH^{'}]^2/[Ba(OH)_2]$	(0·03)
Strontium hydroxide	$[Sr^{\cdot\cdot}][OH^{'}]^2/[Sr(OH)_2]$	(0·03)
Calcium hydroxide	$[Ca^{\cdot\cdot}][OH^{'}]^2/[Ca(OH)_2]$	(0·03)
Ammonium hydroxide	$[NH_4^{\cdot}][OH^{'}]/([NH_4OH] + [NH_3])$	$1{\cdot}8 \times 10^{-5}$
Methylamine	$[CH_3NH_3^{\cdot}][OH^{'}]/([CH_3NH_3OH] + [CH_3NH_2])$	4×10^{-4}
Hydrazine	$[N_2H_5^{\cdot}][OH^{'}]/([N_2H_5OH] + [N_2H_4])$	3×10^{-6}
Pyridine	$[C_5H_6N^{\cdot}][OH^{'}]/([C_5H_6NOH] + [C_5H_5N])$	$1{\cdot}6 \times 10^{-9}$
Aniline	$[C_6H_5NH_3^{\cdot}][OH^{'}]/([C_6H_5NH_3OH] + [C_6H_5NH_2])$	5×10^{-10}
Water	$[H^{\cdot}][OH^{'}]/[HOH]$ at 25°	2×10^{-16}

a strong acid). Of these two indicators only dimethylamino-azo-benzene would be suitable for titrating weak bases (with a strong acid). For titrating acids (with a strong alkali), however, cyanin would have to be used in the case of weak acids but could also be used with strong acids while the very weakly basic dimethylamino-azo-benzene could be used only for strong acids.

As already explained on page 37, the colour change which occurs when alkali or acid is titrated in presence of an indicator takes place when a certain hydrogen ion concentration is reached. This concentration is different for each indicator. Sometimes the colour change is very sharp, but with other indicators it takes place gradually whilst the hydrogen ion concentration increases or decreases through a perfectly definite range. For many analytical purposes a knowledge of the actual hydrogen ion concentration at the moment of the colour change is not necessary. The volume of standard acid or alkali used in the titration gives all the information required provided that the indicator has been properly selected. For many purposes, however, usually of a biological nature, it is necessary to determine the actual hydrogen ion concentration of fluids which are either very weakly acid or very weakly alkaline. The fluids in question are generally of such a character that if an attempt were made to titrate them directly, the hydrogen ion would automatically be renewed for a considerable

time so that the titration would yield quite erroneous results. The hydrogen ion concentration has, therefore, to be determined by some method which does not disturb the ionic equilibria in the fluid. This can be done by means of the hydrogen electrode and this method is the ultimate standard for such determinations. The determinations can, however, be carried out very conveniently and rapidly by the use of suitable indicators. The colour produced by the solution with a suitable indicator is compared colorimetrically with that given by the same indicator with standard solutions of accurately known hydrogen ion concentration. There are a number of such comparison solutions available but it is not proposed to go into details of such determinations. As, however, at the present time indicators are frequently spoken of in terms of the hydrogen ion concentration at which their colour change occurs it is advisable to understand the system of notation which is employed. If the concentration of hydrogen ion in a solution is $[H^{\cdot}]$, then $\log \frac{1}{[H^{\cdot}]}$ (or $-\log [H^{\cdot}]$) is put equal to pH. pH is thus numerically equal to the logarithm of the number of litres of solution which contain one gram of hydrogen ion and instead of saying that the hydrogen ion concentration of the solution has a certain value, the solution is said to have the corresponding pH value. Similarly, indicators are said to change colour at such and such a pH value or to be suitable for use at certain pH values. There are several advantages in this system of notation, and they are discussed by Clark in his book on *The Determination of Hydrogen Ions* (1922, 2nd edition, p. 35). It is to be particularly noted that, since in pure water or an absolutely neutral solution $[H^{\cdot}] = 10^{-7}$, and $-\log(10^{-7}) = 7$, a pH value of 7 corresponds to absolute neutrality. All pH values greater than 7 therefore correspond with alkaline solutions, while pH values less than 7, including negative values, correspond with acid solutions. In the following table is given the range of pH values over which the change of colour of each indicator mentioned on pages 39 and 43 occurs, and also the pH value at which the

colour change has proceeded to the extent of 50 per cent. The figures refer to a temperature of from 18° to 25° :—

Indicator	pH range	pH for 50% change
Methyl orange	2·7–5·4	4
Litmus	5–8	6·5
Phenolphthalein	8·3–10	9
Cyanin	6–9	?
Dimethylamino-azo-benzene	2·9–4	?

For information on the use of indicators for determining the pH of solutions see *The Theory and Use of Indicators* by Prideaux.

Attention must be drawn to the fact that, since the use of indicators depends upon the relative values of their dissociation constants and those of the acids or bases present, any factors which influence these values will affect the results obtained. This applies both to ordinary titrations and to the determination of pH values. Temperature is the factor which influences the dissociation constants most, but these are affected also by the presence of other substances in the solution, more particularly by neutral salts, though this effect is, as a rule, small. The concentration of the solution will also affect the results, partly because of this neutral salt effect. The concentration of the indicator is also important because the intensity of the colour and the readiness with which the colour change can be seen depends upon it. Titrations in hot solutions should usually be avoided, and it is as well to carry out titrations and the standardization of the acid or alkali under as closely similar conditions as possible with regard to temperature, concentration and amount of indicator used.

The Preparation of Standard Solutions of Acid and Alkali

In making up standard solutions of acid or alkali it is convenient to prepare one of them with great care and then to make up the other with its help.

Preparation of Standard Alkali. If it is decided to make up the alkali first then the substance always used is sodium carbonate. This compound can be obtained in great purity, and the requisite amount needs only to be accurately weighed out and dissolved in water, the solution being then made up to the correct volume.

The pure sodium carbonate is obtained by heating the pure bicarbonate to constant weight in a platinum basin or crucible at a temperature below the melting-point of the carbonate. The dissociation pressure of sodium carbonate above its melting-point becomes appreciable, hence the need for care. (For exact details of procedure refer to Treadwell or any other textbook of analysis.)

The need for employing a strongly acidic indicator limits the applicability of standard sodium carbonate solutions. These cannot be used for titrating weak acids, for they can be accurately titrated only in the presence of very weakly acidic indicators such as phenolphthalein.

The titration of weak acids can accordingly be carried out only with standard solutions of strong alkalies such as sodium hydroxide or barium hydroxide; these, on neutralization, give rise merely to a salt and water, which are free from disturbing effects on the weak acidic indicator.

The standard alkali solution most commonly employed for titrating weak acids is one of baryta. This is quite easily prepared by weighing out a little more than the theoretical amount of crystallized barium hydroxide ($Ba(OH)_2 . 8H_2O$), and making it up to the right volume. The solution is left to stand until any $BaCO_3$ present has settled to the bottom.

If standard solutions of sodium or potassium hydroxide are required they are best made from the metal or from potassium hydroxide purified by alcohol. Sodium hydroxide solutions can be readily and safely prepared in quantity by the method of Cornog [1] from metallic sodium. A layer of ether 3 or 4 cms. deep is poured over distilled water, which has been recently boiled to expel carbon dioxide, and pieces

[1] *J. Amer. Chem. Soc.*, 1921, **43**, 2573.

of sodium, not exceeding 1 cm. in diameter, are dropped in. The sodium reacts slowly with the wet ether, and the sodium hydroxide formed passes into the water. When the required amount has been dissolved the bulk of the ether is removed by means of a pipette and the rest by boiling. Potassium hydroxide solutions can be prepared similarly from metallic potassium.

Solutions of barium, sodium, or potassium hydroxide must of course be stored and used under conditions where absorption of carbonic acid from the air is as far as possible prevented. Their exact strength has to be determined by titration with standard acid.

Preparation of Standard Acid. Hydrochloric acid is on the whole the most suitable for this purpose and the most commonly employed. Standard hydrochloric acid is usually made up as follows :—A rough idea of the strength of the ordinary concentrated acid is obtained by taking the specific gravity with a hydrometer and referring to the specific gravity tables. The amount of the concentrated acid required to make standard acid of the desired strength can then be calculated. Slightly more than this amount is weighed out approximately and made up to a little less than the correct volume. The strength of the so diluted acid is then accurately determined, and the additional amount of water (or, if it happens to be a little too weak, of the concentrated acid) which must be added to bring it to the desired strength is calculated. After this further addition and careful mixing the strength should again be determined so as to make certain that it is really correct.

It is not necessary that standard solutions should be exactly normal or decinormal, etc., and in actual practice they seldom are. So long as the correct strength is known, that is sufficient, but it saves trouble in calculations if the solutions are exactly adjusted.

The exact determination of the strength of the acid can be carried out in several ways. If it is a decinormal solution 25 c.c. can be accurately measured out, precipitated with silver nitrate as described on page 114, and the silver chloride

weighed, or it may be titrated with standard silver nitrate solution after carefully neutralizing as already described on page 20. In the case of a normal solution it suffices to precipitate from 2 to 5 c.c., but it is hard to measure out this small amount with sufficient accuracy, and it is therefore best to weigh it out. This necessitates the determination of the specific gravity of the acid which is being analysed so that the exact volume of the amount used for the analysis can be calculated. The determination may be made with an ordinary specific gravity bottle. Or 25 c.c. of the normal acid may be diluted to 250 c.c. and 25 c.c. of the diluted solution used for the standardization with silver nitrate.

If a standard solution of sodium carbonate is available the exact determination of the strength of the acid can be effected by simply titrating it with the carbonate solution in presence of methyl orange.

Standardization of Hydrochloric Acid with Iceland Spar.

Another method which is sometimes useful employs the purest form of calcium carbonate—the mineral Iceland Spar. A fine platinum wire is tied round a fragment of the mineral, and mineral plus wire are accurately weighed. They are then placed in a beaker containing 25 c.c. of the acid which is being standardized and to which one or two drops of methyl orange solution have been added. The carbonate gradually dissolves with effervescence, and is left in the liquid until the pink colour of the methyl orange has become yellow, showing that no free acid remains. This takes some time as the last traces of acid are removed only very slowly. Twenty-four hours or longer may be needed and the contents of the beaker should be stirred occasionally, and, towards the end heated to about 80° in order to drive out all carbon dioxide. The Iceland Spar is then removed from the liquid by means of the wire, washed with distilled water and then dried by rinsing first with alcohol and then with ether. The loss of weight is then ascertained and from that the strength of the acid can at once be calculated. If any tiny fragments of the spar have

broken off they must be carefully collected and weighed with the rest.

The neutralization of the last traces of acid by the spar is, however, so slow that the method which was first suggested by Grandeau,[1] and later by Pincius,[2] is better. A sodium hydroxide solution is prepared of approximately the same strength as the acid to be standardized and the exact relationship between the two solutions is found by titration. A known weight of Iceland Spar is then dissolved in a measured volume of the acid, which is taken in excess. The volume of the sodium hydroxide solution required to neutralize this excess is then determined, and thus by deducting the equivalent volume of acid from the total volume used in the experiment, the amount neutralized by the Iceland Spar is obtained and from that its strength is calculated.

Preparation of Standard Hydrochloric Acid with the Acid of Constant Boiling Point

There is a good method of directly making up a standard solution of hydrochloric acid which requires no further checking. This method makes use of the fact that hydrogen chloride and water form a constant boiling mixture the composition and boiling point of which vary with the atmospheric pressure.

The various compositions obtained at different pressures are accurately known and may be found in reference books.

The constant boiling acid boils at 108·5° under 760 mm. pressure and contains 20·242 per cent by weight of HCl, which is less than that (about 33 per cent) contained in the ordinary concentrated hydrochloric acid. To obtain the constant boiling acid the concentrated acid is diluted until its specific gravity corresponds roughly with that (about 1·102) of the constant boiling mixture. Then on distillation the bulk of the acid will come over at 108·5°, but will be preceded by a small amount of acid boiling at a lower temperature which will

[1] *J. Pharm. Chim.*, 1858 (3), **34**, 209.

[2] *J. pr. Chem.*, 1859, **76**, 171. See also Masson, *Chem. News*, 1900, **81**, 73, and Green, *Chem. News*, 1903, **87**, 5.

be either weaker or stronger than the acid of constant boiling point according to circumstances. The acid passing over at 108·5° is collected separately, and is that required for the above method of preparing standard hydrochloric acid, 180·17 grams of the constant boiling acid being required for one litre of normal acid.

Constant boiling mixtures of maximum boiling point are formed by many binary mixtures. That of hydrochloric acid is perhaps the best known, though others are given by water and most of the strong volatile inorganic acids. Other binary mixtures give rise to constant boiling mixtures of minimum boiling point, which boil at a lower temperature than either constituent. Only where the constituents of a binary mixture are very similar indeed, as, for instance, monochlor-benzene and monobrom-benzene, do the actual vapour pressures and boiling-points of all mixtures lie between those of the pure constituents and agree closely with those calculated from the known composition of the mixtures and the values for the pure constituents.

CHAPTER IV

THE CONNEXION BETWEEN THE SOLUBILITY OF ELECTROLYTES AND "ELECTRO-AFFINITY" OR IONIC STRENGTH

THE intrinsic solubility of compounds, more especially salts, in water, is of fundamental importance in chemical analysis, and it would be of the very greatest assistance if there were some simple theory which would account for the solubilities actually observed. Commonly, this matter is regarded from a purely empirical point of view. Certain compounds are known to be easily soluble, others sparingly soluble, and some so slightly soluble that they are said to be insoluble. It is, however, possible to go beyond this, although one cannot as yet unfortunately give a thoroughly consistent explanation of all the known facts of solubility.

The first serious attack on the problem was made by Abegg and Bodländer,[1] in their theory of electro-affinity. According to these authors, the electro-affinity of an atom or group is its tendency to either lose one or more of its constituent electrons and become a positive ion or else to gain one or more additional electrons, and so become a negative ion. Electro-affinity is best expressed numerically in terms of the electrical potential necessary to replace the lost electron or electrons or to remove the additional electron or electrons. Unfortunately no exact measurement of electro-affinity on this basis is actually possible. The electrode, discharge, or decomposition, potentials of the various ions, however, if determined under comparable conditions of ionic concentration, etc., are probably more or less proportional to their true electro-affinities, and may be used to give an approximately quantitative measure of the magnitude of these. In the following table are given the values of the decomposition potentials of some of the more important simple ions.

[1] *Z. anorg. Chem.*, 1899, **20**, 453.

The table [1] gives the potential difference in volts, calculated for the element named, and an aqueous solution of its ion containing one gram-ion per litre. The potentials given for the gaseous elements represent the potentials of the gases under 760 mm. pressure. The values given are based on the assumption that the absolute zero of potential is at such a point, that the so-called standard normal calomel electrode has a value of + 0·56 volt relative to this zero.[2] Values in parentheses have been estimated by indirect measurements.

Element, Ion	E. P. El., Ion	Element, Ion	E. P. El., Ion
Li, $Li^{\cdot}$ [3]	−2·74	H_2, $H^{\cdot}$	+ 0·277
Na, $Na^{\cdot}$ [4]	−2·44		
K, $K^{\cdot}$ [5]	−2·65	Cu, $Cu^{\cdot\cdot}$	+ 0·606
Rb, $Rb^{\cdot}$ [6]	−2·65		
Ba, $Ba^{\cdot\cdot}$	(−2·54)	As, $As^{\cdot\cdot\cdot}$	< + 0·570
Sr, $Sr^{\cdot\cdot}$	(−2·49)	Bi, $Bi^{\cdot\cdot\cdot}$	< + 0·668
Ca, $Ca^{\cdot\cdot}$	(−2·28)	Sb, $Sb^{\cdot\cdot\cdot}$	< + 0·743
Mg, $Mg^{\cdot\cdot}$	(−2·26)	Hg, $Hg^{\cdot}$	+ 1·027
Al, $Al^{\cdot\cdot\cdot}$	−0·999 ?	Ag, $Ag^{\cdot}$	+ 1·048
Mn, $Mn^{\cdot\cdot}$	−0·798	Pt, $Pt^{\cdot\cdot\cdot\cdot}$	< + 1·140
Zn, $Zn^{\cdot\cdot}$	−0·493	Au, $Au^{\cdot\cdot\cdot}$	< + 1·356
Cd, $Cd^{\cdot\cdot}$	−0·143	F_2, F'	(+ 2·24)
Fe, $Fe^{\cdot\cdot}$	−0·122 ?	Cl_2, Cl'	+ 1·694
Co, $Co^{\cdot\cdot}$	+0·0138 ?	Br_2, Br'	+ 1·270
Ni, $Ni^{\cdot\cdot}$	+0·108 ?	I_2, I'	+ 0·903
Sn, $Sn^{\cdot\cdot}$	< +0·085	O_2, OH'	+ 0·698
Pb, $Pb^{\cdot\cdot}$	+0·129		

Of the positive ions in the above list, the $Li^{\cdot}$ ion has the highest electro-affinity and the $Au^{\cdot\cdot\cdot}$ ion the lowest, while of the negative ions F' has the highest and OH' the lowest electro-affinity.

It should be noted that the electrode potentials tabulated above all refer to a similar electro-chemical process, namely the *gain* of electrons. In the case of cations, therefore, the values refer to the discharge of the ions (in the case of lithium,

[1] See also Stieglitz, *The Elements of Qualitative Chemical Analysis*, 1912, vol. **1**, p. 294.

[2] Ostwald, *Z. physikal. Chem.*, 1901, **36**, 97.

[3] Lewis and Keyes, *J. Amer. Chem. Soc.*, 1913, **35**, 340.

[4] Lewis and Kraus, *J. Amer. Chem. Soc.*, 1910, **32**, 1459.

[5] Lewis and Keyes, *J. Amer. Chem. Soc.*, 1912, **34**, 119.

[6] Lewis and Argo, *J. Amer. Chem. Soc.*, 1915, **37**, 1983.

for instance, to the change $Li^{\cdot} + \ominus \rightarrow Li$, where $\ominus$ is an electron), while for anions the values refer to the formation of the ions (for chlorine the change would be $\frac{1}{2} Cl_2 + \ominus \rightarrow Cl'$). For the converse electro-chemical change occurring with loss of electrons the sign of the electrode potentials would be reversed. The figures as tabulated give a measure of the tendency of the anion-forming elements to ionize, but to get a measure of the corresponding tendency of the cation-forming elements the signs must be reversed.[1]

Electro-affinity is one of the bases of classification and comparison used in Abegg and Auerbach's *Handbuch der anorganischen Chemie*, and is of considerable utility. According to Abegg and Bodländer [2] the solubility of electrolytes in water depends largely upon the electro-affinity of the ion-forming atoms or groups of which they are composed. The greater the electro-affinity of these the greater the solubility and vice versa. Solubility is regarded as the result of a tendency of atoms and groups to reach the ionized condition. Thus most salts of the alkali metals are soluble in water owing to the very high electro-affinities of the alkali metals, while all nitrates are soluble owing to the high electro-affinity of the NO_3' ion. The majority of chlorides, bromides, and iodides are soluble owing to the high electro-affinities of the Cl', Br', and I' ions, although, if these are combined with cations of very low electro-affinity, the resulting compounds may be insoluble. This is the case, for instance, with AgCl, AgBr, and AgI, and if we compare a series of compounds such as the latter with one common ion we find that the insolubility increases as the electro-affinity of the other ion diminishes. One litre of water at 25° dissolves 0·0020 grm. AgCl; 0·000137 grm. AgBr, and only 0·0000028 grm. AgI.

The majority of the cyanides and sulphides are insoluble in water in correspondence with the exceedingly low electro-affinities of the CN' and S'' ions, but, even here, if the cation has a high electro-affinity soluble compounds may be formed; potassium cyanide, for instance, is easily soluble.

Whether the decomposition potentials are those of the simple

[1] See Chapter XIV, p. 245.

[2] *Loc. cit*

ions or of hydrated ions is uncertain, and this may be one reason why it is difficult to trace any very rigid connexion between the solubility of electrolytes and the electro-affinities (as measured by the decomposition potentials) of their constituent ions. It is clear that the decomposition potentials actually give a measure of the total energy change which occurs when an ion is discharged. This may involve quite a chain of events, such as: (1) discharge of a hydrated ion, (2) dehydration of the discharged ion, (3) polymerization of discharged dehydrated ions to neutral molecules, and so on. The signs of the several energy changes may differ, so that the evidence afforded by decomposition potentials is far from being as definite as could be wished. For similar reasons it is not generally possible to get even an approximate measure of the electro-affinities of complex ions by means of electrode potentials.

There is no doubt that the ideas of Abegg and Bodländer marked an important step forward. When properly applied they serve as extremely useful guides, especially when taken in conjunction with two other facts to which Abegg and Bodländer drew attention. These are: (1) the strength of an acid is greater the higher the electro-affinity of its anion, and (2) the electro-affinity of a complex ion is almost always greater than that of the simple ion from which it has been derived. It is possible to get an idea of the electro-affinity of complex anions from measurements of the strength of the complex acids derived from them.

Qualitatively, Abegg and Bodländer's ideas on solubility can be applied pretty widely with fair success, but quantitative agreement is found only in quite restricted series of closely similar compounds. Silver chloride, bromide, and iodide form such a series, so do the corresponding lead and mercuric compounds, and the hydroxides of calcium, strontium and barium. One has to be very cautious in applying conclusions drawn from one such series to another series, however, and this is particularly the case when dealing either with very soluble compounds or with salts derived from both cations and anions of high electro-affinity. The need for such caution will be apparent from a glance at the following table, which

gives the solubilities at 18° of the salts indicated in terms of gram molecules of anhydrous salt per litre of solution. The figures refer to the anhydrous salt or hydrate stable at 18°, and therefore, so far as the solid phases are concerned, the figures are not strictly comparable.

	Cl	Br	I	ClO_3	BrO_3	IO_3	NO_3	SO_4
Mg	5·1	4·57	(?) 4·1	4·6	1·5	0·22	3·95	2·8
Ca	5·4	5·2	4·8	5·3	2·3	0·007	5·2	$1·5 \times 10^{-2}$
Sr	3·0	3·4	3·9	4·6	0·9	0·006	2·7	6×10^{-4}
Ba	1·7	2·9	3·8	1·1	0·02	0·001	0·33	1×10^{-5}

	CrO_4	CO_3	C_2O_4	F	OH
Mg	4·26	(?) 0·1	0·0027	0·012	0·0015
Ca	3×10^{-2}	$1·3 \times 10^{-4}$	$0·4 \times 10^{-4}$	0·0002	0·02
Sr	6×10^{-3}	$0·7 \times 10^{-4}$	$2·6 \times 10^{-4}$	0·0009	0·06
Ba	$1·4 \times 10^{-5}$	$1·1 \times 10^{-4}$	$3·8 \times 10^{-4}$	0·009	0·22

It will be seen that while the chlorides, bromides, and iodides of magnesium and calcium fit in with the views of Abegg and Bodländer in the sense that in each case the chloride is the most soluble and the iodide the least, this does not apply to the corresponding compounds of strontium and barium where the iodides are the most soluble. Again, while the increase in solubility of hydroxides, fluorides, and oxalates in passing from calcium to barium corresponds to the increase in electro-affinity of the cation, all the other salts in the above table exhibit a decrease. The magnesium compounds do not fall into line very well with the others.

An examination of the solubilities of the salts of the alkali metals shows a very similar state of affairs, although there are even more marked irregularities. One very important fact is that salts derived from both cations and anions of high electro-affinity tend to become less soluble the higher the electro-affinity of either the cation or anion. This was recognized by Abegg and Bodländer, but is opposed to their view of the connexion between solubility and electro-affinity. It thus happens that the caesium and barium salts of strong acids (the anions of which have high electro-affinities) are the

least soluble, not the sodium or magnesium salts. The salts of complex cations of high electro-affinity with strong acids also tend to be sparingly soluble. Thus $Co(NH_3)_6Cl_3$ is soluble only to the extent of 4·26 grams (= 0·016 gram mol.) in 100 grams of water at 0°.

The following rather empirical statements may be made in regard to solubility in terms of electro-affinity.

(1) Very soluble compounds are generally derived either (*a*) from an ion of very high positive or negative electro-affinity and an ion of the opposite sign of very low electro-affinity (examples are NaOH, KOH, the common inorganic acids, $AgNO_3$, AgF), or (*b*) from two ions of moderately high, but not the highest, electro-affinity (examples of such compounds being the chlorides, bromides, and iodides of lithium, magnesium or calcium).

(2) Compounds derived from positive and negative ions both of high electro-affinity are sparingly soluble, but very insoluble compounds do not occur in this group.

Examples are $KClO_4$, $Ba(NO_3)_2$, K_2PtCl_6.

(3) Compounds derived from positive and negative ions both of low electro-affinity are generally very insoluble. The oxides, hydroxides, sulphides, and cyanides of the heavy metals are examples of such compounds.

There are many exceptions—or apparent exceptions—to the above statements (which are useful working guides, nevertheless). Thus NH_4NO_3 and $LiClO_3$ are very soluble compounds, though one would have expected them to be sparingly soluble like the nitrates and chlorates of K, Rb, and Cs. The very small solubility of AgCl, AgBr, and AgI and of the sulphates of calcium, strontium and barium is hardly in agreement with the relatively high electro-affinity of the Cl′, Br′, I′, SO_4'', $Ca^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, and $Ba^{\cdot\cdot}$ ions. It is to be noted, however, that within any one such group containing a common ion the solubility may fall off as the electro-affinity of the other ion diminishes.

It is evident that electro-affinity alone does not determine the solubility of salts. There are other modifying influences at work, of which the most important are probably (*a*) polymerization of the salt molecule ; (*b*) hydration of the salt

molecule or its ions ; and (*c*) the condition of the salt molecule with regard to "co-ordination". The consideration of these factors is postponed till Chapter XIII.

The Gravimetric Estimation of Potassium and Nitrate

Two important estimations will now be considered, both of which are interesting as being based on the insolubility of salts derived from two ions of high electro-affinity.

The Estimation of Potassium as Perchlorate [1]

As a rule, this is the most satisfactory method for determining potassium, but careful attention to details is necessary owing to the fact that $KClO_4$ has an appreciable solubility in pure water (0·7 grm. per 100 grms. water at 0° and 2·0 grms. per 100 grms. water at 25°). An aqueous solution containing an amount of the potassium salt which will yield about 0·2 to 0·3 grm. $KClO_4$ is used. The sulphates and phosphates of sodium and potassium are insoluble in 96 per cent alcohol, hence if sulphate and phosphate are present, they are removed by barium chloride and ferric chloride respectively, followed by ammonium hydroxide and carbonate. Mg, Ca, Sr, Ba, and Na may be present, but ammonium salts must be removed by gentle ignition. NH_4ClO_4 has almost the same solubility as $KClO_4$, and would be separated and weighed with the latter. The lowest possible temperature is used to drive off the ammonium salts since potassium salts are appreciably volatile at temperatures above about 600° C. Metals of analytical Groups I, II, III, and IV should be absent, though probably their presence would not matter in most cases, since practically all the metallic perchlorates are soluble.

After removing any objectionable constituents as above, the potassium solution is evaporated to about 20 c.c. in a shallow dish, and while still warm about 5 c.c. of a 20 per cent solution of $HClO_4$ are added. The amount of the $HClO_4$

[1] See Lunge, Keane, *Technical Methods of Chemical Analysis*, 1911, vol. **2**, pt. 1, p. 413 ; also Thin and Cumming, *J. Chem. Soc.*, 1915, **107**, 361 ; Davis, *J. Agric. Science*, 1912, **5**, 52 ; *J. Chem. Soc.*, 1915, **107**, 1678 ; Baxter and Kobayashi, *J. Amer. Chem. Soc.*, 1907, **39**, 248 : 1920, **42**, 735 ; Baxter and Rupert, *J. Amer. Chem. Soc.*, 1920, **42**, 2046.

used should be from $1\frac{1}{2}$ to $1\frac{3}{4}$ times that needed to decompose all the salts present. This may be more or less than the 5 c.c. suggested, and should be adjusted in accordance with the substance being analysed. Cumming [1] has drawn attention to the fact that commercial perchloric acid sometimes contains small amounts of potassium perchlorate. This, if necessary, must be estimated and allowed for. The solution to which the perchloric acid has been added is evaporated on the water bath until the smell of HCl can no longer be detected, and white fumes of $HClO_4$ begin to escape. When cold the residue is treated with 15 c.c. of 96 per cent alcohol and carefully rubbed down with a glass rod to help salts other than $KClO_4$ to dissolve. When the solid has settled the supernatant liquid is filtered through a Gooch crucible, the residue is then twice rubbed up with 96 per cent alcohol, containing 0·2 per cent of $HClO_4$, the washings are decanted and the $KClO_4$ is transferred to the crucible. The $KClO_4$ is then thoroughly washed with alcohol saturated just previously with $KClO_4$ by shaking with excess of the salt for about ten minutes. The total volume of filtrate should amount to about 75 c.c. The $KClO_4$ is weighed after drying at 120–130° for half an hour.

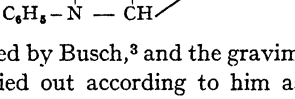
While sparingly soluble in water, $KClO_4$ is much less soluble in 96 per cent alcohol. The solubility of $NaClO_4$ and any other perchlorates which may be present is so much greater that they are readily removed even by 96 per cent alcohol. If alcohol already saturated with $KClO_4$ is used as wash fluid,[2] loss of $KClO_4$ is almost entirely prevented. The alcohol saturated with $KClO_4$ should be used only for the latter part of the washing, since in the early stages where much $NaClO_4$ or other perchlorate has to be removed some $KClO_4$ might be thrown out of solution, as the $NaClO_4$ dissolves, owing to the mass effect of the common ClO_4' ion. Accordingly, in the first stages of the washing, alcohol containing a little perchloric acid is used. The $KClO_4$ is considerably less soluble in this than in the pure 96 per cent alcohol, owing to the effect of the common ion ClO_4', while there is no danger of a high result being obtained owing to displacement of $KClO_4$ from the wash

[1] *Loc. cit.* [2] Due to Davis, *loc. cit.*

fluid. According to Baxter,[1] it is not easy to remove the $NaClO_4$ completely unless, after removing the bulk of it, the $KClO_4$ is dissolved in water and evaporated to dryness before completing the washing with 96 per cent alcohol. This is best done after washing with alcohol containing $HClO_4$ and before washing with alcohol saturated with $KClO_4$.

The Estimation of Nitrate by means of "Nitron"

The NO_3' ion has such a high electro-affinity that all the metallic nitrates are soluble in water even that of caesium, the most electro-positive of the metals. Caesium nitrate is the least soluble of all the metallic nitrates (23 parts $CsNO_3$ per 100 parts H_2O at 20°), but it is not insoluble enough to be used for the gravimetric estimation of nitrate. Of recent years, however, one or two organic bases have been discovered, which form very insoluble nitrates, and one of these, called "nitron", has come into considerable use for estimating nitrate gravimetrically.[2] "Nitron" is the name given to 1 : 4 *Diphenyl* 3 : 5 *endo-anilodihydro-triazole,* which has the constitutional formula :—



It was discovered by Busch,[3] and the gravimetric estimation of nitrate is carried out according to him as follows[4]:—To precipitate the nitrate to be estimated, 10–12 c.c. of a 10 per cent solution of nitron in 5 per cent acetic acid are added all at once to the hot solution (containing about 0·1 gram. HNO_3 in 100 c.c.), to which ten drops of dilute sulphuric acid have been added. The liquid is kept for 1½ to 2 hours at 0°,

[1] *Loc. cit.*

[2] Cinchonamine, one of the quinine group of alkaloids, also forms a very insoluble nitrate and a method for the gravimetric estimation of nitrate has been based on this (Howard and Chick, *J. Soc. Chem. Ind.*, 1909, **28,** 53). The "nitron" method seems to be the better of the two, however.

[3] *Ber.*, 1905, **38,** 856.

[4] *Ber.*, 1905, **38,** 861. See also Gutbier, *Z. angew. Chem.*, 1905, **18,** 494.

and the precipitate is then collected on a Gooch crucible, washed with 10–12 c.c. of ice cold water, dried at 110° and weighed. The precipitate has the composition $C_{20}H_{16}N_4HNO_3$.

The presence of small quantities of chlorides and sulphates does not interfere with the accuracy of the method, but bromides (at a dilution of 1 in 800), iodides (1 in 20,000), nitrites (1 in 4,000), chromates (1 in 6,000), chlorates (1 in 4,000), and perchlorates (1 in 50,000), are also precipitated by nitron (nitrates are precipitated at a dilution of 1 in 60,000). The dilutions refer in all cases to 1 part by weight of the appropriate acid—HBr, HI, etc., in so many parts of slightly acid water. Hydrobromic acid should be previously eliminated by means of chlorine, hydriodic acid by means of an iodate, the bromine or iodine liberated being driven off by boiling the solution. Nitrous or chromic acid should be removed by hydrazine sulphate. (The chromic acid would be reduced to an ordinary chromium salt.)

In order to estimate a nitrate in presence of a nitrite, the solution of the salts (0·2 grm. substance in 5–6 c.c. of water) is added to finely powdered hydrazine sulphate, which completely destroys the nitrite.[1] The nitrate is then precipitated by means of nitron as described above, and very good results are obtained. Thiocyanic, hydroferrocyanic, hydroferricyanic, picric, and oxalic acids also form salts with nitron which are not very soluble. They should therefore be absent when the method is used for the determination of nitrate. The results obtained by the nitron method are very good, so it may be that the slight solubility of the nitron nitrate is compensated for by slight occlusion or adsorption of nitron, nitron acetate, etc., by the nitron nitrate precipitate.

Although relevant data are not available, there seems little doubt that the positive ion of the nitron salts ($C_{20}H_{16}N_4H^{\cdot}$) has a high electro-affinity—even higher than that of the $NH_4^{\cdot}$ ion—and that the insolubility of nitron nitrate is of the type found with salts derived from two ions of very high electro-affinity. The insolubility of the perchlorate and chlorate supports this view, as also does the fact that the

[1] Forming hydrazoic acid HN_3.

chlorine ion which has a considerably lower electro-affinity than the NO_3', ClO_4' or ClO_3' ions, gives rise to the considerably more soluble nitron chloride. One would have expected the chromate, iodide, and nitrite to have been still more soluble, and in view of their small solubilities it must be concluded that some other factor is operative. Although the ion of the nitron salts ($C_{20}H_{16}N_4H^{\cdot}$) has a high electro-affinity, there is a considerable tendency for it to decompose, thus: $C_{20}H_{16}N_4H^{\cdot} \rightleftarrows C_{20}H_{16}N_4 + H^{\cdot}$ owing to the insolubility of free nitron ($C_{20}H_{16}N_4$) in water.[1] If, therefore, the solution is not sufficiently acid, free nitron might be precipitated and the concentration of the ion $C_{20}H_{16}N_4,H^{\cdot}$ might become too small for a satisfactory and complete precipitation of the nitrate as nitron nitrate. This is the reason for adding a little dilute sulphuric acid to the nitrate solution before introducing the nitron reagent. Since the nitron nitrate is the salt of a strong acid, its solubility in dilute acids is hardly, if at all, greater than its solubility in pure water.[2]

[1] Compare the case of the $NH_4^{\cdot}$ ion. See page 76.

[2] See page 63.

CHAPTER V

THE SOLUBILITY OF SALTS IN ACIDS

FOR analytical purposes the solubility of salts in acids is of very great importance, and we must now consider the factors which are operative in this case.

The effect of even strong acids in small amounts upon the insoluble salts of strong monobasic acids [1] is very slight. It is of the same order and due to exactly similar causes as the effect of neutral salts which was considered in connexion with the estimation of barium.

Insoluble salts of weak monobasic acids are, however, not precipitated in presence of a strong acid. Practically the only salts of this class which have to be considered are cyanides. The cyanides of most of the heavy metals are insoluble in water, but dissolve in dilute mineral acids. Nickel cyanide, for example, is insoluble in water, but easily soluble in hydrochloric acid. On treating the $Ni(CN)_2$ with HCl the following equilibria adjust themselves :—

$$\begin{aligned} Ni^{\cdot\cdot} + 2CN' &\rightleftarrows Ni(CN)_2 \text{ (dissolved)} \rightleftarrows Ni(CN)_2 \text{ (solid)} \\ H^{\cdot} + Cl' &\rightleftarrows HCl \\ Ni^{\cdot\cdot} + 2Cl' &\rightleftarrows NiCl_2 \\ H^{\cdot} + CN' &\rightleftarrows HCN \end{aligned}$$

Now HCN is a very weak acid, and consequently ionized only to a very small extent in dilute solution. It is clear from the mass-action equation $\frac{[H^{\cdot}][CN']}{[HCN]} = K$ that if hydrogen ions are added to a solution containing CN′ ions the concentration of the latter must diminish and that of the undissociated HCN consequently increase in order that the above equation may be fulfilled. As fast as the CN′ ions are removed in the form of undissociated HCN they are replaced by the ionization of more undissociated $Ni(CN)_2$ which will

[1] If the acid is present in large amount it may greatly increase the solubility owing to formation of complex acids (e.g. $HAgCl_2$ from AgCl and HCl).

be replaced by the solution of more of the solid; this will continue until all the solid $Ni(CN)_2$ has dissolved, provided that the concentration of the hydrogen ions is sufficient.

In the case of salts of polybasic acids, there is an additional factor to be considered, owing to the fact that the first hydrogen of such an acid has a far greater (a hundred to a hundred thousandfold in different cases) tendency to ionize than has the second, which, again, has a much greater tendency than the third (see p. 38). Thus, for example, the ionization of a tribasic acid, such as phosphoric acid, takes place in three stages, each of which is regulated by its own equilibrium constant. We have :—

$$H^{\cdot} + H_2PO_4' \rightleftarrows H_3PO_4 \qquad \frac{[H^{\cdot}][H_2PO_4']}{[H_3PO_4]} = K_1$$

$$H^{\cdot} + HPO_4'' \rightleftarrows H_2PO_4' \qquad \frac{[H^{\cdot}][HPO_4'']}{[H_2PO_4']} = K_2$$

$$H^{\cdot} + PO_4''' \rightleftarrows HPO_4'' \qquad \frac{[H^{\cdot}][PO_4''']}{[HPO_4'']} = K_3$$

Now, so far as the first stage of the ionization is concerned, H_3PO_4 is a moderately strong acid, i.e. the ion H_2PO_4' has a relatively high electro-affinity. As a result of this, the majority of the salts derived from it are soluble in water (e.g. AgH_2PO_4).

In respect to the second stage of ionization, H_3PO_4 behaves as a weak acid, for the HPO_4'' ion has only a small electro-affinity. Most of its salts are in consequence only very slightly soluble in water (e.g. Ag_2HPO_4).

So far as the third stage of ionization is concerned, H_3PO_4 is an exceedingly weak acid, and the PO_4''' ion has such a small electro-affinity that, with the exception of those of the alkali metals, all its salts are very insoluble in water (e.g. Ag_3PO_4). Similar considerations apply to all other polybasic acids, but, of course, the strength of the acids associated with the first, second, and third stages of ionization, varies from case to case.

It is now easy to see in what way the addition of acid to the salts of polybasic acids will affect their solubility. By the addition of acid the hydrogen ion concentration of the solution

is increased, and this at once disturbs the conditions of equilibrium, which have to readjust themselves in accordance with the several mass-action equations involved. The result is that the ions of low electro-affinity unite with hydrogen ions to form ions of higher electro-affinity. The salts derived from these are more soluble, so that the insoluble salt originally present dissolves, or, vice versa, the insoluble salt cannot be precipitated in presence of the free acid. These points are best illustrated by considering a concrete example, and the conditions under which calcium oxalate can be precipitated will be discussed for this purpose.

Calcium oxalate is very sparingly soluble in pure water (as are the majority of oxalates, for the C_2O_4'' ion has a very small electro-affinity), but dissolves readily in dilute mineral acids.

The solubility in water is regulated by the usual relation :—

$$Ca'' + C_2O_4'' \rightleftarrows CaC_2O_4 \text{ (dissolved)} \rightleftarrows CaC_2O_4 \text{ (solid)}$$

In a dilute solution of HCl we should have the further equilibria :—

$$\begin{aligned} H^{\cdot} &+ Cl' &&\rightleftarrows HCl \\ Ca'' &+ 2Cl' &&\rightleftarrows CaCl_2 \\ H^{\cdot} &+ HC_2O_4' &&\rightleftarrows H_2C_2O_4 \\ H^{\cdot} &+ C_2O_4'' &&\rightleftarrows HC_2O_4' \end{aligned}$$

The hydrogen ions derived from the HCl unite with the C_2O_4'' ions to form HC_2O_4' ions, but the place of the C_2O_4'' ions thus removed is at once taken by others derived from the undissociated CaC_2O_4 the concentration of which is kept up by solution of some of the solid. This process will go on until equilibrium is reached, and this will occur only when all the solid CaC_2O_4 present has dissolved, provided that sufficient HCl is present.

When equilibrium has thus been finally restored there may be still a few C_2O_4'' ions present, but their concentration will be in any case insufficient for the solubility product of CaC_2O_4 to be reached. Under the new conditions the following equilibria are the important factors :—

$$\begin{aligned} H^{\cdot} &+ Cl' &&\rightleftarrows HCl \\ Ca'' &+ 2Cl' &&\rightleftarrows CaCl_2 \\ H^{\cdot} &+ HC_2O_4' &&\rightleftarrows H_2C_2O_4 \\ Ca'' &+ 2HC_2O_4' &&\rightleftarrows Ca(HC_2O_4)_2 \end{aligned}$$

Of course, if the solutions are sufficiently concentrated for the solubility products of either of the solids $H_2C_2O_4$ or $Ca(HC_2O_4)_2$ to be reached that solid would separate, but under the conditions of analysis this should never happen.

The Determination of Calcium as Oxide

It is plain then that for the quantitative precipitation of calcium as oxalate the concentration of the hydrogen ion must be very low. This is usually attained by carrying out the precipitation in a solution made faintly alkaline by addition of ammonia. If this is done, however, there is almost certain to be trouble with the filtration, the precipitate tending to pass through the filter, for owing to the very small solubility of the precipitate in alkaline solution it separates rapidly in a fine state of division. The difficulty can be overcome by increasing its solubility in the early stages of the precipitation by having the solution faintly acid, and making it alkaline with ammonia only after all the oxalate has been added.[1] The procedure is then as follows :—

A suitable amount of the substance in which calcium is to be determined (which should contain no other metals, excepting magnesium or alkalies) is dissolved in 20 to 30 c.c. of water, with the aid of hydrochloric acid if necessary (e.g. when analysing calcium carbonate). The solution is nearly neutralized with ammonia, or made faintly acid as the case may be and heated to incipient boiling ; the requisite amount of boiling ammonium oxalate solution is then added drop by drop with constant stirring (about 10 c.c. of a cold saturated solution is required for each 0·1 gram CaO). Dilute ammonia ($2\frac{1}{2}$ per cent) is then added drop by drop until the solution is weakly alkaline. The precipitate should be left to stand for three or four hours before filtration, for in

[1] The same end may be attained by adding a considerable amount of ammonium chloride to the solution. This increases the solubility in the manner discussed under the estimation of barium. The method given above is, however, far preferable as the factor causing the increased solubility is removed at the end of the precipitation.

this way the particles become coarser, as explained in connexion with the precipitation of barium sulphate. The calcium oxalate is then filtered off and washed with 2½ per cent ammonia.

Calcium oxalate is appreciably soluble in pure water (100 c.c. dissolve 0·00068 grams at 25°). There are sufficient hydrogen ions in the water to lead to the formation of appreciable amounts of HC_2O_4' ions ; the solubility observed is due chiefly to this, and can be almost entirely prevented by adding to the water a small amount of ammonia. The concentration of hydrogen ions in the ammoniacal solution is excessively low.

The washed precipitate is dried, ignited strongly, and weighed as calcium oxide. The ignition should be carried out first over the bunsen until all the carbon of the filter paper has disappeared, and then over the blowpipe ; a platinum crucible should be employed as a much higher temperature can be reached thereby. Ten minutes ignition over the blowpipe is usually more than sufficient for constant weight to be reached. The ignited calcium oxide should be allowed to cool in a desiccator and weighed quickly, as it readily absorbs moisture from the air.

On ignition the calcium oxalate decomposes first into carbonate, which is then further converted into oxide :—

$$CaC_2O_4 \rightarrow CaCO_3 + CO\,; \quad CaCO_3 \rightleftarrows CaO + CO_2$$

The formation of the carbonate from the oxalate is not a reversible process (at any rate under any easily attainable conditions), but the decomposition of the carbonate is, and at any given temperature, if the heating took place in a closed space decomposition would proceed only until the equilibrium pressure of CO_2 at that particular temperature was reached. Accordingly the CO_2 formed during the ignition of the precipitate should be given plenty of opportunity to escape by occasionally removing the lid of the crucible. (The equilibrium pressure reaches one atmosphere at about 900°.)

Some workers prefer to ignite the calcium oxalate at a low temperature, and convert it only into carbonate. This procedure is much more troublesome, but the difficulty of

preventing the formation of some oxide may be overcome by adding a small piece of ammonium carbonate to the ignited calcium carbonate and driving it off by gentle heat. This process is repeated until the weight of the calcium carbonate is constant. It is much better, however, to convert it directly into oxide.

Determination of Calcium in Presence of Phosphate

The method just described can be employed in the very important case of the estimation of calcium in the presence of phosphates.

To the acid solution dilute ammonia is added until a slight permanent precipitate of calcium phosphate is formed. This is then dissolved by the addition of a few drops of dilute hydrochloric acid, and the precipitation of calcium oxalate is then proceeded with exactly as described above.

This estimation depends upon the fact that CaC_2O_4 is more insoluble under the conditions of precipitation than any of the calcium phosphates. By the time the solution is alkaline so much C_2O_4'' ion is present that the calcium is practically completely precipitated as CaC_2O_4 before the solubility product of any of the calcium phosphates is reached. In presence of phosphate the solution must be acid initially. The alternative method is useless.

The Estimation of Barium

This estimation has already been described on page 11. The only additional point to note is that the barium sulphate can be redissolved either partially or completely by the addition of a large amount of strong sulphuric acid. The presence of much hydrochloric or nitric acid may also prevent the complete precipitation of the barium. This may cause trouble in certain cases, and is of course due to the removal of SO_4'' ions and the formation of HSO_4' ions :—

$$Ba^{\cdot\cdot} + SO_4'' \rightleftarrows BaSO_4 \text{ (dissolved)} \rightleftarrows BaSO_4 \text{ (solid)}$$
$$SO_4'' + H^{\cdot} \rightleftarrows HSO_4'$$
$$Ba^{\cdot\cdot} + 2HSO_4' \rightleftarrows Ba(HSO_4)_2 \text{ (dissolved)}$$

The Estimation of Lead as Sulphate

This is a very instructive estimation on account of the methods adopted for rendering the solubility of the lead sulphate suitable for quantitative purposes.

On the supposition that no other metal is present to interfere with the estimation, or, that if originally present, it has been separated, the estimation is carried out as follows :—

To the solution containing 0·1 gram lead there is carefully added 0·5–2 c.c. of concentrated sulphuric acid. If nitric acid was originally present, as, for instance, would almost certainly be the case in the analysis of an alloy, the solution is evaporated down on the water bath in a porcelain dish until nitric acid fumes cease to be evolved. The contents of the dish are then diluted to 20–50 c.c., according to the amount of H_2SO_4 used, and after being well stirred up, are left to stand for 4–12 hours before filtration. If no nitric acid had to be removed it is necessary only to concentrate the solution to the above volume, and then leave it to cool and stand some hours before filtering. The lead sulphate is filtered off either through a Gooch crucible or a weighed filter paper, and is washed once or twice with 2–5 per cent sulphuric acid and then with 50 per cent alcohol. The washing with alcohol is continued until all the free acid has been washed out. Then the precipitate is dried at 100° and weighed. If other metals have to be estimated the alcohol washings are collected separately and added to the main filtrate only after removal of the alcohol by evaporation.

The solubility product of lead sulphate, although small, is sufficiently large to render special care necessary in the estimation of lead as sulphate if accurate results are to be obtained. Use is made of the fact that by increasing the concentration of the SO_4'' ion the amount of lead remaining in solution will be much diminished. This is the reason for using such a large amount of sulphuric acid. If, however, the concentration of the latter is unduly increased, there will be a disappearance of SO_4'' ions with formation of HSO_4' ions and as a result some lead sulphate will pass into solution. During the evaporation to remove nitric acid this is liable

to occur, and thus it is necessary to add water subsequently until the concentration has been reduced to such an extent that the full beneficial effect of the SO_4'' ions in diminishing the solubility can be exerted without any trouble arising from the presence of HSO_4' ions.

In common with all other sulphates, lead sulphate is much less soluble in a mixture of alcohol and water than in pure water ; that is the reason for washing it with such a mixture. As, however, there is some danger of causing precipitation of other suphates if these are present in the solution in large amount, it is best to wash the precipitate first with dilute sulphuric acid before using the dilute alcohol. Care must be taken to wash out all traces of free acid, otherwise the filter paper will be charred during the drying.

The effect of sulphuric acid in first of all diminishing the solubility of lead sulphate (at 18°) and, when present in higher concentrations, increasing it, can be seen from the following table.[1] The $PbSO_4$ dissolved is expressed in terms of lead.

Grm. H_2SO_4 per litre	Grm. mols. H_2SO_4 per litre	Grm. Pb per litre
0	0	0·0261
0·0049	0·00005	0·0228
0·0098	0·00010	0·0209
0·0245	0·00025	0·0133
0·0490	0·00050	0·0089
0·490	0·00500	0·0035
976	9·96	0·0346
1540	15·70	0·1346
1780	18·20	0·4903

Lead sulphate is very much more soluble in solutions of ammonium or sodium acetate than in pure water, a fact which is of some analytical importance. It enables lead sulphate to be separated from barium sulphate (the solubility of which is very slightly affected by the soluble acetate), quartz, etc., in analyses of sulphide or other ores containing lead. In the weaker acetate solutions the increased solubility seems to be mainly due to the small electrolytic dissociation [2]

[1] See Abegg and Auerbach, *Handbuch der anorg. Chem.*, 1909, vol. **3**, pt. 2.

[2] See page 20.

of lead acetate. In stronger solutions complex ions introduce complications. Noyes and Whitcomb's figures for the solubility in ammonium acetate are as follows [1] (Temp. 25°).

Grms. $NH_4C_2H_3O_2$ per litre	Grms. $PbSO_4$ per litre
0	0·041
7·98	0·636
15·96	1·38
31·92	3·06

[1] *J. Amer. Chem. Soc.*, 1905, **27**, 756.

CHAPTER VI

THE CONDITION OF AMMONIA IN AQUEOUS SOLUTION

Determinations Involving Precipitation with Ammonium Phosphate

THE exact nature of many of the commonest laboratory reagents is very frequently not properly appreciated. As this statement applies among other things to the ordinary solution of ammonia, it seems advisable to consider briefly the conditions there prevailing, more especially as a due appreciation of the equilibria concerned must precede any attempt to understand the complicated mechanism of the phosphate precipitations discussed in this chapter.

That some chemical reaction occurs when NH_3 dissolves in water is abundantly shown by many facts, such as the high value of the heat of solution, the basic properties of the latter, and so on.

The Condition of Ammonia in Aqueous Solution

The view generally held up to the present [1] has been that the trivalent nitrogen atom of NH_3 becomes pentavalent, enabling NH_4OH to be formed by addition of water. This NH_4OH is capable of ionization into $NH_4^{\cdot}$ and OH' ions to the presence of which the electrical conductivity and basic properties of the solution are due. On this view of the matter the following equilibria would have to be considered :—

$$\underset{\text{gas}}{NH_3} \rightleftarrows \underset{\text{dissolved}}{NH_3}$$

$$\underset{\text{dissolved}}{NH_3} + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4^{\cdot} + OH'$$

[1] See Abegg and Auerbach, *Handbuch der anorg. Chem.*, 1907, vol. **3**, pt. 3, pp. 71–6.

That the ions are chiefly OH' and $NH_4^{\cdot}$, at any rate in dilute solutions, is certain, and is shown for example by the fact that the electrolytic dissociation of aqueous ammonia is diminished not only by OH' but also by $NH_4^{\cdot}$ ions.

That some of the dissolved ammonia is present in the form of NH_3 molecules and some of it in a hydrated condition is shown by a consideration of the partial pressures of NH_3 and H_2O over solutions of ammonia and by the manner in which ammonia distributes itself between water and chloroform.

For weak solutions of ammonia in water Henry's law very nearly holds, that is to say, the ratio $\frac{\text{partial pressure of } NH_3 \text{ in vapour}}{\text{conc. of dissolved } NH_3}$ is approximately constant. This can be seen from the following table, the figures in which hold for a temperature of 25°. p is the partial pressure of NH_3 (in mm. of mercury), g the number of grams, and n the number of gram mols. of NH_3 in one litre of solution.

p	g	n	$\frac{p}{n}$
5·97	7·752	0·456	13·1
6·71	8·602	0·506	13·2
9·35	11·93	0·702	13·3
13·45	17·00	1·0	13·45

Even in these weak solutions it will be seen that the partial pressure of the ammonia decreases more rapidly than the concentration of the dissolved ammonia, which indicates that a small portion of the latter is held back in some kind of combination. The higher the temperature the more nearly is Henry's law obeyed, indicating that the proportion of combined ammonia diminishes with rise of temperature.

If one litre of ammonia solution containing 2·125 grams NH_3 (= 0·125 gram mol.) is shaken with one litre of air at 25° only 0·00136 gram NH_3 passes into the air space, corresponding with a partial pressure of NH_3 of 1·486 mm. mercury and a value of 12·9 for the ratio $\frac{p}{n}$. As the partial pressure of NH_3 over weak solutions is so small it is not

surprising that loss of ammonia by evaporation is comparatively slow under these conditions.

It is to be noted that the presence in the aqueous solution merely of NH_4OH in addition to NH_3, related by the equilibrium $NH_3 + H_2O \rightleftarrows NH_4OH$, would not explain the deviations from Henry's law. The amount of NH_4OH present would be directly proportional to the concentration of NH_3 and to the partial pressure of the latter. In other words, there would be a constant ratio between the partial pressure of the NH_3 and the total concentration of dissolved ammonia ($NH_3 + NH_4OH$), and Henry's law would be strictly obeyed. A consideration of the following equations will show that the $NH_4^{\cdot}$ ion concentration is only proportional to the square root of the NH_3 concentration, and therefore of the NH_3 partial pressure. This follows from

$$[NH_4'][OH'] = K_1[NH_4OH] = K_1K_2[NH_3][H_2O]$$

which, if it is assumed that $[NH_4^{\cdot}] = [OH']$, gives

$$[NH_4^{\cdot}]^2 = K_1K_2[NH_3][H_2O]$$

or $[NH_4^{\cdot}] = C\sqrt{[NH_3]}$

where C is a constant (in dilute solutions $[H_2O]$ can be taken as constant). Hence the concentration of total dissolved ammonia (including $NH_4^{\cdot}$ ions) will increase more slowly than the partial pressure of the NH_3 which accounts for the slow increase in the ratio $\frac{p}{n}$ in the above table with increasing concentration. Actually matters would be more complex than has been assumed, since the OH' concentration would be slightly greater than that of the $NH_4^{\cdot}$—some OH' being derived from the water.

If the $NH_4^{\cdot}$ ion is supposed to result from direct combination of NH_3 and $H^{\cdot}$, the concentration of total dissolved ammonia will still increase more slowly than its partial pressure, for the amount of $NH_4^{\cdot}$ which can be formed is essentially dependent on the amount of $H^{\cdot}$ ion available.

The distribution of ammonia between chloroform and water has been studied by several investigators,[1] and the observed

[1] See particularly Dawson, *J. Chem. Soc.*, 1906, **89**, 1668.

deviations from constancy of the distribution coefficient $\frac{\text{molar concentration of ammonia in water}}{\text{molar concentration of ammonia in chloroform}}$ are satisfactorily accounted for on the above basis, coupled with the assumption that $NH_4^{\cdot}$ ions are not soluble in chloroform. The following table gives Dawson's results. C is the molar concentration of ammonia in water, c' that in chloroform, and $\frac{C}{c'}$ is the distribution coefficient.

C	0·1540	0·1885	0·2011	0·2074
c'	0·005919	0·007283	0·007759	0·008028
$\frac{C}{c'}$	26·01	25·87	25·92	25·83

C	0·3336	0·3958	0·4898	0·5207
c'	0·01299	0·01545	0·01923	0·02043
$\frac{C}{c'}$	25·67	25·61	25·46	25·49

C	0·6247	0·6674	0·7554	0·8796
c'	0·02463	0·02646	0·03005	0·03522
$\frac{C}{c'}$	25·36	25·23	25·14	24·98

The figures show that the concentration of the total ammonia (including $NH_4^{\cdot}$ ion) dissolved in the water increases more slowly than the concentration of ammonia dissolved in the chloroform.

The nature of the hydrated molecules present in the aqueous solution is at present uncertain, and although they are commonly supposed to consist of NH_4OH (or $NH_3.H_2O$) there is some doubt about this. It should also be noted that NH_4OH would not necessarily be identical with $NH_3.H_2O$. The isolation of the solid hydrates $2NH_3.H_2O$ and $NH_3.H_2O$ at low temperatures by Rupert [1] is

[1] *J. Amer. Chem. Soc.*, 1909, **31**, 866.

interesting in this connexion, but does not necessarily prove that they are present in ordinary solutions.

According to Hantzsch, whose view is supported by Abegg, the formation of $NH_4^{\cdot}$ ions takes place directly by addition of an NH_3 molecule to a $H^{\cdot}$ ion thus :—$NH_3 + H^{\cdot} \rightleftarrows NH_4^{\cdot}$, the weak $H^{\cdot}$ ion being greatly strengthened by the process and yielding the $NH_4^{\cdot}$ ion of high electro-affinity. Regarded in this light an aqueous solution of ammonia will be the seat of the following equilibria :—

$$x\mathrm{NH_3} + y\mathrm{H_2O} \rightleftarrows (\mathrm{NH_3})_x\ (\mathrm{H_2O})_y$$
(dissolved)

$\mathrm{NH_3}$ (gas) $\rightleftarrows \mathrm{NH_3}$ (dissolved)

$\mathrm{H^{\cdot}} + \mathrm{OH'} \rightleftarrows \mathrm{HOH}$

$\mathrm{NH_4^{\cdot}} + \mathrm{OH'} \rightleftarrows \mathrm{NH_4OH}$

$\mathrm{NH_3} + \mathrm{H^{\cdot}} \rightleftarrows \mathrm{NH_4^{\cdot}}$
(dissolved)

As it is probable that the electro-affinity of the $NH_4^{\cdot}$ ion is even greater than that of the $K^{\cdot}$ ion, the apparent weakness of ammonia as a base is quite anomalous. This has been generally supposed to be due to the very small amount of ammonium hydroxide present. Thus the latter might be a strong base (i.e. almost completely ionized into $NH_4^{\cdot}$ and OH') yet its instability and consequent decomposition into NH_3 and H_2O might be so great that the solution as a whole behaves like a very weak base. In other words in the two mass-action equations :—

$$[NH_4^{\cdot}][OH'] = K_1[NH_4OH]\ ;\ [NH_4OH] = K_2[NH_3][H_2O]$$

K_1 has a large and K_2 a small value.

Since, in dilute solutions, $[H_2O]$ can be taken as constant the expression $[NH_4OH] = K_2[NH_3][H_2O]$ can be simplified to $[NH_4OH] = K_3[NH_3]$, but the numerical values of K_2 and K_3 will, of course, be different.

The dissociation constant of ammonia, as usually calculated, gives the value, K, of the expression :—

$$\frac{[NH_4^{\cdot}][OH']}{[\text{Total } NH_3 \text{ in solution other than } NH_4^{\cdot} \text{ ions.}]} = \frac{[NH_4^{\cdot}][OH']}{\{[NH_3] + [NH_4OH]\}} = \frac{[NH_4^{\cdot}][OH']}{[NH_3]\ (1 + K_3)}$$

K correctly represents the efficiency of a solution of ammonia as a base, but not the basic strength of NH_4OH. The latter is correctly represented by K_1.

The distribution of ammonia between water and chloroform has been used by Moore [1] as a basis for calculating the true dissociation constant $K_1 = \frac{[NH_4^{\cdot}]\ [OH']}{[NH_4OH]}$ of ammonium hydroxide and of the constant K_3 in the expression $[NH_4OH] = K_3[NH_3]$. The values he obtains at 20° are :—

K_1 = between $6{\cdot}5 \times 10^{-5}$ and $4{\cdot}0 \times 10^{-5}$
K_3 = between 0·42 and 0·70.

According to this value for the true dissociation constant, NH_4OH would be a far weaker base than NaOH or KOH, but in view of the remarkable similarity between ammonium and potassium salts and the undoubted high electro-affinity of the $NH_4^{\cdot}$ ion it is difficult to believe that the above values are correct. It is possible that what has been taken as NH_4OH by Moore is really a mixture of a small proportion of the ionizable ammonium hydroxide, NH_4OH, and of a much larger proportion of a non-ionizable hydrate of ammonia $NH_3.H_2O$.[2]

Looked at from Hantzsch's point of view, in the two equations :—

$$[NH_3][H^{\cdot}] = K[NH_4^{\cdot}]; \quad [H^{\cdot}][OH'] = K_w$$

K has a relatively small value, that is to say, the tendency for NH_3 to add on $H^{\cdot}$ is great, but owing to the small ionic product K_w of water the tendency cannot be satisfied (because there are so few $H^{\cdot}$ ions present, and they are being competed for by both NH_3 and OH').

It appears from the results of Gaus [3] and Hantzsch and Sebaldt [4] that although addition of OH' ions to a solution of ammonia in water increases the partial pressure of NH_3 and also the proportion which dissolves in chloroform, the addition of $NH_4^{\cdot}$ ions is without effect. The addition of either OH' or $NH_4^{\cdot}$ ions would have been expected to produce the same effect as is actually observed in the case of the

[1] *J. Chem. Soc.*, 1907, **91**, 1379.
[2] These points have been discussed recently by Caven, *Chemistry and Industry* (1923), 164, 448, and 744, and Moore, *ibid.*, 343 and 641.
[3] *Z. anorg. Chem.*, 1900, **25**, 236.
[4] *Z. physikal. Chem.*, 1899, **30**, 258.

OH' ions by diminishing the proportion of ionized ammonia present. That $NH_4^{\cdot}$ ions produce no effect is perhaps explicable by supposing that, while there is actually a diminution in the amount of ionized ammonia, there is at the same time formation of some $NH_4(NH_3)_x^{\cdot}$ ions. The NH_3 so rendered inactive may just balance the effect due to the decrease in the amount of ionized ammonia. There is some evidence for the existence of such $NH_4(NH_3)_x^{\cdot}$ ions. Thus $(NH_4)_2O$ (= $NH_4.NH_3\,OH$) was obtained at low temperatures by Rupert,[1] while Troost [2] obtained $NH_4Cl.3NH_3$ and $NH_4Cl.6NH_3$ as solid crystalline compounds melting respectively at $+7°$ and $-18°$ by the action of NH_3 on dry NH_4Cl.

From an analytical point of view it must be remembered that a solution of ammonia contains a small number of $NH_4^{\cdot}$ and OH' ions, a relatively large amount of free NH_3 and some NH_3 in the form of hydrated molecules.[3] These several substances are all in equilibrium with one another, and the concentration of one of them cannot be altered in any way without the concentrations of the others being simultaneously affected. Whether the $NH_4^{\cdot}$ ions are formed by ionization of previously formed NH_4OH or by direct addition of NH_3 to hydrogen ions is of minor importance from the analyst's point of view.

Estimation of Ammonia by Distillation into Standard Acid

This is the most generally applicable method of estimating ammonia whether dissolved as such or in the form of solid ammonium salts. It depends on the fact that the partial pressure of NH_3 above its solutions is a good deal greater at their boiling point, and is still further increased by excess of NaOH. The equilibria concerned have already been considered. In carrying out the estimation care is necessary that all the ammonia shall be driven over without loss into the standard acid.

A suitable amount of the substance being analysed

[1] *Loc. cit.*
[2] *Compt. rend.*, 1879, **88**, 578.
[3] Perman, *J. Chem. Soc.*, 1903, **83**, 1168.

(dissolved in dilute acid, if necessary) is placed in a 400 c.c. flask. The total volume of liquid in the flask should be 100 to 200 c.c. The flask is closed with a two-holed cork or rubber bung, through one hole of which passes the stem of a dropping funnel for introducing alkali,[1] while through the other passes the stem of a bulb trap which prevents alkaline spray escaping from the flask during boiling, while it allows free passage of steam and ammonia. The other end of the trap is connected to a small condenser which leads down to the vessel containing the standard acid. The end of the condenser tube, fitted with an adapter if necessary, dips just below the surface of the standard acid contained in a conical flask. Sufficient NaOH solution is added through the dropping funnel to liberate all the ammonia and leave in addition about 10 c.c. of 2N.NaOH. The contents of the flask are then boiled until about half the water present has been distilled over. As the condensed water collects in the standard acid the flask containing this should be lowered occasionally so that the end of the condenser tube is kept just below the level of the acid, which is shaken occasionally. Special flasks with side tubes and bulbs sealed on at the bottom may be used for holding the standard acid, but they are not really needed. In this case the end of the condenser does not dip into the acid, but passes through the cork closing the flask, and the condensed water with dissolved ammonia simply drips into the acid. The flask is inclined slightly so that the side opening is just closed by the acid. The air driven out of the apparatus at the beginning of the distillation has to bubble through the acid before escaping by the side tube, and any ammonia is thus retained. If possible, an amount of the substance being analysed should be used which will yield sufficient ammonia to neutralize from 15 to 20 c.c. of $\frac{N}{2}$ acid, or otherwise, of $\frac{N}{10}$ acid. Sharper end points are obtained with $\frac{N}{2}$ acid and alkali than with $\frac{N}{10}$

[1] If the apparatus is all connected up, the alkali added quickly, and the cork carrying the bulb trap quickly replaced, the dropping funnel can be dispensed with.

solutions, for the acid used to absorb the NH_3 becomes considerably diluted during the distillation. When about half the liquid originally present in the distillation flask has been boiled over all the NH_3 has usually been expelled. If there is any doubt about this an additional amount should be driven over and tested for ammonia. After the distillation the acid which has been used for absorbing the ammonia is titrated with the standard alkali. As ammonia is a weak base a strongly acid indicator such as methyl orange has to be employed.

The Estimation of Magnesium

Metals of groups 1, 2, 3, 4, and 5, and also lithium, must be removed previous to the estimation of magnesium.

To the moderately acid solution containing the magnesium there is added a solution of ammonium phosphate (about 1 gram phosphate for every 0·1 gram MgO present). If the solution does not contain much ammonium salt or free acid it is well to add also some ammonium chloride (from 5 to 10 c.c. of a 2N. solution). There should be sufficient acid present to prevent the formation of a permanent precipitate on adding the phosphate solution. If the volume of solution per 0·1 gram MgO is greater than about 50 c.c. the proportions of phosphate and ammonium chloride used should be correspondingly increased.

The solution is now precipitated (it may be either hot or cold) by adding dilute ammonia (2½ per cent) drop by drop, stirring all the while, until the liquid is markedly alkaline to litmus. A crystalline precipitate of magnesium ammonium phosphate is obtained ($MgNH_4PO_4.6H_2O$ is precipitated at room temperature; $MgNH_4PO_4.H_2O$ is precipitated above about 50°). The beaker and contents are allowed to stand for 6–12 hours before filtration. The precipitate is best filtered on an ordinary filter, washed with 2½ per cent ammonia solution, dried in the steam oven and ignited, first over the bunsen burner, and then for a few minutes over the blowpipe. During the ignition magnesium pyrophosphate is formed, and that is what is weighed—

$$2MgNH_4PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O.$$

The filter paper must be ignited apart from the precipitate, and it takes a long time for the carbon to burn off completely owing to partial fusion of the pyrophosphate causing the formation of a protective coating over particles of carbon. For the same reason the pyrophosphate obtained by ignition of the precipitate is nearly always grey in colour owing to the presence of particles of carbon. The amount of carbon, however, is unweighable.

During the ignition of the magnesium ammonium phosphate it will be noticed that at a certain point an incandescence spreads for a moment throughout the several lumps, accompanied by a noticeable diminution in volume of the latter. Sometimes this incandescence occurs during the heating over the bunsen, sometimes not before the final ignition over the blowpipe—depending upon the thickness of the crucible employed, the exact conditions of the precipitation, and so on Sometimes it is hardly noticeable, but the shrinkage always occurs. The completion of the incandescence or shrinkage may usually be taken as indicating that the ignition has been sufficient and may be stopped. The incandescence occurs above the temperature at which all the water and ammonia have been driven off from the original $MgNH_4PO_4$, and is probably due to some sort of polymerization of the $Mg_2P_2O_7$. The fact that the mass incandesces indicates the evolution of a considerable amount of heat during this polymerization.

The magnesium ammonium phosphate may also be precipitated by first making the magnesium solution alkaline with ammonia in presence of ammonium salts, and then adding the phosphate solution drop by drop. Experience and theoretical considerations, however, seem to point to the first method being the more accurate, although in the majority of cases the two methods give practically identical results.

The Estimation of Phosphoric Acid

The estimation of phosphoric acid in compounds or mixtures free from the metals of groups 1, 2, 3, 4, and 5, and lithium is practically the inverse of the above estimation of magnesium.

The reagent employed for precipitating the phosphoric acid in the form of $MgNH_4PO_4$ is known as magnesia mixture, and is made by dissolving 50 grams $MgCl_2.6H_2O$ in 650 c.c. water, adding 70 or 150 grams NH_4Cl and making up to a litre with concentrated ammonia or water respectively. Ten c.c. of this reagent is sufficient to precipitate 0·1 gram P_2O_5. The precipitation is carried out either by adding the ammoniacal magnesia mixture drop by drop to the alkaline phosphate solution or, better still, by adding the requisite amount of the non-ammoniacal magnesia mixture to the sufficiently acid phosphate solution and then precipitating the magnesium ammonium phosphate by slowly adding 2½ per cent ammonia until the solution is strongly alkaline.

The Estimation of Arsenic Acid as $Mg_2As_2O_7$

This estimation is carried out in precisely the same way as the estimation of phosphoric acid. The precipitated magnesium ammonium arsenate should, however, be filtered on a Gooch crucible and first dried at 110°. The Gooch crucible is then fitted into a somewhat larger crucible with a ring of asbestos, so as to keep the crucibles from touching one another, with an air space of a few millimetres between the two. The outer crucible is then heated gradually to redness, a few crystals of solid ammonium nitrate being placed on the precipitate beforehand.

100 c.c. of water dissolve 0·17 gram $MgNH_4AsO_4$, but the compound is practically insoluble in 2½ per cent ammonia.

From the ionic point of view the precipitation of $MgNH_4PO_4$ is rather complex. The salts of polybasic acids ionize in steps, just as do the acids themselves (see page 38). One would expect the NH_4^+ ion to split off first rather than the Mg^{++} ion, both because it is monovalent and because it has a somewhat higher electro-affinity then the bivalent Mg^{++} ion. The difference of electro-affinity is comparatively small, however, and, in view of the fact that the $MgNH_4PO_4$ is always formed in, and separates from, solutions containing considerable amounts of NH_4^+ ions, it is probable that the

ionization is into $Mg^{\cdot\cdot}$ and NH_4PO_4'' in the first instance according to the equation—

$$MgNH_4PO_4 \rightleftarrows Mg^{\cdot\cdot} + NH_4PO_4''$$

rather than into $NH_4^{\cdot}$ and $MgPO_4'$ according to the alternative equation—

$$MgNH_4PO_4 \rightleftarrows NH_4^{\cdot} + MgPO_4'$$

The NH_4PO_4'' ion will dissociate to some extent into $NH_4^{\cdot}$ and PO_4''' (and probably to some extent into NH_3 and HPO_4''). We are thus concerned with the following equilibria :—

$$\underset{\text{solid}}{MgNH_4PO_4} \rightleftarrows \underset{\text{dissolved}}{MgNH_4PO_4} \rightleftarrows Mg^{\cdot\cdot} + NH_4PO_4''$$
$$NH_3 + HPO_4'' \rightleftarrows NH_4PO_4'' \rightleftarrows NH_4^{\cdot} + PO_4'''$$
$$NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4^{\cdot} + OH'$$

HPO_4'' and $(NH_4)_2\,PO_4'$ ions will usually be present in small amounts, too :—

$$PO_4''' + H^{\cdot} \rightleftarrows HPO_4''$$
$$NH_4PO_4'' + NH_4^{\cdot} \rightleftarrows (NH_4)_2\,PO_4'$$

Hence it will be primarily the concentration of NH_4PO_4'' ions which will regulate the precipitation in the above experiment. If one considers the above ionic equilibria it is clear that an increase in the $NH_4^{\cdot}$ ion concentration will cause an increase in the NH_4PO_4'' ion concentration by simply throwing back the dissociation of the NH_4PO_4'' ion in the normal way. Excess of ammonia by preventing the formation of HPO_4'' from NH_4PO_4'' will also be favourable to the latter.

Owing to the solubility product of $MgNH_4PO_4$ being very small, only a small excess of either phosphate or of magnesium is required to precipitate all the magnesium or all the phosphate as $MgNH_4PO_4$.

The concentration of NH_4PO_4'' ions is probably much greater than that of the PO_4''' ions, for even a very low concentration of the latter would almost certainly lead to the precipitation of $Mg_3(PO_4)_2$ rather than of $MgNH_4PO_4$, for it is probable that the solubility product of the former is considerably smaller than that of the latter. This conclusion seems to be of some importance, since there are a number of quantitative estimations which make use of phosphate solutions containing ammonia and ammonium salts.

It will appear from the above that the main function of the ammonium salt and of the excess of ammonia is to increase the concentration of the NH_4PO_4'' ion, and to diminish that of PO_4''' or $MgPO_4'$. The ammonium salts play also another part in preventing the precipitation of magnesium hydroxide. The latter compound, although not very insoluble, can be precipitated by ammonia if the latter is added in sufficient amount, for although the hydroxyl ion concentration in fairly strong ammonia solution is very low, it is just sufficient for the solubility product of $Mg(OH)_2$ to be reached, provided that the Mg ion concentration is not too low. The addition of ammonium salts, however, reduces the hydroxyl ion concentration to such an extent that the solubility product value for $Mg(OH)_2$ is never reached.

It does not require very considerable changes in the conditions of precipitation to cause an increase in the concentration of some of the other ions sufficient to cause trouble. This explains why the ratio of MgO to P_2O_5 in the precipitate is sometimes greater than and sometimes less than that corresponding with $MgNH_4PO_4$; in the first case, probably from the presence of $Mg_3(PO_4)_2$, owing to an undue PO_4''' or $MgPO_4'$ ion concentration, and in the second case probably owing to the presence of $(NH_4)_3PO_4$ or $Mg(NH_4)_4(PO_4)_2$ caused by the presence of $(NH_4)_2PO_4'$ ions.

$(NH_4)_3PO_4$ is readily precipitated from a moderately strong ammonium phosphate solution by addition of ammonia, and there can be little doubt that this is because the solubility product $[NH_4^{\cdot}][(NH_4)_2PO_4']$ is relatively small.

$$NH_4^{\cdot} + (NH_4)_2PO_4' \rightleftarrows (NH_4)_3PO_4 \rightleftarrows (NH_4)_3PO_4$$
dissolved solid.

If the concentration of $(NH_4)_2PO_4'$ ion becomes unduly large there is danger of such separation of $(NH_4)_3PO_4$ occurring during precipitation of $MgNH_4PO_4$. The formation of $(NH_4)_2PO_4'$ ions will obviously be favoured by a high concentration of $NH_4^{\cdot}$ ions :—$NH_4^{\cdot} + NH_4PO_4'' \rightleftarrows (NH_4)_2PO_4'$.

As already pointed out on page 83, HPO_4'' may be formed from the NH_4PO_4'' ions, and free ammonia is added to prevent this occurring. Should, for any reason, the HPO_4'' ion concentration become considerable, $MgHPO_4$ may be pre-

cipitated, and this does sometimes occur during the early stages of the precipitation of $MgNH_4PO_4$ before enough ammonia has been added to lower the HPO_4'' concentration sufficiently.

For a similar reason the $MgNH_4PO_4$ is liable to become partially converted into $MgHPO_4$ if washed with pure water, and it is to prevent this occurring that the $MgNH_4PO_4$ precipitate is washed with $2\frac{1}{2}$ per cent ammonia. $MgHPO_4$ is considerably more soluble than $MgNH_4PO_4$ so the formation of the former should be avoided, although on ignition it also would yield $Mg_2P_2O_7$.

It will be evident from what has been said above that a very nice adjustment of the various ionic concentrations is necessary if exact quantitative results are to be obtained in the precipitation of $MgNH_4PO_4$. An immense amount of work has been done on this question mainly in connexion with the estimation of phosphoric acid in fertilizers. On the whole, it appears that the best results are obtained if the magnesium and phosphate solutions are mixed in suitable proportions in acid solution and the mixed solution then precipitated by slow addition of ammonia with continuous stirring.

The dangers to be avoided are rather different according as one is estimating magnesium or phosphate. The former estimation is, as a matter of fact, the less troublesome. The various sources of error have been the subject of important investigations by Neubauer,[1] and it has been found that the best results are obtained when working as above.[2]

If a considerable excess of ammonia is added quickly to the mixed $Mg—PO_4$ solution, there is a possibility in both cases of $Mg(OH)_2$ separating. If, however, the ammonia is added gradually there is no danger of this in the Mg estimation, but the possibility is present in the P_2O_5 estimation if too much $MgCl_2$ is used.

On the other hand, the possibility of $(NH_4)_3PO_4$ separating is really present only in the Mg estimation ; to prevent

[1] *Z. anorg. Chem.*, 1892, **2**, 45 ; 1893, **4**, 251.
[2] See also Bube, *Z. anal. Chem.*, 1910, **49**, 525.

it, excess of phosphate solution should be avoided, as well as excessive concentration of ammonium salts or ammonia.

The danger of $Mg_3P_2O_8$ separating is present in both cases, and more especially at the beginning of the precipitation. (When precipitating the mixed Mg–PO_4 solution by ammonia, there are in the case of a magnesium estimation many $Mg^{\cdot\cdot}$ and a few PO_4''' ions at the beginning, while in the case of an estimation of P_2O_5 much the same applies.) To avoid this sufficient ammonium salts must be present, and the precipitation must be carried out slowly. Any tribasic phosphate first formed can then change over to $MgNH_4PO_4$ before it becomes enveloped in the latter, as soon as the decrease of $Mg^{\cdot\cdot}$ ions and increase of $NH_4^{\cdot}$ ions renders $Mg_3(PO_4)_2$ unstable and $MgNH_4PO_4$ stable.

The object of leaving the magnesium precipitate to stand some time before filtration is partly to give the $MgNH_4PO_4$ time to separate as completely as possible from solution, for the solution of this compound is somewhat prone to remain supersaturated even in contact with the solid phase. The precipitate often separates in the amorphous condition (this is probably largely tribasic magnesium phosphate) to begin with, but rapidly becomes crystalline. The standing also enables the last traces of the amorphous form, or of tribasic phosphate, to change over into crystalline $MgNH_4PO_4$. The amorphous form, as in all cases, is more soluble than the stable crystalline form, hence the latter separates out from a solution saturated with respect to the former.

The estimation of phosphoric acid in presence of metals of groups 1, 2, 3, 4, and 5 will be considered later.

The Estimation of Zinc as Pyrophosphate [1]

This most excellent method for estimating zinc is much to be preferred to any other, and is applicable in the majority of cases. It is very similar to the estimation of magnesium.

A few drops of methyl orange are added to the solution containing zinc, which is neutralized by the addition of either

[1] W. E. Garrigues, *J. Amer. Chem. Soc.*, 1897, **19**, 934. The process is originally due to Tamm, *Chem. News*, 1871, **24**, 148.

ammonia or hydrochloric acid according to circumstances. (If the acid originally present was acetic then litmus must be used instead of methyl orange.) The neutralized solution, occupying 50–100 c.c. per 0·1 gram zinc, is then precipitated cold by the addition of ammonium phosphate (using from 1 to 2 grams $(NH_4)_2HPO_4$ dissolved in a small amount of water for every 0·1 gram of zinc). The precipitate is flocculent and amorphous at first, but after warming at 70°–90° for some time becomes crystalline and settles well. Should this not occur it is a sure sign that insufficient $(NH_4)_2HPO_4$ is present, and more should be added. This crystalline precipitate is $ZnNH_4PO_4$, with more or less water of crystallization. The liquid is allowed to cool down to room temperature, and the crystalline precipitate then filtered off either on a Gooch or an ordinary filter paper. The filtrate should give no precipitate when tested with H_2S. The precipitate is washed with cold distilled water, and is then dried to constant weight at 100°, when the water of crystallization is driven off, leaving anhydrous $ZnNH_4PO_4$, or it can be ignited and weighed as $Zn_2P_2O_7$. If a filter paper has been used the precipitate must be separated before burning the paper. During this process the colour of the flame shows that a slight amount of reduction occurs, but in the author's experience this is negligible.

The Estimation of Manganese and Cobalt as Pyrophosphate

These estimations are carried out in exactly the same way as the above estimation of zinc. Since, however, in these two cases there is no fear of reduction and volatilization of the metals, the precipitates should always be ignited and weighed as pyrophosphate, though they can also be weighed as the double phosphate after drying at 100°.

Theoretical Aspect of the Phosphate Precipitation of Zinc, Manganese, and Cobalt

$ZnNH_4PO_4$, $MnNH_4PO_4$, and $CoNH_4PO_4$ appear to be less soluble than $MgNH_4PO_4$, which no doubt explains why addition of free ammonia is unnecessary for their quantitative precipitation, provided sufficient ammonium salts and

especially sufficient excess of $(NH_4)_2HPO_4$ are present to increase the concentration of NH_4PO_4'' ion to its necessary value. In fact, in the estimation of zinc and cobalt, free ammonia must on no account be added, for in that case the precipitation would be incomplete or not occur at all. The zinc and cobalt ammonium phosphates, in fact, dissolve in ammonia owing to the formation of soluble complex compounds yielding cations such as $[Zn(NH_3)_6]''$ and $[Co(NH_3)_6]''$. Manganese does not yield such compounds, and excess of ammonia does not matter.[1]

For the same reason too great an excess of $(NH_4)_2HPO_4$ must be avoided, since in solution this gives rise to a considerable amount of NH_3 which causes some of the zinc or cobalt to remain dissolved.

The principles underlying the estimation of zinc, manganese, and cobalt as pyrophosphate are identical with those discussed in the case of magnesium. The facts observed in these cases help, moreover, to confirm the views with regard to the mechanism of the precipitation developed above.

The precipitation of these three metals as metal-ammonium phosphate is complete only in solutions which are neutral or faintly alkaline to methyl orange or litmus, and in which there is considerable excess of ammonium phosphate (rather more than five times that theoretically needed). If there is insufficient phosphate present, the metal may be completely precipitated, but the precipitate will

[1] This fact is, indeed, the basis of a method for separating zinc and manganese (G. Luff, *Chem. Zeit.*, 1922, **46**, 365). The weakly acid solution containing the metals is treated with about a quarter of its bulk of dilute ammonia (sp. gr. 0·923) followed by a good excess of ammonium phosphate dissolved in the minimum amount of water. The solution is allowed to stand for a few hours, the precipitate filtered, washed with dilute ammonia, ignited and weighed as $Mn_2P_2O_7$. The filtrate is made just neutral to litmus with hydrochloric acid, and the precipitated zinc ammonium phosphate, after standing some time, is washed with cold water, ignited, and weighed as pyrophosphate. The precipitation of the manganese must be carried out in a flask filled with hydrogen or coal gas and the flask must be kept stoppered during the standing. This is because in alkaline solution divalent manganese compounds are slowly oxidized by atmospheric oxygen with formation of hydrated Mn_2O_3 or MnO_2, which is precipitated.

not become crystalline and has an indefinite composition. The amorphous precipitate produced at first in all cases is probably of indefinite composition. It has been formed in presence of a relatively large number of $Zn^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, or $Co^{\cdot\cdot}$ ions, and contains tribasic phosphate, which, however, under the final conditions, is unstable and changes into MNH_4PO_4, where M represents Zn, Mn, or Co.

On account of the insolubility of the tribasic phosphate in these cases, it is necessary to keep the concentration of the PO_4''' ion as low as possible, while a considerable excess of ammonium phosphate is required to give the requisite NH_4PO_4'' ion concentration. It is, therefore, not possible to use these three precipitations in the converse operation of estimating phosphoric acid.

In the case of cobalt, atmospheric oxidation may lead to formation of very stable, soluble, cobaltic amines. Probably for this reason, as much as one per cent of the cobalt may remain in solution. Estimation of cobalt as pyrophosphate is not to be recommended. If the method is ever employed the cobalt left in the phosphate solution must be separated by means of H_2S.

It is worth noting that when precipitating Mg, Zn, Mn, or Co ammonium phosphate, or $MgNH_4AsO_4$, it is better to employ only ammonium salts. Potassium salts, in particular, should be avoided, as the precipitates are very liable to carry down some potassium, which doubtless replaces ammonium isomorphously. There does not appear to be much danger of this happening with sodium. It is better, however, to avoid the use of sodium compounds if possible.

Supersaturation

In many cases it is possible to obtain solutions containing a good deal more salt in solution than suffices to saturate it. Such solutions are said to be supersaturated with respect to that salt, and as a rule are most readily prepared by treating water with rather more of the salt than is sufficient to saturate it at the required temperature, and then heating the mixture to a higher temperature until the salt has completely dissolved. The hot solution is then allowed to stand

quietly and cool to the desired temperature, the entrance of particles of dust and especially of particles of the salt being carefully prevented.

Now the readiness with which such supersaturated solutions can be obtained, as also their stability and degree of supersaturation, varies very greatly. So also does the time required to saturate water with a salt when that liquid is shaken up with excess of the latter. It is found, in fact, that the above and many other properties of electrolytes (such as the readiness with which they can be supercooled when in the fused state without crystallizing, and indeed the readiness with which any unstable form changes into the form more stable under the conditions of experiment) run closely parallel. Van't Hoff [1] has shown that the higher the valency of the ions which the electrolyte can yield the greater is the tendency for unstable conditions to persist.

Occasionally this tendency to form supersaturated solutions or to persist in other unstable conditions causes trouble in analytical operations. The determination of magnesium (or phosphoric acid) described above is one of the cases where this tendency must be allowed for by leaving the precipitate to stand before filtering. In spite of the presence of the solid magnesium ammonium phosphate, an appreciable time is required for that compound to separate completely from solution. As the corresponding zinc, manganese, and cobalt compounds are similarly constituted one would have expected them to show the same behaviour, but apparently the greater insolubility of those compounds seems to exercise such a modifying effect that long standing of the precipitates is unnecessary.

It is not easy to find a theoretical explanation of the above connexion between the valency of the ions and the permanency of unstable conditions, but possibly it is somehow due to the complicated ways in which compounds derived from polyvalent ions can ionize, coupled with the fact that in these cases the polyvalent ions often take part in other side equilibria.

[1] Van't Hoff, *Sitzungsber. Preuss. Akad. Wiss., Berlin*, 1907, p. 659.

CHAPTER VII [1]

THE SIGNIFICANCE OF COLLOIDAL CHEMISTRY IN QUANTITATIVE ANALYSIS

CRYSTALLINE, AMORPHOUS, AND COLLOIDAL STATES OF "SOLID" MATTER

AT one time a solid used to be defined as a substance which could offer permanent resistance to shearing stress, but it is impossible to give any rigid definition since there is every imaginable gradation between solids and liquids which the above or any other definition is not sufficient to cover.

There is now a certain tendency to restrict the use of the term "solid" to crystalline forms of matter (excepting liquid crystals) but this also is quite unsatisfactory for it is impossible to draw a sharp line of division between crystalline and non-crystalline forms of matter.

The characteristic and distinctive geometrical forms of crystals are due to the possession of certain directive forces of attraction by the molecules which build up the crystals. These forces cause a definite orientation of the molecules, so that the resulting structure has a definite geometrical form. The nature and magnitude of these forces vary with the nature of the atoms composing the molecules, but under given conditions are constant for molecules of the same sort. The admission that the molecules possess directive forces of attraction ultimately forces one to admit that each individual molecule is in this sense crystalline,[2] whether

[1] A considerable portion of this chapter is taken by permission of the Controller of H.M. Stationery Office from an article by the present writer on "Colloid Problems in Analytical Chemistry", in the *Fourth Report on Colloid Chemistry* (British Association for the Advancement of Science. Published by H.M. Stationery Office, 1922).

[2] Though the crystal molecule may possibly be a polymer of the chemical molecule: Fedorov, *Z. Kryst.*, 1913, **52**, 22; Bragg, *J. Chem. Soc.*, 1922, **121**, 2766.

it forms part of a solid, liquid, or gas. The forces of attraction between the molecules of liquids are not sufficient to bring about a definite geometrical form, although in the case of " liquid crystals " there is sufficient orientation to produce characteristic optical properties.

The majority of liquids have a relatively low viscosity and are hence unable to resist a shearing stress and, for instance, will take the shape of any vessel in which they are placed. The greater the viscosity the less ready the response to the shearing stress, so that, for example, a lump of pitch placed in a vessel may take months before it has taken up the shape of the latter. Pitch is commonly regarded as a solid, although undoubtedly a liquid.

Many crystalline solids have a definite melting point (under a given pressure), above which they cannot be heated without melting. The resulting liquid, however, can often be cooled far below the melting point without crystallizing. It remains in the liquid state, and is said to be superfused. Now, the viscosity of a liquid increases with fall of temperature —as a rule rapidly—so it often happens, especially if the melting point is high, that the viscosity of the superfused liquid, when cooled to the ordinary temperature, is exceedingly large. This is the case with ordinary glass or with the quartz glass now largely used for making some kinds of chemical apparatus. From the ordinary point of view we are certainly justified in calling these materials " solids ", though in reality they are superfused liquids. The realization of this has led to the view that all non-crystalline or amorphous " solids " are in reality superfused liquids.

In the case of a great many amorphous solids the corresponding crystalline form has no melting point—except possibly under very high pressure—owing to decomposition occurring long before a temperature sufficient to cause melting is reached. The view that all amorphous solids are really superfused liquids is, therefore, somewhat artificial and unsatisfactory, although many of the differences between crystalline and amorphous solids can be satisfactorily explained on that basis.

Another view, and one which has been championed more

especially by von Weimarn,[1] is that all amorphous and colloidal forms of solids are in reality crystalline, although very minutely so. Whilst this view is very difficult to prove, a great deal can be said for it, but before discussing it more fully we must first consider some of the properties of colloidal solutions.

Colloidal solutions or suspensions are liable to be formed under the most varied circumstances whenever a liquid or solid suddenly separates from the condition of vapour or from solution either as a result of chemical reaction or in other ways. They differ from true solutions in that the presence of individual particles of the dissolved or suspended substance can be demonstrated by suitable microscopic or other methods. Every possible gradation, however, can exist between true solutions and mechanical suspensions, colloidal solutions being the intermediate stage.

When a beam of light is passed through a colloidal solution the light is scattered and partially polarized, which indicates the presence of discrete particles in the solution (the Tyndall effect). The presence of such particles can, moreover, be demonstrated by means of the ultra-microscope, which shows them in a state of vigorous movement (Brownian motion). Although discrete particles are present, the solid colloid cannot be separated from such a solution by filtration through any ordinary filtering paper—the particles are far too small. Colloids cannot diffuse through animal membranes or parchment paper, however, upon which fact depend the ordinary processes for purifying colloids from admixed crystalloid matter.

Ultra-microscopic investigations (Zsigmondy and others) have shown that the size of the colloidal particles varies within very wide limits—from about 1 to 3 μ in colloidal gold solutions which appear opalescent, 32 to 60 $\mu\mu$ in average dilute gold solutions ($1\mu = 0{\cdot}001$ mm., $1\ \mu\mu = 0{\cdot}000001$ mm.; the diameter of a H_2 molecule is about $0{\cdot}00022\ \mu = 0{\cdot}22\ \mu\mu$; limit of visibility with ultra-microscope is about 6 $\mu\mu$). The other properties of colloidal solutions vary *pari passu*

[1] *Kolloid Z.*, from 1907 onwards.

with the size of particles—the smaller the particle the greater the osmotic pressure (very small in any case)—the larger the particles the less marked the Brownian movement, and so on.

Another important fact is that the colloidal matter in solution is associated with charges of electricity, the sign of which may be positive or negative. Consequently, if two electrodes are dipped into a colloidal solution and connected with poles of a battery the colloidal matter will slowly travel either to the cathode or the anode, according as it is positively or negatively charged.

The most important of all the properties of colloidal solutions from the analytical point of view is that of being coagulated under certain conditions. When this occurs the colloid which was previously in solution (the " Sol ") separates out in a flocculent condition (the " Gel ") and can be removed by filtration.

This coagulation can be brought about in several ways. In many cases it occurs spontaneously after a shorter or longer interval of time. Boiling the colloidal solution will frequently cause coagulation, but the most general of all methods is the addition of electrolytes. Practically every inorganic colloidal solution can be precipitated by the addition of salt solutions, but the amount of the latter necessary varies within wide limits. Some colloids are very sensitive to salts, and are precipitated by very small amounts whilst in other cases large amounts are required. It has, however, to be borne in mind that an excess of electrolyte may favour the formation of a colloidal solution : a small quantity will cause coagulation and precipitation of the colloid, but a larger amount may cause its re-solution. This is very liable to happen, for instance, when the electrolyte is caustic soda or potash. It is partly on account of this effect of excessive amounts of electrolyte that the analyst avoids working with too concentrated solutions, for under these conditions he is liable to get slimy gelatinous precipitates which filter badly, or else no precipitates at all—only a colloidal solution.

It has been found that the coagulating power of salts

depends markedly upon the valency of the constituent ions—the higher the valency the greater the power of coagulation as a rule.[1] There is good reason for thinking that this action of electrolytes is in some way connected with a neutralization of the electrical charges on the colloidal particles by the electrical charges on the ions, for it is found that positively charged ions (cations) are most effective in coagulating negatively charged colloids, while positively charged colloids are best precipitated by negatively charged ions (anions). The increased activity of polyvalent ions is also intelligible on this view. It is, however, certain that other factors are operative as well, for there are very marked differences in the coagulating powers of different salts, although these may yield ions of the same valency. Then again it must be remembered that it is impossible to study the effect of one ion without having the oppositely charged ion present also. The electrical theory very satisfactorily explains the fact that two opposite y charged colloids mutually precipitate each other, while similarly charged ones have no such effect. Of the colloids which usually carry a positive charge may be mentioned the metallic hydroxides ; while the metallic sulphides, metals, AgCl, silicic and stannic acids and gum generally carry negative charges when in colloidal solution.

Colloid phenomena play a more fundamental part in most analytical operations than is generally realized. Much still remains obscure, but sufficient is now known about colloids and their behaviour under different circumstances to give the chemist sure guidance through most of his analytical difficulties.

The Formation of Precipitates

The last stage in the formation of a precipitate is, in many cases, the coagulation by electrolytes of a colloidal solution. To what extent all precipitates pass through this, or a similar stage, is somewhat doubtful, but a consideration of the conditions which lead to precipitation will give some clue

[1] H. Schulze, *J. pr. Chem.*, 1882, **25**, 431 ; 1883, **27**, 320.

to the probable course of events. The question of the coagulation of colloidal solutions and the re-solution or peptization of the precipitates obtained has been considered very fully and with a wealth of references by Bancroft in the Second Report of the Committee on Colloid Chemistry and its Industrial Applications, 1918, pp. 2–16.

The part played by the solubility product in determining the conditions under which precipitation takes place has been previously considered. The deductions made are, however, independent of the mechanism of the final stage of precipitation, and would be the same whether that were of the nature of ordinary crystallization or of electrolytic coagulation.

It is the stage of precipitation prior to the actual settling out of the solid which would appear to depend directly on the solubility product, and for the present purpose it can be assumed that the law of mass action does apply to the initial stages of all precipitation.

On mixing solutions of two electrolytes, which by double decomposition can give rise to a less soluble compound, the latter will sooner or later separate from solution when its solubility product has been overstepped. The time taken for this to occur may vary greatly according to circumstances, and so also will the degree of supersaturation required. It is important to bear in mind that the solubility of a substance depends upon the size of the particles. The solubility is practically independent of size if the particles are greater than 0·02 mm. in diameter, but there is a well-marked increase when they become much smaller than this. When their magnitude approaches that of an isolated molecule, their solubility may be many times greater than that characteristic of large particles. It is because of this increased solubility of fine particles that in the absence of the solid phase, some supersaturation is inevitable prior to precipitation. Its degree will depend upon such factors as (*a*) presence or absence of dust or other nuclei; (*b*) physical conditions of the experiment, such as temperature, rate of admixture of reactants, etc.; (*c*) specific characteristics of the substance being precipitated.

The unstable supersaturated condition breaks down more or less suddenly, but the degree of suddenness varies from case to case, being influenced by temperature and many factors such as rate of movement of the solution.

A number of polymolecular nuclei now form in the solution. Their number will depend chiefly upon (*a*) the degree of supersaturation, (*b*) the suddenness with which the condition of supersaturation breaks down, (*c*) the total concentration of the compound about to separate, (*d*) the temperature—this mainly as affecting (*a*), (*b*), and (*c*).

If the individual molecules in these primary nuclei are all oriented in the same way, the latter must be regarded as being crystalline, and it seems likely that this is the case except possibly with substances of very high molecular weight. The number of individual molecules in the primary nuclei may well vary considerably.

From the work of Perrin [1] we know that, on the one hand, such nuclei will behave like large molecules. They are able to diffuse, exert osmotic pressure, etc., in virtue of their molecular motion (the Brownian movement), which, however, is slow and corresponds to their high molecular weight (that of the aggregate regarded as one molecule). On the other hand, the particles will have the properties characteristic of a sol, although probably some of these properties are the result of interaction between the nuclei originally separating out and the surrounding solution.

As soon as the nuclei appear they are subject to the influence of all the constituents present in the surrounding medium—molecules and ions of both solvent and dissolved substances. Molecules of the same kind as those present in the primary nuclei tend to attach themselves bodily and regularly, so increasing the size of the crystal which would ultimately become large enough to settle out provided no other complicating factor came into play. In many cases the minute growing crystal (which, as has been mentioned, can be regarded as a single molecule) may be expected to have some tendency

[1] *Chem. News*, 1912, **106**, 189, 203, 215. (A summary of his work given in a lecture at the Royal Institution.)

to split off one or more ions, and the electrical charge, which such particles usually carry, is probably to some extent due to such ionization. This ionization probably occurs in such a way as to give one or more simple ions of small mass and a heavy residue. Whether the light ions so split off are positive or negative will depend upon the chemical nature of the ionizing particle, but this spontaneous ionization would certainly be largely influenced by other ions present in the solution, a question which will be considered presently.

It seems reasonable to think that the transition from the stage in which a substance is dissolved in the simplest molecular condition to that where it separates in the solid (or liquid) state, either visibly or ultramicroscopically, is really continuous, although the whole transition may occur over such an excessively small range as to make its actual observation very difficult. The charged (ionized) colloidally suspended crystalline particle would thus be the result of gradual polymerization (or growth) of the simple molecules. There is evidence to show that a kind of polymerization and ionization similar in character to that just imagined does occur in solutions of many salts at concentrations far below those at which even ultra-microscopic particles begin to form. There seems no reason why it should not continue right to the limit of crystallization. Cases of this kind have been investigated by Donnan and Bassett [1] and by Watkins and Denham,[2] where the polymerization and ionization was of such a character as to give simple metallic cations ($Co^{\cdot\cdot}$, $Cu^{\cdot\cdot}$), and heavier complex anions such as $Co\,Cl_4''$ or $Cu\,Cl_4''$.

Now in most cases the crystalline particle forms and grows in a solution containing simple molecules and ions other than those which go to build it up, and it is to be expected that some interchange of ions will occur. A particle ionizing into a heavy complex cation, and one or more simple anions such as OH', Cl', or SO_4'', will exchange some of the latter for any other negative ions also present in the solution.

[1] *J. Chem. Soc.*, 1902, **81**, 939.
[2] *J. Chem. Soc.*, 1919, **115**, 1269.

The extent of this interchange will depend, among other things, upon the relative proportions of the foreign anions and those characteristic of the particle. This would be perfectly analogous to the process by which, for example, some KBr is formed in a solution obtained by mixing solutions of NaBr and KCl, and it would seem to be one reason for the almost constant presence of some foreign acid radicles in many precipitates. Where the particle ionizes into heavy complex anion and one or more simple cations, the latter will similarly be exchanged to some extent for other positive ions present in the solution. It will be realized that ions thus taken up by the particle may themselves be of a composite character and contain both metal and acid radicle.

The more or less ionized particles are also subject to other influences, not precisely of an ionic character, in which the solvent molecules, as also other molecules present, play an important part. Some of these various molecules attach themselves to the surface of the suspended particles—so-called surface adsorption. This has generally been regarded as a physical process, though the work of Langmuir [1] has shown that it is probably essentially chemical in nature and due to more or less marked residual affinity of the surface layer of the adsorbing particle. The work on crystal structure by Bragg and others [2] clearly shows that the atoms in the outermost layers of crystals are not fully saturated, so that such surface additions of foreign molecules need not be regarded as very remarkable. The firmness with which they are held will naturally depend both on the nature of the adsorbing particle and on that of the foreign molecules. As it is a surface phenomenon, it is well marked only in cases where the adsorbing substance is in a fine state of division. In aqueous solutions a sheath of water molecules appears to be so held, containing, however, other molecules as well.

There seems no reason why some of the molecules so held should not still ionize in more or less the usual way, which really amounts to the same thing as saying that certain

[1] Summarizing paper in *J. Amer. Chem. Soc.*, 1916, **38**, 2221.

[2] *X-Rays and Crystal Structure*, 4th ed., 1924, by W. H. and W. L. Bragg; also W. H. Bragg, *J. Chem. Soc.*, 1916, **109**, 260.

ions are removed from the solution and adsorbed by the colloidal particles, which would at the same time receive the ionic charges. The usually accepted view is that the charges carried by colloidal particles originate in this way by ionic adsorption, but it seems a mistake to ignore the possibility of spontaneous ionization of the particles themselves.

The sheath of adsorbed water (or solvent) molecules round the particles in a colloidal suspension probably plays an important part in preventing coalescence and settling out when the particles collide. As a rule the particles have the same electric charge and so repel one another, but uncharged particles can remain in colloidal suspension in some cases, and even in cases where most of the particles are charged it must be supposed that some kind of equilibrium exists between the charged particles, their ions, and the uncharged particles. Some collisions between the latter probably take place, therefore, and in time coalescence and settling out might be expected to occur, and in many cases actually does occur. Any adsorption sheath, either of water or other molecules, would tend to prevent coalescence occurring on collision. The action of so-called "protective" colloids and, in certain cases, of crystalloidal non-electrolytes, in preventing the formation of precipitates is explicable in this way.

That colloidal suspensions may be coagulated by the addition of electrolytes has already been mentioned, but the mechanism of the process is doubtful. It probably occurs in two stages, the neutralization of the charged particles being followed by their coalescence. The neutralization is generally regarded as being due to the adsorption of that ion of the added electrolyte of opposite charge to the colloidal particle, and doubtless this is correct. It seems reasonable to look at the matter from the ordinary ionic point of view. The process may be akin to the throwing back of the ionization of an ordinary electrolyte by the mass influence of the added ion which is common to the two electrolytes. Neutralization might also be due to the electro-affinity of the ion which causes coagulation being smaller than that of the simple

ion split off from the colloidal complex. Having a smaller tendency to remain in the ionic state, it combines with the charged colloidal particle more readily than the simple ion originally present.

Other things being equal, the efficiency of salts as coagulants might be expected to depend upon the electro-affinity of the anions in the case of positive sols and of the cations in the case of negative sols, and this may well be the basis of Schulze's law,[1] for in a general way electro-affinity falls off with increasing valency. The many exceptions to Schulze's law would also be explicable, for electro-affinity depends upon many other factors than valency.[2]

The matter is, however, complicated by adsorption of the un-ionized electrolyte and in many other ways, so that when different electrolytes are arranged in their order of effectiveness as coagulants, that order is not always easy to explain, while the amounts of the ions adsorbed are not even approximately equivalent.[3] The high efficiency of acids as coagulants for negative colloids seems more satisfactorily accounted for by the low electro-affinity of the $H^{\cdot}$ ion than by its high ionic conductivity, and in fact most of Westgren's results[4] seem more intelligible when so explained. Thus the fact that, of the three sodium salts ($NaIO_3$, NaCl, NaOH) examined, the first is the most efficient coagulator for negative gold sols, and the third is the least efficient, falls naturally into line with the fact that the IO_3' ion has the highest electro-affinity and the OH' ion the least. The IO_3' ion will most readily surrender its $Na^{\cdot}$ ion to the negative colloidal particles, while the OH' ion will do so least readily.

In certain cases polyvalent ions may assist the process of coagulation in another way by actually linking together two or more of the colloidal ions.

The mutual precipitation of oppositely charged colloids can obviously be regarded as a special case of the process

[1] See p. 95.

[2] Abegg and Bodländer, *Z. anorg. Chem.*, 1899, **20**, 453.

[3] Compare Weiser and Sherrick, *J. Physical Chem.*, 1919, **23**, 205; Weiser and Middleton, *J. Physical Chem.*, 1920, **24**, 30.

[4] *Arkiv Kem. Min. Geol.*, 1918, **7**, No. 6, 1–30.

outlined above, and in that sense is to be frankly regarded as ionic and chemical.

No simple stoicheiometrical relationship is to be expected between the positive and negative constituents of the precipitates obtained by coagulating colloidal solutions, either by electrolytes or by other colloids, but this does not necessarily mean that the process is not chemical in the broader sense.

After neutralization, coalescence of the particles follows more or less rapidly as a result of molecular collisions. The frequency of these depends mainly upon the concentration of the particles and their velocity, which again depends upon their mass and upon the temperature.

There seems no doubt that the adsorbed water (degree of hydration) plays a very important part at this stage, and that coalescence of individual particles to form the secondary aggregates is largely due to capillary [1] forces between the particles coming into play. If these forces are small or the degree of hydration large the secondary aggregates are not very stable and are easily broken down again—and this is in full agreement with the well-established fact that lowering the interfacial tension between solid and liquid (or liquid and liquid) favours the formation of colloidal suspensions. If, however, the original degree of hydration is too slight (as with metallic particles), or if the aqueous envelopes surrounding the particles become broken, so that the particles come within the range of their cohesive [1] forces then the secondary aggregates formed are much more stable and the transformation is not reversible. It is partly to enable such changes to occur in the secondary aggregates—changes which may sometimes amount to actual crystallization—that precipitates are frequently allowed to stand or are even digested for some time before filtration.

Edser,[2] who seems inclined to interpret all colloidal solutions in terms of the contact angle between particle and liquid,

[1] On Langmuir's view of the matter (*loc. cit.*) these forces are essentially chemical.

[2] *Fourth Colloid Report of the British Association for the Advancement of Science*, 1922, pp. 311–13.

considers that minute air bubbles play a very important part in promoting flocculation of precipitates by moving about and collecting the suspended particles. He points out that it is customary to stir or shake during precipitation, and that this is well adapted to produce aeration. It may well be that this is one of the ways in which the neutralized sol particles become flocculated, but they must be neutralized first. The electrical theory of colloidal solutions is too useful and supported by too much evidence to be discarded lightly.

It will be realized that in any individual case the formation of a precipitate may be due to ordinary crystalline growth of the separating particles until they are sufficiently large to settle out, or the primary crystalline particles formed may be coagulated by the action of electrolytes present or by the action of oppositely charged particles, or by a combination of these. It may not be easy to say which course is followed in any given case, but the more soluble a compound, the more likely is its precipitation to be due to simple crystalline growth and conversely.

It can, however, be asserted with confidence that, provided the precipitate is sufficiently insoluble, the more its formation depends upon simple crystalline growth the better from the analyst's point of view, owing to the greater readiness with which such a precipitate can be filtered and washed and because of its greater purity.

It is evident that, as far as actual precipitation is concerned, all efforts should be concentrated on obtaining a crystalline precipitate or, if that is out of the question, an amorphous precipitate as dense as possible, that is to say, one formed by coagulation of the largest possible colloidal particles. Precipitation must, therefore, be carried out as slowly as possible, and this is done by adding the precipitating solution very slowly, stirring all the time, to the other solution. Both solutions should be moderately dilute, the dilution permissible or necessary depending on the true solubility of the substance to be precipitated. Only a moderate excess of the precipitating solution should normally be employed, for with a large excess there is danger of formation of crystalloidal

complex salts and re-solution of the precipitate. A very slight excess of precipitant may not be satisfactory, as in such cases the slight excess may, with amorphous precipitates, cause peptization of the precipitate and formation of a colloidal solution, as in the case of silver chloride.[1] A moderate excess of reagent is nearly always satisfactory as by its ionic effect it diminishes the solubility of crystalline precipitates and also helps the coagulation of amorphous ones—this being regarded as also an ionic effect in reality.

Conditions should moreover be such as to ensure the greatest possible solubility (within reason of course) of the precipitate at the actual time of its formation. An elevated temperature is generally favourable to this, and in many cases proper attention to the acidity, etc., of the solutions may be very helpful. Once precipitation has been effected, the solubility is again lowered by allowing to cool and by complete or partial neutralization of any acidity, or possibly by other means. An elevated temperature may sometimes accelerate the electrolytic coagulation of sols, and this would be unfavourable to the formation of dense precipitates. A moderate temperature may therefore be better than either a lower or higher one for the precipitation of amorphous precipitates. This applies, for example, to aluminium hydroxide, which is best precipitated at 66°.[2] Digestion subsequent to precipitation, or even standing for some time at the ordinary temperature before filtration, is also favourable owing to the opportunities so given for crystalline particles to grow at the expense of any very fine and more soluble ones that may be present, or for amorphous precipitates to undergo those secondary changes which may amount to crystallization and at least cause them to become denser.

Owing to the need for postponing the electrolytic coagulation as long as possible, the concentration of electrolytes present should be as small as is consistent with the general requirements of the experiment. The unfavourable effect of high salt concentrations on the character of precipitates is well

[1] Lottermoser, see later, pp. 108, 114.
[2] Taylor, *Chem. News*, 1911, **103**, 169.

known. The nature of the electrolytes present can also sometimes be controlled in the sense of ensuring the absence of those of very high coagulating power.

Purity, Filtration, and Washing of Precipitates

In those cases where precipitation is due entirely to crystalline growth the purity of the precipitate will normally be of a high order. Impurities are present only in a form readily removable by washing, viz. as a thin layer adsorbed on the surface of the particles. The coarser the precipitate the less is its surface and the more readily can it be washed. As this form of precipitation is most likely to occur with compounds which are not highly insoluble the minimum amount of wash-water should be used.

Impurity of such precipitates, other than that which is due to surface adsorption and readily removable, is to be feared only in cases where isomorphous replacement is possible, as, for example, in separating calcium, strontium, and barium. Crystalline precipitates, moreover, are not likely to pass into colloidal solution again during the process of washing, their passage back into solution being determined by ordinary solubility.

The above statements would apply also to those precipitates which are crystalline owing to secondary charges in a primary precipitate formed by electrolytic coagulation of a sol. They would also apply in some measure even if the rearrangement of the primary precipitate was only sufficient to cause rupture of the adsorbed water layers without actual crystallization.

The case is very different, however, when the precipitate has separated wholly owing to electrolytic coagulation and without any subsequent rearrangement of the secondary aggregates. With this type of precipitate there is much more general surface adsorption because of the finer state of aggregation, but material so adsorbed is doubtless fairly readily removable by washing. One has, in addition, to deal with the much more intimately combined acidic or basic atoms or radicles, which played such an important part in discharging the original charged sol particles or which had been taken up by them by the method of ionic interchange

suggested previously. Atoms or radicles so attached will generally lie just on or in the surface of the constituent particles of the secondary aggregates composing the precipitate. Steric considerations will usually prevent their actual adsorption into the crystalline particles unless there is possibility of some isomorphous replacement. The finer the sol particles are at the moment of coagulation the more serious is contamination of this kind likely to be, and, moreover, it cannot as a rule be removed by simple washing.

The attachment of such contaminating groups or atoms has been attributed to ordinary chemical forces supported firstly by the mass effect (concentration) of the ion which becomes so attached, and secondly—especially in the case of polyvalent ions—by its relatively low electro-affinity. Which of these two factors is the more important will vary from case to case, and the behaviour of the precipitate on washing will largely depend upon which predominates. If the mass effect of the discharging ion is of much importance a relatively high concentration is required for the complete neutralization of the charged sol particles, which must precede their coagulation. On washing the coagulum the mass effect is no longer sufficient, and although the contaminating radicle is thereby gradually removed, such removal is fatal to the continued existence of the precipitate. The radicle once more passes into the ionic state, leaving its complementary particle in the precipitate charged, and in a short time the precipitate disintegrates, the individual charged particles again passing into colloidal solution. Where the contaminating or discharging ion is mainly attached by virtue of its low electro-affinity such removal on washing is much slower, and the precipitate does not so readily pass back again into colloidal solution.

Washing a precipitate with a solution of an electrolyte may be expected to counteract any such tendency to pass into colloidal solution and is indeed a well-known analytical artifice. When the washing electrolyte is suitably chosen it may be possible to eliminate undesirable constituents from the precipitate almost completely and to obtain after ignition a product of the correct composition.

Generally it will not be possible to wash an amorphous precipitate entirely free from foreign radicles. As a consequence of this the weight, after drying or igniting the precipitate, may be what it should be from stoicheiometric considerations, but it is much more likely to be slightly greater or even less, according to the nature of the foreign radicles in the precipitate. If the latter contains an element or group subsequently to be determined in the filtrate, the results obtained for it will be too low. The amount of any foreign radicles present in a precipitate depends very intimately on many factors, which makes the application of any empirical correction very uncertain even if great care is taken to carry out the precipitations always in the same way.

Now, though the coagulating effect of an electrolyte has to be ascribed essentially to either the anion or the cation derived from it, it must be remembered that the other ion of same sign as the colloidal particles has a disturbing effect which may nullify or even reverse this coagulating effect. The first effect may well be neutralization of the colloidal particles, but before these have time to coalesce they become charged once more, but in the opposite sense, either by direct adsorption of the opposite ion or by loss of its partner after preliminary adsorption of the un-ionized molecule.

From what has been said previously it follows that this effect should be largely dependent upon the electro-affinity of the ion of same sign as the original sol particles, and it was actually found that in the case of negative gold sols NaOH was much the least efficient coagulator of the sodium salts tried and OH′ was the anion of lowest electro-affinity.[1] The stabilizing effect of the strongly adsorbed H· ion of low electro-affinity is also marked in the coagulation of positive ferric hydroxide sols.[2]

The stabilizing effect of the one ion of the electrolyte may come into action even after coagulation of the discharged sol particles and cause disintegration—peptization—of the

Westgren, *Arkiv Kem. Min. Geol.*, 1918, **7**, No. 6, 1–30.
Weiser and Middleton, *J. Physical Chem.*, 1920, **24**, 30.

precipitate; this occurs readily in the case of the hydrated colloids where secondary changes due to rupture of the water sheaths either do not occur or only very slowly. In such cases, too, it is also found that ions of low electro-affinity are frequently good peptizing agents. Thus alumina, which is a positive colloid, is readily peptized by acids.[1]. Of course, the peptization depends to some extent also on the colloid and in some cases ions of high electro-affinity may be adsorbed as in the peptization of silver halides by the corresponding potassium halide owing to adsorption of the halogen ions.[2]

The peptization of a gel, such as that of silver chloride by a solution of KCl owing to adsorption of Cl′ ions, is so remarkably similar to the passage of a gel like silver cyanide into true solution in KCN owing to addition of CN′ ion that there seems no reason to doubt the complete analogy of the two processes. The negatively charged sol particles are to be regarded as complex ions in which the "neutral part" (in the terminology of Abegg and Bodländer, loc. cit.) consists, in this instance, of the original uncharged particle of silver chloride, while in the crystalloidal cyanide solution the complex ion is $Ag(CN)_2'$ and its "neutral part" consists of a single molecule of AgCN. But the analogy goes even further, for under suitable conditions the colloidal solution of silver chloride in KCl passes into a crystalloidal solution containing the complex anion $AgCl_2'$ whilst weak solutions of KCN will peptize silver cyanide which forms a colloidal solution owing to adsorption of CN′ ions.[3]

In striking confirmation of these views is the fact that corresponding with the colloidal solutions of silver halides in $AgNO_3$, in which the sol particles are positively charged and owe their stability to adsorbed $Ag^{\cdot}$ ions, there are known definite crystalline compounds Ag_2ClNO_3, etc., which ionize into complex *cations* $Ag_2Cl^{\cdot}$, etc.[4] It is probable that the passage into true solution of a gel under the influence of any

[1] Weiser, *J. Physical Chem.*, 1920, **24**, 277, 505.

[2] Lottermoser, *J. pr. Chem.*, 1903, **68**, 341; 1905, **72**, 39; 1906, **73**, 374; *Z. physikal. Chem.*, 1908, **62**, 359.

[3] Lottermoser, *J. pr. Chem.*, 1905, **72**, 39.

[4] Hellwig, *Z. anorg. Chem.*, 1900, **25**, 183.

electrolyte is, in all cases, preceded by a stage in which a colloidal solution is formed owing to adsorption of one or other ion. This certainly appears to occur when compounds such as aluminates and zincates are formed by the action of caustic alkalis on metallic hydroxides, and even when the latter dissolve in acids. Such a transition has been studied in an interesting manner in the case of silicic acid dissolving in ammonia.[1]

Many organic colloids are peptizable by pure water, yielding sols containing either positively or negatively charged particles. Such colloids have a marked effect in preventing the coagulation of other colloids of similar sign to themselves, and in that case are called " protective " colloids. One can suppose that the one colloid is neutralized normally by the electrolyte added but is at once peptized by the water-soluble colloid. That is to say the charged protective colloid particle is adsorbed by the neutral particles of the other colloid.

Such water-soluble colloids—and indeed other colloids too, though not in such a marked way—also have a great effect on the precipitation of many inorganic compounds. In the presence of protective colloids, compounds which normally separate in coarse crystals tend to separate in very minute crystals, while those normally separating in a fine state of division will separate in a flocculent condition and in extreme cases no separation at all occurs. These effects are all attributable to the formation in the solution of adsorption complexes, or complex ions, between the protective colloid and one or other of the ions of the compound being precipitated. This renders precipitation of the compound either impossible or at least difficult. It is well known that the presence of colloidal organic matter in solution is liable to give trouble in many inorganic estimations and that it should always be removed or destroyed if possible.

Colloid Properties of the Filter Paper, Surfaces of Vessels, etc.

Effects due to the colloid character of the filter paper (or indeed of other filtering materials) are sometimes not

[1] Schwarz and Liede, *Ber.*, 1920, **53**, B. 1509.

properly appreciated. The filter paper fibres are negative colloids, and when a precipitate which has resulted from the coagulation of a positive colloid is filtered through the paper a sort of double decomposition occurs with attachment of the particles of the positive colloid to the negative filter paper. If the individual particles are sufficiently small this occurs in the pores of the paper, completely blocking them up and making filtration extremely slow. This sort of thing happens with aluminium hydroxide as usually precipitated, and with zinc sulphide when precipitated from alkaline solution, and indeed is liable to happen with any similar positive colloid.[1]

Owing to their large surface and their colloid character, the fibres readily adsorb dissolved substances from solution and also water. This adsorption is perhaps mainly due to the simple surface action, but it is partly of the more profound kind which occurs when a sol is neutralized by an electrolyte. It follows that a filter paper may not only remove soluble constituents from a solution being passed through it, but it may be extremely difficult to wash these out again. Errors can obviously be caused in this way. The weight of precipitate obtained after drying or ignition may be too great, while values found for constituents subsequently estimated in the filtrate may be too low. In extreme cases traces of substances may be entirely removed from solution by filter papers and so escape detection, though in suitable cases their removal by such means may be made the basis of a method for separating and estimating them. In cases where filter papers are used which are not of the ashless variety, disturbances may be caused by replacement of the inorganic constituents of the paper, which are probably present in the adsorbed condition, by other substances derived from the solution being filtered. The correction subsequently applied for the ash of the filter may then be wide of the mark.

Mainly on account of these adsorption effects the size of the filter paper used should always bear a reasonable proportion

[1] Kolthoff, *Pharm. Weekblad*, 1920, **57**, 1510.

to the amount of precipitate being filtered. Adsorption of water by filter paper is troublesome in those cases where a precipitate cannot be ignited but has to be weighed on the filter. It is well known that the amount of moisture held by the paper varies considerably with the conditions, and that great care must be taken when working with weighed filter papers in order to get trustworthy results. Other filtering materials show similar adsorption effects, though to a different extent.

It must be remembered that all surfaces, whether crystalline or amorphous, have some capacity for adsorbing substances either from solution or from the gaseous condition, and the aspect of this matter which is of most importance to the analyst is the adsorption of moisture from the air. This effect must be allowed for by such precautions as (1) never weighing substances in larger crucibles, glass vessels, etc., than are essential for the operation in hand, (2) igniting substances or at least drying them at as high a temperature as possible before weighing, (3) keeping the atmosphere in which vessels are allowed to cool before weighing and that in which they are weighed in as constant a condition as possible with respect to moisture by the use of desiccators and by having some drying agent in the balance case, (4) making the complementary weighings (e.g. empty and full crucible) at as short a time interval as possible, (5) using a second vessel of similar size and weight as a counterpoise.

Except in the most refined work it is not as a rule difficult to eliminate the troubles due to this moisture adsorption, but there are a few notorious cases, such as those of ignited alumina and silica, which readily retain and take up moisture, where special care is needed.

It is probable that the tenacity with which some precipitates, especially sulphides and oxides, adhere to the sides of beakers, etc., in which they have been precipitated, is to be accounted for in terms of the mutual precipitation of two oppositely charged colloids—the glass in the cases mentioned acting as the negative colloid.

Application of the Foregoing Considerations to some Special Cases

Estimation of Lead Sulphate[1]

Owing to the relatively high solubility of $PbSO_4$, its precipitation is probably entirely a matter of crystalline growth.

Separation of Calcium as Oxalate[2]

Calcium oxalate has a very small solubility product, and when precipitated from ammoniacal solutions, as frequently recommended, often gives trouble by running through the filter paper. This is because it has separated under conditions of great insolubility and probably by coagulation of a finely divided sol. The C_2O_4'' ion is very sensitive to hydrogen ions, and readily yields the HC_2O_4' ion; calcium oxalate therefore readily dissolves in dilute acids, and even in water dissolves more than might be expected owing to the $H^{\cdot}$ ions present in the water.

If, therefore, the precipitation is carried out in weak acid solution, the solution being made ammoniacal at the end of the precipitation, the precipitate forms much more slowly and probably entirely on lines of crystalline growth, and no trouble is experienced with the filtration. When the method of Järvinen[3] is used glittering crystals of calcium oxalate are obtained.

The Estimation of SO_4

Although this is simply the inverse of the estimation of barium (already discussed on p. 11) it is more liable to give trouble. The excess of sulphuric acid present in the one case renders adsorption of ions other than SO_4'' more difficult.

The moderately dilute sulphate solution (which must be acid and should occupy about 30 c.c. for every 0·1 gram $BaSO_4$) is heated to boiling and precipitated by slowly adding with constant stirring a hot solution of barium chloride until the latter is present in small excess. The precipitate is allowed to settle, then filtered, washed with hot water, and ignited as already described under the estimation of barium.

[1] See p. 69.
[2] See p. 66.
[3] *Z. anal. Chem.*, 1904, **43**, 559.

Precipitation of Barium Sulphate

It seems likely that barium sulphate represents a border line case, and that by very carefully regulated slow precipitation from hot solutions the forces of crystallization are just sufficient to cause precipitation independently of electrolytic coagulation. As a rule, perhaps, the precipitate results from such coagulation, but even then there is a marked tendency for the precipitate to undergo secondary changes and become denser, either on digestion with the mother liquor or on standing. These secondary changes are not necessarily profound enough to eliminate troubles due to adsorption, which may be very serious. The precipitation of barium sulphate has been very carefully examined, largely on account of its importance in connexion with the estimation of sulphur in iron pyrites. An interesting account of this work is to be found in Classen's *Ausgewählte Methoden der analytischen Chemie*, 1903, vol. **2**, pp. 305–18.[1] Heavy metals and various acid radicles are readily carried down by the barium sulphate, the most important cases practically being those of ferric iron and sulphate. Colloidal solutions of barium sulphate are usually positive, due to strong preferential adsorption of $Ba^{\cdot\cdot}$ ions; and all the experimental evidence supports the view that other metals are carried down owing to combination of negative complex ions such as KSO_4' or $Fe_2(SO_4)_4''$ with the positive particles of the barium sulphate sol. When this occurs low results are obtained for SO_4. High results for SO_4 are, however, obtained when chlorine or similar ions are removed from solution by the barium sulphate. In so far as Cl' ion has combined with a sol particle owing its positive charge to $Ba^{\cdot\cdot}$ ions it is quite correct to say, as is generally done, that the precipitated barium sulphate has carried down barium chloride.

Slow precipitation from hot dilute solution goes a long way towards ensuring a pure precipitate, but in presence of ferric iron and similar metals the only safe mode of procedure is to separate the metal first as in Lunge's well-known method for iron,[2] or the modification proposed by Küster and Thiel.[3]

[1] See also Taylor, *J. Soc. Chem. Ind.*, 1923, **42**, 294T.
[2] *Z. anal. Chem.*, 1880, **19**, 419.
[3] *Z. anorg. Chem.*, 1899, **19**, 97.

Gravimetric Estimation of Chloride as AgCl

If the solution contains only metals of the alkalis or alkaline earths it is moderately acidified with nitric acid and precipitated in the cold by slow addition of silver nitrate solution. It should be stirred vigorously all the while, and will become suddenly much clearer when a slight excess of silver nitrate has been added. The liquid is then heated nearly to boiling (if the precipitate has settled well this can be dispensed with), allowed to settle, and filtered either through a Gooch crucible or an ordinary filter. It is washed with cold, very dilute nitric acid—not with pure water—as otherwise the colloidal AgCl begins to pass through the filter. The nitric acid is finally removed by a couple of washings with alcohol. If a Gooch crucible has been used the precipitate is dried at 130°–150° and weighed. If a filter paper has been used, then, after drying in the oven, the paper is ignited apart from the precipitate. The small amount of reduced silver in the ash is reconverted to chloride by moistening with a drop of nitric acid and one of hydrochloric and driving off the excess by gentle heat. The rest of the AgCl is then added, and the crucible is heated over a small flame until the chloride just begins to melt.

AgCl is a typical colloid and as such is liable to contamination by adsorption under certain conditions. This is especially the case if it is precipitated from solutions containing salts of the heavy metals, in particular the less basic ones such as $Fe^{\cdot\cdot}$ or $Sn^{\cdot\cdot\cdot\cdot}$. In these cases the AgCl is liable to carry down some of the metallic hydroxide—an effect that may be ascribed to the mutual precipitation of two oppositely charged colloids. The AgCl is negatively charged while any of the metallic hydroxide formed by hydrolysis would be positively charged. As heating the solution favours hydrolysis this should be avoided, while a considerable amount of free acid should be present so as to reduce hydrolysis to a minimum. It may be still better to remove the heavy metal before the silver chloride is precipitated.

Silver chloride is very readily peptized by alkali chlorides so that neutral solutions of these on treatment with silver

nitrate solution do not flocculate readily until enough of the silver solution has been added to react with the whole of the chloride. This peptizing effect of the chloride is very marked in decinormal and weaker solutions. With much stronger solutions, however, the excess of chloride tends rather to coagulate the silver chloride than to peptize it. If other salts or electrolytes are present the peptizing effect of the chloride is much less marked, which is one reason for carrying out the precipitation in presence of nitric acid.

The precipitation of silver chloride is a case in which the beneficial effect of vigorous stirring, with its consequent aeration, in promoting flocculation of the precipitate is most marked. (See *ante*, page 102.)

During the whole process of precipitation, filtration, etc., the silver chloride should be exposed to bright light as little as possible. Under the influence of the latter, as is well known, it gradually becomes pinkish or violet and finally black. This is due to decomposition, in the course of which chlorine is evolved according to one or other of the equations :

$$AgCl = Ag + Cl$$
$$2\ AgCl = Ag_2Cl + Cl$$

(The decomposition almost certainly yields chlorine atoms in the first instance, which then at once combine to form molecules.) Although there is no doubt about the evolution of chlorine, it is still uncertain whether metallic silver or the subchloride is formed. There are good reasons for thinking that it is really a colloidal solution of silver in AgCl which is actually formed. In any case, the amount of chlorine lost by the silver chloride during an ordinary analysis is far too small to cause any appreciable error.[1]

A precisely similar reaction occurs when a photographic plate is exposed, though in that case it is usually AgBr or AgI which is concerned and not AgCl.

The decomposition of silver chloride in light is one of those very numerous reactions which require the presence of traces of water. Perfectly dry AgCl will not darken when

[1] See Hartung, *J. Chem. Soc.*, 1922, **121**, 682.

exposed to light in a sealed tube.[1] It is not known for certain what part the moisture plays in such cases.

Gravimetric Determination of Bromide, of Iodide, and of Silver

The estimation of bromide or of iodide is carried out in exactly the same way as that of chloride.

The gravimetric determination of silver as chloride is simply the converse of that of chloride.

[1] Baker, *J. Chem. Soc.*, 1892, **61**, 735.

CHAPTER VIII

AMPHOTERIC COMPOUNDS

Quantitative Precipitations and Separations as Oxide or Hydroxide

IT is characteristic of acids that on solution in water (or other ionizing solvent) they split off hydrogen ions while bases on the contrary give hydroxyl ions.[1]

But there are numerous compounds which give rise to both hydrogen and hydroxyl ions and which accordingly function both as acids and bases, although sometimes the acid character predominates, sometimes the basic. Such compounds are said to be amphoteric. The simplest amphoteric compound is water, which gives equal numbers of hydrogen and hydroxyl ions.

It is necessary that in all aqueous solutions the product of the hydrogen and hydroxyl ion concentration should have the value K_w, the ionic product of water, hence one can never have a solution containing either hydrogen or hydroxyl ions without a certain amount of corresponding hydroxyl or hydrogen ions. In the solution of a strong acid the concentration of the hydroxyl ion is vanishingly small, while that of the hydrogen ion is vanishingly small in the case of a strong base. In such cases the minute amount of hydroxyl or hydrogen ion is derived entirely from water.

Arsenious "acid" is a typical amphoteric compound. In the solid state it exists as the anhydrous oxide As_2O_3, but doubtless in solution this becomes hydrated to form, e.g. $As(OH)_3$, which ionizes thus :—

$$As(OH)_3 \rightleftarrows H^{\cdot} + H_2AsO_3' \\ \rightleftarrows OH' + H_2AsO_2^{\cdot} \text{ (or } As(OH)_2^{\cdot})$$

[1] The term base is applied both to the oxide and to the hydrated oxide, e.g. to Na_2O and NaOH. It is perhaps best restricted to the hydrated oxide which alone can give hydroxyl ions.

The concentration of $H^{\cdot}$ and OH' in the equilibrium set up depends on the value of K_a and K_b (below).

Since both the acidic and basic functions of $As(OH)_3$ are very feeble, it is only the tendency to lose one $H^{\cdot}$ or one OH' ion which is measurable (see the section on the ionization of acids, page 38). It is true that potentially there are three $H^{\cdot}$ or three OH' ions available, and in presence of a large excess of alkali or of acid all three might act. In presence of moderate amounts of alkali, however, it behaves like a monobasic acid [1] and with acids doubtless as a monacid base.

The basic and acidic dissociation constants have been determined by Wood,[2] who found—

$$\begin{cases} K_a = \dfrac{[H^{\cdot}][H_2AsO_3']}{[As(OH)_3]} = 6{\cdot}3 \times 10^{-10} \\ K_b = \dfrac{[OH'][H_2AsO_2^{\cdot}]}{[As(OH)_3]} = \text{about } 1 \times 10^{-14} \end{cases}$$

These figures indicate that the acid character of $As(OH)_3$ is far more marked than the basic, and that arsenious acid is approximately of the same strength as boric acid.

It need hardly be mentioned that by the addition of acid or base to such a solution the equilibria are disturbed. If an acid is added, its $H^{\cdot}$ ions, by combining with OH' ions, derived from the $As(OH)_3$, will shift the equilibria $H^{\cdot} + H_2AsO_3' \rightleftarrows As(OH)_3 \rightleftarrows OH' + H_2AsO_2^{\cdot}$ from left to right, and so cause the $As(OH)_3$ to act only as a base. When a base is added its OH' ions will produce precisely the opposite effect and cause the $As(OH)_3$ to act only as an acid.

The majority of the metallic hydroxides have well marked amphoteric characters, and it is on that account that they are often soluble in strong alkalies.

As a rule these hydroxides are very insoluble in water, but the small amount that does dissolve splits off hydrogen or hydroxyl ions or both as the case may be. The hydroxyl ions are most numerous usually, since the basic character

[1] Zawidzki, *Ber.*, 1903, **36**, 1427.
[2] *J. Chem. Soc.*, 1908, **93**, 411.

of these compounds is the more pronounced. It is the hydroxyl ions which come into play when the hydroxide is dissolved in acid; thus, taking $Cu(OH)_2$ as an example :—

$$\underset{\text{solid}}{Cu(OH)_2} \rightleftarrows \underset{\text{dissolved}}{Cu(OH)_2} \rightleftarrows Cu^{\cdot\cdot} + 2OH' \xrightarrow{2HCl} Cu^{\cdot\cdot} + 2Cl' + 2H_2O$$

Since, however, $Cu(OH)_2$ splits off also a few hydrogen ions it will dissolve in strong alkali. Thus :—

$$\underset{\text{solid}}{Cu(OH)_2} \rightleftarrows \underset{\text{dissolved}}{Cu(OH)_2} \rightleftarrows CuO_2'' + 2H^{\cdot} \xrightarrow{2KOH} CuO_2'' + 2K^{\cdot} + 2H_2O$$

But $Cu(OH)_2$ is an exceedingly weak acid, and therefore a very large excess of KOH has to be used in order to overcome hydrolysis.[1] In all cases where precipitated hydroxides redissolve in excess of potash or soda the phenomena can be explained in this manner. When they dissolve in excess of ammonia it is usually for a totally different reason, which is dealt with in Chapters XII and XIII.

The strength of aluminium hydroxide as a weak acid has been examined by Wood.[2] It behaves as a monobasic acid ionizing thus :—$H^{\cdot} + H_2AlO_3' \rightleftarrows Al(OH)_3$, and Wood found that the dissociation constant

$$K_a = \frac{[H^{\cdot}][H_2AlO_3']}{[Al(OH)_3]} = 6{\cdot}3 \times 10^{-13}$$

The basic character of $Al(OH)_3$ is much stronger than its acidic character, but it was not found possible to determine the actual value of the basic dissociation constant. It is to be noted, however, that the basic ionization almost certainly takes place according to the equation $Al(OH)_3 \rightleftarrows OH' + Al(OH)_2^{\cdot}$ in the first instance. All polyacid bases probably ionize in stages just as do polybasic acids, but this is much more difficult to prove in the case of the bases. In some cases, e.g. $Fe(OH)_3$, although the acidic function of the hydroxide is so weak that it will not dissolve in aqueous alkali, because sufficient excess cannot be added to overcome

[1] See Creighton, *J. Amer. Chem. Soc.*, 1923, **45**, 1237, and Müller, Kahlert, Wiegand, Ernst, and Keil, *Z. physikal. Chem.*, 1923, **105**, 73.
[2] *J. Chem. Soc.*, 1908, **93**, 417.

hydrolysis, yet derivatives of the acid forms can often be obtained by igneous methods. Fe_2O_3ZnO is an instance of such a compound. It has been prepared artificially by Gorgeu,[1] and in its native form constitutes the mineral Franklinite.

Heyrovsky [2] considers that the process by which aluminium hydroxide dissolves in alkali is by complex ion formation, $Al(OH)_3 + OH' \rightleftarrows Al(OH)_4'$, and not by sending into solution one, two, or three of its hydrogen atoms as hydrions. On this view the hydrolysis of aluminates is not due to scarcity of hydrions but to incompleteness of the complex formation. The solution of other hydroxides in alkali can be explained in a similar manner. Solution of the hydroxides in this way would be entirely comparable to their peptization by adsorption of OH' ions. The degree of hydration of the aluminate ion would differ by a molecule of water according to whether its formation is due as above to addition of an OH' ion or to loss of an H' ion $Al(OH)_3 \rightleftarrows AlO(OH)_2' + H'$, though it is to be noted that the $Al(OH)_4'$ ion could lose a molecule of water subsequent to its formation and yield $AlO(OH)_2'$. Our knowledge of the precise degree of hydration of ions is very incomplete.

Both of the above alternative views regarding the process of solution of hydroxides in alkali have points in their favour, but it hardly seems possible at present to say which is the more correct.

There is, however, another aspect of metallic hydroxide precipitates which must be considered, and that is the colloidal one. Practically all such precipitates which are of importance as a means of separating and estimating a metal are very insoluble, and hence are " amorphous ", being formed as the result of electrolytic coagulation of a sol. The precipitates are typical gels, and are readily peptized by suitable ions, especially hydrogen or hydroxyl ions. There seems no doubt that the initial stages of the solution of these gels in either acid or base consists in a peptization and formation of a

[1] *Compt. rend.*, 1887, **104**, 580.
[2] *Chem. News*, 1922, **125**, 198.

colloidal solution. In the acid solution positive particles which owe their charge to adsorbed hydrogen ions or to loss of hydroxyl ions are present, while the alkaline solutions contain negative particles owing their charge to adsorbed hydroxyl ions or to loss of hydrogen ions. If sufficient excess of acid of alkali is used these colloidal solutions pass into crystalloidal ones containing the salts of the amphoteric forms of the particular hydroxide concerned. The readiness with which this change to the crystalloidal condition occurs will depend not only on the strength of the acid or alkali but also upon the basic and acidic characteristics of the hydroxide. If the basic character is too weak the hydroxide may not pass beyond the stage of a colloidal suspension in acid solution, though it may do so in alkaline solution. Silicic acid is such a substance. On the other hand, if the acidic character is too weak just the reverse may hold, as it does with ferric hydroxide.

Owing to the amorphous character of most of the metallic hydroxides, and this applies also to acidic hydroxides such as silicic acid, the water they contain is much more vaguely and loosely held than that present in crystalline hydrates, and is often regarded as held merely by adsorption. At the same time there are strong reasons for regarding these substances as hydroxides. In some cases, e.g. $Al(OH)_3$ perfectly definite crystalline compounds can be obtained as well as the more indefinite amorphous gels.

The case of cupric hydroxide is interesting. Copper is sometimes precipitated as that compound, but under the conditions of the usual analytical procedure dehydration of the sol occurs simultaneously with or shortly after its coagulation with formation of what is essentially copper oxide. After thorough washing and ignition, the weight of oxide obtained is generally only very slightly higher than the theoretical. According to Kohlschütter and Tüscher [1] the elimination of water from copper hydroxide is due to amphoteric ionization and neutralization of molecular complexes of colloidal dimensions. This apparently indicates

[1] *Z. anorg. Chem.*, 1920, **111**, 193.

that the hydroxide in its acidic and basic forms acts as its own coagulator, and so has little tendency to be coagulated by and adsorb foreign ions. If dehydration occurs subsequent to coagulation any foreign radicles present would probably be expelled at the same time. In certain cases, however, marked adsorption may occur. A good quantitative separation of copper and zinc, for instance, cannot be obtained by precipitation with excess of caustic soda or potash. Although the bulk of the zinc hydroxide dissolves in the excess, the copper oxide always retains a little, owing no doubt to its having taken part in the above indicated amphoteric neutralization of the copper hydroxide. Other similar well-known cases of separations which are unsatisfactory quantitatively but work well enough qualitatively may possibly be explicable in a similar way. Such cases are the separation of ferric iron from aluminium with excess of caustic soda and the separation of ferric iron from manganese, zinc, nickel, or cobalt by means of ammonium hydroxide in presence of ammonium salts. In some of these cases atmospheric oxidation plays a part.[1]

The well-known fact that many hydroxide precipitates gradually become less reactive, and less readily soluble in acids, may well be due in part to some such process as that outlined for copper hydroxide, though not proceeding to the same degree of dehydration. There seems little doubt at any rate that it is connected with some loss of water either from the sol particles or from the gel.

A similar change seems to be the cause of the instability of the solutions of many hydroxides (e.g. that of aluminium) in caustic soda, or in ammonia (e.g. chromium hydroxide) or even in acids (e.g. the slow hydrolysis of ferric chloride solutions) although the type of crystalloidal compound initially present in the solution is quite different in the three cases. If the concentration and proportion of caustic alkali, ammonia, or acid are not excessive, the metallic hydroxide molecules formed by hydrolysis gradually unite to form highly disperse sol particles which in time coalesce, undergo

[1] Compare Treadwell, *Schweiz. Chem. Zeit.*, 1918, **2**, 59, 71.

some dehydration, and ultimately separate in a relatively dense and unreactive condition.

Gradual loss of water accompanied by decreased reactivity and decreased tendency to revert to the sol condition is shown by practically all inorganic colloids and is much accelerated and intensified by desiccation. Use is sometimes made of this fact during analysis as for instance in the estimation of silica which is always evaporated to dryness before filtration so that it may become less soluble (colloidally and otherwise). The phenomena observed are somewhat complex, and have been studied especially by van Bemmelen.[1]

Quantitative Precipitations and Separations as Oxide or Hydroxide

Owing to the well-marked amphoteric character of most of the metallic hydroxides precipitation by means of sodium or potassium hydroxide is satisfactory as a quantitative method in only a few cases. In practice it is limited to copper, ferric iron, nickel, and cobalt (as $Ni(OH)_3$ and $Co(OH)_3$). The less basic solution of ammonia has a much smaller tendency to bring out the acid character of an amphoteric hydroxide than has soda or potash, but even it can be used as a quantitative precipitant only in very few cases—those of ferric iron, aluminium, and chromium.

This is owing to the fact that ammonia dissolves many hydroxide precipitates, not by bringing out their acid character but by the formation of complex ammonia compounds, such as $Cr(NH_3)_6(OH)_3$, which will be considered later.

The Estimation of Copper as Cupric Oxide

To the hot acid solution of the cupric salt, which must be free from organic substances and ammonium salts, there is added a small excess of a solution of potassium hydroxide. A greenish-blue precipitate of cupric hydroxide is obtained which, however, soon loses water and is converted into dark brown cupric oxide.

The mixture is kept heated nearly to the boiling point until the change is completed. The precipitate is then

[1] See his work on silicic acid. *Z. anorg. Chem.*, 1896, **13**, 233–356.

filtered off and well washed, first by decantation with boiling water until the wash waters are no longer alkaline. The precipitation should be carried out in a porcelain dish, as glass is more attacked by the hot alkali. It will often be found that a little copper oxide remains very tenaciously attached to the dish. This is best removed as follows, after rinsing the rest of the precipitate on to the filter. A couple of drops of dilute nitric acid are added, and by means of a glass rod this is spread over all those parts of the dish to which any oxide has adhered and should suffice to dissolve it all. The solution so obtained is caused to collect near the lip of the dish by inclining the latter, it is heated to boiling over a small flame, and precipitated by adding potash solution drop by drop until the precipitate turns brown. The precipitate is then quickly rinsed into a separate small filter paper and thoroughly washed with boiling water.

The precipitate is dried and detached from the filter paper. The latter is ignited separately, the ash treated with a drop or two of nitric acid, which is then carefully evaporated and the residue ignited. Any reduced copper is thus converted into nitrate, and this on ignition gives cupric oxide. The rest of the copper oxide is then added, and the whole is ignited and weighed. The method gives excellent results when properly carried out, though slightly high results are apt to be obtained, for it is almost impossible to wash out completely any alkali and salts held adsorbed by the precipitate.

A large excess of potash should be avoided in this precipitation, because cupric oxide dissolves slightly in strong alkali giving a blue solution. It appears to be better to use potassium hydroxide rather than sodium hydroxide, as it seems to be less strongly adsorbed by the cupric oxide; the excess is therefore washed out more easily.

Precipitation of Nickel and Cobalt as Hydrated Peroxides with KOH and Bromine

The nickel (or cobalt) solution is heated to boiling in a porcelain dish and precipitated by addition of a solution of pure potash to which bromine water has just been added.

A moderate excess of alkali should be used.

A nearly black flocculent precipitate of the nickelic or cobaltic oxide is obtained which is filtered and washed (first by decantation) with hot water. The precipitate is ignited (filter paper separately), and in the case of nickel weighed as NiO. It is better to moisten the ignited oxide with water and test with litmus paper to see if any alkali is present. If so it must be washed and again ignited and weighed.

Nickel can be precipitated as hydrated NiO by the action of potash alone, but the green precipitate filters very badly and is liable to go into colloidal solution during the washing. Moreover, the precipitate adsorbs potash very tenaciously (it can be removed by washing the ignited precipitate). The much denser nickelic oxide does not suffer appreciably from either of these drawbacks. It is, however (in common with the NiO obtained by precipitating with potash alone), liable to contain a little silica (from the dish), and for very accurate work this must be estimated and taken into account.

Cobalt is precipitated exactly as above in the form of hydrated cobaltic oxide, which, however, is not quite so easy to deal with as the corresponding nickel compound. It has some tendency to pass through the filter on washing, but this can be avoided by using the very best and finest grained filter paper. After ignition the oxide must be washed with water to remove alkali, which, owing to strong adsorption, can never be completely removed before ignition. The washed oxide is finally ignited in a current of dry hydrogen, either in a Rose crucible or in a porcelain boat contained in a tube, and weighed as metal.

As the nickel oxide and cobalt metal are always liable to contain silica derived from the action of alkali on the porcelain dish, they should, after weighing, be dissolved in the crucible by warming with a little strong hydrochloric acid. The solution is evaporated to dryness, the residue moistened with a drop or two of concentrated hydrochloric acid, water added, and any silica filtered off and its weight deducted from that of the NiO or Co.

As is well known, cobalt in its chemical behaviour shows

considerable resemblance to iron, while the resemblances between iron and nickel are much less pronounced.

The resemblances between the oxides are, however, very marked in both cases. By precipitation under suitable conditions from aqueous solutions the three metals give respectively the hydrated oxides:—

FeO . aq.	CoO . aq.	NiO . aq.
Fe_2O_3 . aq.	Co_2O_3 . aq.	Ni_2O_3 . aq.

It is to be noted, however, that according to Bellucci and Clavari[1] both Ni_2O_3 and Ni_3O_4 are in reality mixtures of NiO with an oxide NiO_2.

The oxides of the divalent metals are very similar as regards solubility—they can all be precipitated by potash or soda, but not by ammonia in presence of ammonium salts—as the solubility is such that the hydroxyl ion concentration in the latter solutions is not sufficient to yield a precipitate. FeO oxidizes very readily to Fe_2O_3; CoO less readily and NiO still less readily, while in agreement with this the stability of Fe_2O_3 is greatest and that of Ni_2O_3 least.

Salts derived from Fe_2O_3 are quite stable; only a few very unstable simple salts derived from Co_2O_3 are known (but many very stable complex derivatives), while none derived from Ni_2O_3 have been obtained.

When a cobalt or nickel salt solution is treated with potash and bromine (that is to say with a strongly oxidizing solution containing hypobromite) some of the $Co^{\cdot\cdot}$ or $Ni^{\cdot\cdot}$ ions are oxidized to the corresponding $Co^{\cdot\cdot\cdot}$ or $Ni^{\cdot\cdot\cdot}$ ions probably by the BrO' ion. Thus $2Co^{\cdot\cdot} + 2H^{\cdot} + BrO' = 2Co^{\cdot\cdot\cdot} + Br' + H_2O$. The $Co^{\cdot\cdot\cdot}$ or $Ni^{\cdot\cdot\cdot}$ ions are at once practically entirely precipitated as the very insoluble hydroxides by the large excess of OH' ions present. According to Howell,[2] the precipitates obtained by the action of sodium hypochlorite and alkali on solutions of cobalt or nickel salts are mixtures of hydrated Co_2O_3 and CoO_2, or Ni_2O_3 and NiO_2.

Fe, Co, and Ni form also the oxides Fe_3O_4, Co_3O_4, and Ni_3O_4, the stability of which rapidly decreases in the order given. Now at any given temperature each of the three

[1] *Atti R. Accad. Lincei*, 1905, [5], **14**, ii, 234.
[2] *J. Chem. Soc.*, 1923, **123**, 65, 669, 1772.

oxides of these three metals has a definite dissociation pressure—which is not exactly known in any of the cases. We do know this, however, that when strongly ignited over a good bunsen the dissociation pressure of Fe_2O_3 is much less than the partial pressure of atmospheric oxygen, so that under such treatment Fe_2O_3 is unaltered while FeO or Fe_3O_4 absorb oxygen more or less rapidly until converted into Fe_2O_3. At a very high temperature Fe_2O_3 loses oxygen and is converted into Fe_3O_4. In the case of cobalt under similar conditions of ignition one gets a mixture of CoO and Co_3O_4, which varies according to the exact conditions showing that the decomposition pressure of Co_3O_4 is about equal to the atmospheric oxygen pressure under these conditions. This is why cobalt has to be weighed as metal.

In the case of nickel under the same conditions the oxides Ni_2O_3 and Ni_3O_4 have decomposition pressures considerably greater than the atmospheric oxygen pressure, and they are therefore soon converted into NiO.

Determination of Aluminium as Al_2O_3

Other metals which are precipitated by ammonia must be absent, as well as phosphoric acid.

The acid solution containing the aluminium is heated to 66° and precipitated at that temperature by the addition of a slight excess of ammonia. The solution is then heated to boiling and filtered.[1]

The aluminium hydroxide obtained under these conditions filters well and fairly rapidly, whereas the filtration is often exceedingly tedious if the precipitation is carried out from a boiling solution or in the cold with subsequent heating to boiling, as is often recommended. The precipitate is thoroughly washed with hot water containing a little ammonia and ammonium nitrate to minimize any tendency of the precipitate to become slimy or pass through the filter. It is advantageous to wash by decantation several times before transferring the precipitate to the filter. It should be ignited wet and weighed as Al_2O_3. Strong ignition over the blowpipe should be used finally and, owing to the tendency of ignited

[1] Taylor, *Chem. News*, 1911, **103**, 169.

Al_2O_3 to absorb moisture from the air, it should be weighed as rapidly as possible and then ignited and weighed again to make sure that a constant weight has been obtained. There seems little doubt that this method of precipitating aluminium hydroxide, which has been found empirically to give the densest and most easily filterable precipitate, does so because at 66° the mobility of the simple $Al(OH)_3$ molecules first formed and their true solubility is such that they are able to form relatively large crystalline particles before coagulation by the electrolytes present takes place. At other temperatures coagulation occurs before such large particles have been formed, so that the resultant precipitate has a much greater power of adsorption for water, salts, etc., and is of a gelatinous nature.[1]

According to Fresenius, aluminium hydroxide precipitated in the cold is slightly soluble in excess of ammonia, but this solubility is greatly diminished by ammonium salts. This suggests that the solubility is due to the hydroxyl ions from the ammonium hydroxide bringing out the acid character of the aluminium hydroxide and causing the formation of some aluminate, whilst ammonium salts prevent this by lowering the hydroxyl ion concentration.

It is probable, however, that the slight solubility of aluminium hydroxide in ammonia solution is best regarded as a purely colloidal phenomenon, and due to peptization by the hydroxyl ions. Ammonium salts, by lowering the hydroxyl ion concentration, would have a depressing action on the peptization. It is unlikely that in weak ammoniacal solutions the action would go further than simple peptization, though in strong caustic alkali the sol is converted into a crystalloidal solution.[2] It is in any case improbable that the slight solubility in ammonia is due to formation of complex ammonia compounds, for no such derivatives of aluminium are known in aqueous solution.

When aluminium is precipitated as above by Taylor's method it does not appear to be necessary to add the ammonium salts usually recommended for precipitation

[1] See *ante*, Chapter VII, page 104.

[2] See *ante*, Chapter VIII, page 120.

from nearly boiling solutions. The hydroxide precipitated at 66° is dense enough to be relatively insensitive towards peptization. It is inadvisable to use more than a slight excess of ammonia, however, and the solution should be tested with litmus paper to see when this has been added.

The optimum conditions of acidity for the complete precipitation of aluminium by ammonia have been studied by Blum [1] who states that $[H^+]$ should be between $10^{-6\cdot5}$ and $10^{-7\cdot5}$.

Determination of Iron as Fe_2O_3

If the iron is not all present in the ferric state the solution must be heated with sufficient nitric acid to oxidize any ferrous iron. The solution is then heated to about 70°, precipitated by adding a small excess of ammonia, raised to the boiling point, and the precipitated ferric hydroxide allowed to settle. The supernatant liquid is run through the filter paper, and the precipitate then transferred to, and thoroughly washed on, the filter with hot water. The precipitate is then dried and strongly ignited over a good bunsen burner. It should not be ignited over the blowpipe, as at high temperatures the dissociation pressure of ferric oxide becomes greater than the partial pressure of oxygen in the air and some Fe_3O_4 may be formed.

As ferric hydroxide is a positive colloid its coagulation is brought about by negative ions. It is, therefore, difficult to wash the precipitate entirely free from adsorbed acid radicles. So far as the estimation of the iron is concerned, this is of little moment in most cases, as the acid radicles are either decomposed (e.g. NO_3, SO_4) or replaced by oxygen (e.g. Cl)[2] on ignition so that pure Fe_2O_3 is obtained. When, however, the precipitation and separation of the ferric hydroxide is preliminary to the estimation of sulphate in the filtrate as in Lunge's method for the estimation

[1] *J. Amer. Chem. Soc.*, 1916, **38**, 1282.

[2] Possible loss of $FeCl_3$, suggested by Classen (*Ausgewählte Methoden der Analytischen Chemie* (1901), vol. **1**, p. 445), seems very unlikely unless much chlorine remained in the precipitate. The chlorine is much more likely to be eliminated either as HCl by the action of water during drying and ignition or as Cl_2 by the action of oxygen during ignition.

of sulphate in presence of iron,[1] it is most important that no sulphate radicle shall be carried down by the ferric hydroxide. This is achieved by using a moderate excess of ammonia in the precipitation and heating for 10–15 minutes at 60° to 70°, but not boiling, before filtration. The mass effect of the OH′ ions practically entirely prevents adsorption of SO_4'' ions, though, even with considerable excess of ammonia, heating to boiling seems to facilitate some interchange between SO_4'' ions and OH groups from the ferric hydroxide precipitate and must therefore be avoided.

Separation of Iron and Aluminium by means of Caustic Soda

Under ordinary circumstances ferric iron is always precipitated with ammonia and not with potash or soda, because in the latter case the precipitated hydroxide is liable to be contaminated with adsorbed alkali, which is difficult to remove by washing. In some cases, however, such as in the analysis of clays or where a very high order of accuracy is not required and it is desired to estimate iron and aluminium in presence of one another, use is made of the fact that aluminium hydroxide dissolves in excess of potash or soda, whereas ferric hydroxide does not.

The solution containing the iron and aluminium is nearly neutralized and gradually added to a considerable excess of almost boiling caustic soda solution (about twice normal) in a platinum basin. If platinum is not available, porcelain, which is less attacked by alkali than glass, can be used, but there is then danger of contamination with silica.

The mixture is well diluted with water before filtering off the insoluble ferric hydroxide, which must be well washed with hot water. It is often found that there is a tendency for a small amount of ferric hydroxide to pass through the filter paper in colloidal suspension in the strongly alkaline solution. Any error so caused tends to balance another error, due to the fact that the ferric hydroxide always retains a little aluminium hydroxide.

As the ferric hydroxide obstinately retains adsorbed

[1] See *ante*, Chapter VII, p. 113.

alkali, it is redissolved in a little hot hydrochloric acid and reprecipitated with ammonium hydroxide.

The caustic soda filtrate from the ferric hydroxide is acidified with hydrochloric acid and the aluminium precipitated with ammonium hydroxide.

The retention of a small amount of alumina by the ferric hydroxide is probably due to slight interaction between the acidic form of the aluminium hydroxide and the basic form of ferric hydroxide. Though the acidic character of the latter is very feeble, the fact that it is peptized to some extent by strong alkali, and also adsorbs some of this very strongly, are indications that it has a tendency to act as an acid even in presence of water.

Estimation of Chromium as Cr_2O_3 after Precipitation as Hydroxide

The solution, which must contain all the chromium in the trivalent condition, is heated nearly to boiling, and ammonia solution added in slight excess. The temperature is maintained until the solution is colourless and practically all excess of ammonia has been driven off. The solution should remain faintly alkaline to litmus paper. The precipitate is well washed by decantation, then transferred to a filter, washed thoroughly with hot water, dried, ignited, and weighed as Cr_2O_3.

The precipitation of the chromium is not complete in presence of organic matter, either owing to this acting as a protective colloid, or owing to the formation of complex ions, according to the nature of the organic matter. If the precipitation of the chromium hydroxide has been carried out in glass vessels the precipitate is very liable to retain traces of silica owing to adsorption—and this applies to most other hydroxide precipitates.

Chromium hydroxide is soluble to a small extent in ammonia owing to formation of complex chrome-ammonia compounds, such as $Cr(NH_3)_6(OH)_3$, which impart a purple colour to the solution. These purple ammoniacal solutions are, however, unstable, and even at the ordinary temperature decompose slowly with deposition of the dissolved hydroxide.

This process is much hastened by heating, and occurs the more readily the less ammonia is present. The removal of ammonia accordingly promotes the decomposition of the complex, and hence it is best to drive off nearly all excess of ammonia. The instability of solutions of chromium hydroxide in ammonia has already been referred to on page 122.

The Estimation of Tin as SnO_2 after Separation as so-called Metastannic Acid

When tin or alloys containing tin are oxidized with strong nitric acid the tin is converted into metastannic acid, which is insoluble in nitric acid. This gives a method for estimating tin in alloys such as bronze or soft solder which contain neither arsenic nor antimony.

About half a gram of the alloy is placed in a small covered beaker and 3 to 4 c.c. of strong nitric acid (1·5 gravity) added. About 2 c.c. of water is then allowed to run in slowly, so that attack of the alloy occurs gradually. When the reaction is finished the mixture is heated to boiling and diluted with 25 c.c. of hot water. After settling, the mixture is filtered, best through a hardened filter, and the metastannic acid well washed with hot water to which a little ammonium nitrate has been added. After drying, the precipitate is detached from the paper, which is burned separately. In order to reconvert any reduced metal to oxide the ash is treated with a drop of nitric acid in a weighed porcelain crucible, dried, and ignited. The rest of the precipitate is then added to the ash, and the whole is ignited finally over the blowpipe and weighed as SnO_2. The latter has to be examined for its purity, as described below.

Lead, copper, etc., when present are estimated in the filtrate from the metastannic acid by suitable methods. As a rule, the first step consists in evaporation of the filtrate with sulphuric acid to eliminate nitric acid.

Metastannic acid is a colloid and is liable to go into colloidal solution as soon as it is washed free from electrolytes, although its tendency to do this varies a good deal according to the exact conditions under which it has been separated. Metastannic acid, however, is always troublesome to filter unless

a very close-grained filter is used, and it should not be washed with pure water.

Stannic acid can be obtained either by the action of alkalies on solutions of stannic salts (so-called α-stannic acid) or by the action of strong nitric acid on tin or tin alloys (so-called β- or meta-stannic acid). The substances prepared by these two methods show such marked differences in their chemical behaviour that they were long regarded as different compounds.

The freshly prepared α-stannic acid is readily soluble in mineral acids and alkalies, while the β-stannic acid—especially if it has been prepared some time—is either insoluble or soluble only with great difficulty in acids, though more easily in alkalies.

The work of numerous investigators, including van Bemmelen [1] and quite recently Collins and Wood,[2] has shown however, that all intermediate stages occur between the extreme α and β forms. The differences in chemical reactivity which are observed are due to the gradual loss of water, and condensation between the molecules of stannic hydroxide. The decrease in reactivity during the gradual transition from the α to the β form is very probably associated with interaction between the acidic and basic forms of stannic hydroxide, as Collins and Wood suppose. The phenomenon is, however, not restricted to stannic acid, though particularly well marked with that compound. A similar behaviour is observed to a greater or less extent with almost all hydroxide and also sulphide precipitates.

All inorganic colloid precipitates, indeed, tend to become less reactive on ageing, and though the amphoteric character of most hydroxides and sulphides doubtless facilitates the process, it occurs also in cases where an amphoteric character can hardly be assumed. It is in fact associated with a gradual increase in the molecular complexity of the particles of which the gel is built up, no matter what the cause of the increased

[1] *J. pr. Chem.*, 1881, **23**, 324 : *Z. anorg. Chem.*, 1900, **23**, 111; 1905, **45**, 83.

[2] *J. Chem. Soc.*, 1922, **121**, 441, 1122, and 2760, and Weiser, *J. Physical Chem.*, 1922, **26**, 654.

complexity. As the molecular complexity increases the surface available for chemical interaction with a liquid, or gas diminishes, and this is partly, if not mainly, the cause of the diminished reactivity.

The behaviour of the stannic acids towards mineral acids, though complex, is most instructive. The freshly precipitated α acid dissolves readily in mineral acids forming solutions—which are in the main crystalloidal—of stannic salts. The β acid, however, behaves rather differently. Most acids (as also alkali) are markedly adsorbed by it, and the manner in which it removes acids from solutions of different concentrations is typical of an adsorption process. So long as excess of mineral acid is present the metastannic acid is kept in the coagulated condition and remains insoluble. If the acid is largely diluted or removed by washing then in the case of hydrochloric acid the metastannic acid goes into colloidal solution—being in fact peptized by the acid. Excess of mineral acid (including hydrochloric acid) added to the solution so obtained will cause the stannic acid to separate again as a gel.

With sulphuric acid, metastannic acid shows a much smaller tendency to be peptized and even less with nitric acid. In the case of sulphuric acid this may be connected with the divalent character of the SO_4'' ion and its somewhat lower electro-affinity, which would make H_2SO_4 a better coagulator and worse peptizing agent than HCl for stannic acid. Such an argument fails in the case of nitric acid, however, and the very small tendency for metastannic acid to be peptized by nitric acid may be owing to the coagulating effect of metastannic acid itself on any solution which started to form. Collins and Wood [1] found that metastannic acid does coagulate its own solutions.

The stannic acid solutions in course of time pass into crystalloidal solutions if the amount of acid present and the temperature are suitable. The sol stage is very persistent in the case of metastannic acid, but with freshly precipitated α-stannic acid is not so easily observed. It is probable that

[1] *Loc. cit.*

in all cases where a gel is dissolved to form a crystalloidal solution the first stage in the process consists in a peptization of the gel and formation of a sol.

Examination of the Ignited SnO_2 for Purity

Whether or not such examination is necessary will depend largely upon the other metals present in the alloy being analysed. The SnO_2 is certain to contain iron if that was present in the alloy, and may contain also traces of copper and other metals. Even when only very little iron is present in the alloy a large proportion of it is carried down by the metastannic acid, whereas very little copper or lead is carried down even when the alloy is rich in those metals. This rather indicates that the amount of the contaminating metal adsorbed by the metastannic acid is in some way related to the extent to which the salts of that metal are hydrolysed. In presence of excess nitric acid, copper or lead salts would not be appreciably hydrolysed, whereas ferric salts would be. Colloidal ferric hydroxide produced by such hydrolysis might readily take part in the amphoteric neutralization of the stannic acid and so be carried down by it.

The ignited SnO_2 is ground as finely as possible in an agate mortar, losing as little as possible in the process, and mixed in a porcelain crucible with six times as much of a mixture of equal parts anhydrous sodium carbonate and flowers of sulphur—a mixture which reacts as though it consisted of sodium polysulphide. The mixture is heated over a small flame in the covered crucible until the excess of sulphur is nearly removed. It requires some practice to hit off this point, which may be taken as reached when the smell of SO_2 ceases to be strong and when the blue sulphur flame round the lid of the crucible is scarcely visible.

After cooling, the contents of the crucible are treated with a small quantity of hot water. The tin goes into solution as sulphostannate, Na_2SnS_3, while iron, copper, etc., remain insoluble as sulphides. These are filtered off, washed with H_2S water, dried, ignited, and weighed as oxides. The total weight of contaminating oxides so obtained is deducted from the original weight of ignited SnO_2 before the percentage

of tin is calculated. They are dissolved in a small quantity of hot strong hydrochloric acid, and the solution added to the filtrate from the original metastannic acid.

If the heating of the sodium carbonate + sulphur mixture has not been continued long enough to decompose the major part of the polysulphide the solution obtained on subsequent addition of water may be deep brown or nearly black in colour owing to the sulphides of iron, etc., remaining in colloidal suspension. They are peptized by the polysulphide ions and can be precipitated by the addition of sodium sulphite, which reacts with the polysulphides to form thio-sulphate and mono-sulphide.

It may happen that not all the SnO_2 is converted into sulphostannate after one fusion. This is detected by the gritty nature of the insoluble residue obtained on the addition of water, which can be felt on stirring with a rounded glass rod. In such cases the insoluble residue must be filtered off and again fused with the mixture of sodium carbonate and sulphur.

Determination of Silicic Acid in a Silicate

If the silicate is one which can be decomposed by acid directly (e.g. blast furnace slag), the finely powdered material (1 gram) is treated with 10 c.c. of water in a small wide beaker. The water is gently boiled and 15 c.c. of concentrated hydrochloric acid added at such a rate that the boiling is not disturbed. This mode of dissolving siliceous bodies prevents the undissolved portions being coated over with gelatinous silica.[1] When decomposition is complete the solution is evaporated to approximate dryness on the water bath. The subsequent procedure is then identical with that given below for the analysis of silicates which are insoluble in acids.

A silicate which is not decomposed by hydrochloric acid must first be fused with sodium carbonate.

The Grinding of the Sample.

The success of the fusion depends very largely upon excessively fine grinding of the silicate, especially if this is of

[1] Brearley and Ibbotson, *Analysis of Steel-Works Materials* (1902), p. 224.

a refractory nature. It is first roughly crushed into small fragments. This can be done in a steel mortar, but according to Hillebrand [1] such treatment is liable to lead to contamination by particles of metal. He recommends the use of a hard steel plate 10 cm. square and about 4½ cm. thick on which is placed a steel ring 2 cm. high and about 6 cm. in diameter to prevent undue flying of fragments when the sample is broken by a hardened steel hammer. The sample crushed in this way is ground to an impalpable powder in an agate mortar. The final grinding should be carried out with very small quantities at a time, and continued until the powder does not feel gritty when rubbed between the first finger and thumb.

The Fusion.[2]

One gram of the finely ground silicate sample is thoroughly mixed with four to six times its weight of ignited pure sodium carbonate in a large platinum crucible. The lid is placed on the latter, and the crucible is heated for a considerable time over a small flame in order to drive off all moisture from the contents. The temperature is then gradually raised until finally the crucible is heated with the full flame of a Teclu burner or a blowpipe. As soon as the molten contents of the crucible have become quiet, showing that all evolution of carbon dioxide has ceased, the heating can be stopped. During the fusion, in order to ensure that there shall be an oxidizing atmosphere within the crucible,[3] the flame should not be directed vertically against the bottom of the crucible, but at an angle against the side and bottom, nor should the flame be allowed to envelop the whole crucible. When fusion is complete the crucible is gripped by the tongs, which should be platinum-tipped, and dipped in cold water, but without allowing any of the latter to enter the crucible. After this sudden cooling the solidified fusion cake can usually be readily removed by tapping the inverted crucible. A

[1] Hillebrand, *Some Principles and Methods of Rock Analysis* (1900), p. 31, *Bulletin No.* 176 *of the United States Geological Survey.*

[2] See Mellor, *A Treatise on Quantitative Inorganic Analysis* (1913), p. 163.

[3] Hillebrand, *loc. cit.*, p. 51.

better method still, according to Hillebrand, is to grip the crucible by means of bow-shaped (platinum-covered) crucible tongs and, whilst the contents are solidifying, to spread them in a thin sheet over the sides and bottom by an appropriate rotating motion with the arm. The thin crusts obtained in this way generally separate readily from the crucible and are decomposed by acid more quickly than is the solid cake obtained by the other method.

The contents of the crucible are placed in a rather tall covered beaker with some water, and hydrochloric acid of 1·1 specific gravity is added in excess. There is vigorous evolution of carbon dioxide, which slackens as the dissolving material becomes coated over with the silica which separates. The small quantity of material still adhering to the crucible is dissolved in water and hydrochloric acid and rinsed into the beaker. The latter is placed on the water bath and when disintegration, assisted with gentle pressure of a blunt glass rod, is complete, the contents are transferred to a roomy porcelain (or, better, platinum) basin and evaporated to dryness on the water bath.

After evaporation the residual mass is moistened with concentrated hydrochloric acid and left to stand at the ordinary temperature for 20 or 30 minutes, in order to redissolve any basic oxides, such as Fe_2O_3, which may have been formed by hydrolysis during the evaporation. When solutions of salts of the less basic oxides with volatile acids are evaporated there is almost invariably some formation of metallic oxide, or at least of insoluble basic salts intermediate between the oxide and the normal salt.

Water, 50–100 c.c., is then added to the contents of the basin, which is heated on the boiling water bath for a short time. After the silica has settled the solution is filtered and the silica thoroughly washed with hot water, first by decantation and then on the filter paper. The filtrate may still contain up to 2 per cent of the total silica originally present, and must be evaporated to complete dryness and treated as before to render this dissolved silica insoluble.[1]

[1] If a complete analysis of a rock or silicate is being made, this second evaporation can be dispensed with, provided that silica is determined in

The silica so obtained is filtered through a second small filter and both quantities of silica are ignited and weighed together. The filtrate from the second lot of silica may still contain up to 0·15 per cent of the total silica, but this, as a rule, can be neglected.

In order to obtain the silica perfectly anhydrous before weighing it is best to ignite it to constant weight in a platinum crucible over a Teclu burner or the blowpipe. Silicic acid being a colloid, one would expect it to adsorb certain substances to a considerable extent, as it actually does. The ignited silica obtained as above is never pure, and is especially liable to contain ferric and aluminium oxides. After ignition and weighing the silica is therefore treated with 2 to 3 c.c. water, one drop of concentrated sulphuric acid and 3 to 5 c.c. of pure hydrofluoric acid. (For small quantities of silica smaller quantities will, of course, be used.) The platinum crucible and contents are then heated on the water bath or hot plate until only the sulphuric acid remains, and that is then driven off by careful heating with a free flame. The SiO_2 is entirely removed as SiF_4 by this treatment, and after strong ignition the residual oxides (Fe_2O_3, Al_2O_3, etc.) are weighed and their weight deducted from the original weight of impure SiO_2.

When a complete analysis of the silicate is being made these oxides from the silica must either be analysed separately or dissolved by digestion with some HCl and added to the filtrate from the silica before proceeding with the separation of the bases present.

The behaviour of silicic acid resembles in many respects that of the stannic acids. The gelatinous silica which separates when the silicate is treated with acid is easily peptized, yielding a highly disperse sol. This indicates that the primary particles of which the gel is composed are exceedingly small, and they are evidently highly hydrated from the character of the gel. As the silicic acid gel loses

the precipitate (Fe_2O_3, Al_2O_3) subsequently obtained with ammonia. All silica remaining in solution is carried down by the ferric hydroxide + aluminium hydroxide precipitate (Wells, *J. Amer. Chem. Soc.*, 1922, **44**, 2187).

water it becomes at the same time much less capable of peptization. It is necessary to evaporate to dryness the mixture in which the silicic acid is suspended in order to dehydrate the silica partially before filtration; otherwise a large proportion of the silica would remain in solution and dissolve during the washing. As it is, owing to the tenacity with which the silica adsorbs water it is not possible to dehydrate it sufficiently by one evaporation when much is present. Consequently, the filtrate always contains a little silica and has to be evaporated a second time. In order to hasten the dehydration and make one evaporation suffice textbooks frequently suggest heating the evaporation residue at 110–120° before proceeding further. According to Hillebrand,[1] even this does not render all the silica insoluble while the silica so obtained is considerably less pure. He strongly recommends double evaporation on the water bath as being the best and most accurate method.

There are a few points of some theoretical interest in connexion with the fusion of silicates with alkali carbonate which may be referred to. The melting-point of sodium carbonate is about 810° while that of potassium carbonate is about 885°,[2] but the melting-point of either is lowered by the presence of the other and the equimolecular mixture has the lowest melting-point of any mixture—at about 690°. The so-called " fusion mixture " is an equimolecular mixture of the two carbonates, and is frequently used instead of pure sodium carbonate for alkali fusions. Its use is, however, unnecessary, for there is no difficulty in maintaining a high enough temperature to obtain a fluid melt with sodium carbonate alone. It has, moreover, been pointed out by Dittrich[3] that potassium salts are washed from the different precipitates, later on, with greater difficulty than sodium salts. In quantitative work, therefore, the use of sodium carbonate alone is preferable to that of " fusion mixture ".

For a complete understanding of the reactions which occur during the fusion of silicates with sodium carbonate

[1] *Loc. cit.*, p. 52.

[2] Le Chatelier, *Bull. Soc. Chim.*, 1887, (2), **47**, 300.

[3] *Anleitung zur Gesteinanalyse*, Leipzig (1905), p. 5.

much more information is required than is actually available. Elaborate Phase Rule investigations of the more or less complex systems consisting of sodium carbonate, silica, various metallic oxides, and other acids (phosphoric, sulphuric, etc.) would have to be carried out before one could say what products were obtained as a result of the alkali fusion. This, of course, applies equally to other fusions with sodium hydroxide, sodium peroxide, etc. A large amount of such work has actually been carried out in connexion with cement clinker and silicate mineral formation by the Geophysical Laboratory at Washington and published in their memoirs.

Suffice it to say that, as a result of the high temperature fusion with a large excess of alkali, the acid-insoluble silicates, etc., are broken down and converted into mixtures of alkali-rich silicates, together with alkali aluminates, manganates, ferrates, etc., which are readily decomposed by acids.

Distinction between Soluble and Insoluble Silica in Soil Analyses

Attempts to distinguish so-called soluble or amorphous silica from other forms have long been made in soil and clay analyses, and many different solutions and methods have been put forward for the purpose. They all give different results, however, and none of them are trustworthy.[1] The fact of the matter is that most soils and clays contain various transition stages between quartz and colloidal silica. The differences in reactivity of these made use of in the attempt to separate them are of degree only and not of kind, so that the results obtained must depend most intimately on concentration, temperature, time of contact with the extracting solution, state of division of the silica, etc., and no complete separation can be possible.

In the case of clays to be used in some technical processes, it is probably of some value to be able to make an approximate estimation of the silica present as quartz. The clay is heated with strong sulphuric acid to decompose the kaolin, water is then added, and the insoluble residue filtered off. This

[1] von Horváth, *Z. anal. Chem.*, 1916, **55**, 513; *Bied. Zentr.*, 1918, **47**, 97.

residue is then extracted with a solution containing 10 grams of crystallized sodium carbonate and 1 gram of sodium hydroxide per 100 c.c. This treatment practically dissolves only the silica resulting from decomposition of the kaolin,[1] together with any amorphous silica originally present in the clay, while the quartz remains insoluble. For full details the reader is referred to Lunge-Keane, *Technical Methods of Chemical Analysis*, 1908, vol. **1**, part 2, pp. 585–8, where a discussion of other proposed methods is also given.

Estimation of Silicon in Alloys

In metals and alloys silicon is usually present as silicides, but sometimes (e.g. in aluminium) partially as free silicon. In either case it is separated as silicic acid and weighed as silica after oxidation by suitable means. The precise method of procedure depends on the metal or alloy being analysed. As an illustration, the determination of silicon in ferro-silicon containing 10 to 15 per cent silicon will be given.[2] For ferro-silicon richer in silicon other methods of decomposition must be used.[3] Sufficient of the sample is ground as finely as possible in an agate mortar and two grams are weighed out for the analysis. 50 c.c. of concentrated hydrochloric acid are added, followed by 10 to 20 c.c. of nitric acid (conc.). The mixture is boiled until decomposition of the alloy is complete, which takes about 15 minutes, about twice the volume of water is added, and the silicic acid is filtered off at once. It is washed with cold dilute hydrochloric acid, ignited and weighed as SiO_2 in a platinum crucible. The silica so obtained is white, and the residue after treatment with hydrofluoric acid does not exceed two or three milligrams. To the result obtained 0·1 per cent should be added as a correction for the soluble silica remaining in the filtrate. This soluble silica could, of course, be removed by evaporation

[1] It is this silica resulting from the action of acid on the kaolin or other silicate which is usually referred to as soluble silica in analyses of soils, clays, or rocks.

[2] See Brearley and Ibbotson, *The Analysis of Steel-works Materials* (1902), p. 117.

[3] Brearley and Ibbotson, *loc. cit.*, p. 120.

of the filtrate to dryness as in the silicate analysis previously described, but this requires considerable time and is not necessary in most cases, since the silica formed as a result of the oxidation with nitro-hydrochloric acid is in a comparatively dense state and practically insoluble in the strong acid. After dilution, especially if the solution is boiled, a considerable amount will pass into solution in the course of a few hours, hence the need for filtering it off directly after the dilution. This procedure is advantageous also for another reason: if the solution obtained by the nitro-hydrochloric acid is evaporated to dryness to render all the silica insoluble, the residue treated with hydrochloric acid and the silica then filtered off, it is found that the silica obtained is contaminated with a considerable amount of oxide of iron. If one operates as described above, a silica almost free from iron is obtained. This suggests that during the evaporation and consequent partial dehydration of the silicic acid the adsorbed iron compounds actually share in the dehydration process with formation of indefinite SiO_2–Fe_2O_3 complexes, from which it is impossible to remove the iron by washing. It is an illustration of the important part played by dehydration in the contamination of precipitates by so-called adsorption.

The Estimation of Tungsten as WO_3

In view of the modern uses of tungsten in the manufacture of special steels and in the electric lamp industry, its estimation is an important one. It is usually separated from solution either as tungstic acid or as mercurous tungstate, and weighed as WO_3 after ignition. The separation as tungstic acid will be considered as it is the most generally applicable.

The initial difficulty consists in attacking and getting into solution the material under examination. The most suitable method depends on the composition of the material. Sometimes it can be decomposed satisfactorily by digestion with nitro-hydrochloric acid, in other cases a preliminary fusion (e.g. with sodium carbonate) may be necessary in order to convert all tungsten into soluble sodium tungstate,

or some other method may be better. Methods of analysis suitable for the majority of cases likely to occur in practice will be found in Brearley and Ibbotson's book, to which reference has already been made (p. 142). As an example, one method of estimating tungsten in ferro-tungsten is given here.

The alloy is ground as finely as possible in an agate mortar,[1] and from one to two grams are weighed into a beaker or porcelain dish. Concentrated hydrochloric acid, 50–100 c.c., is added, and the mixture is digested just short of the boiling point. The iron is easily attacked but the tungsten is not. On adding a few drops of concentrated nitric acid, the ferrous changes to ferric chloride, and then the tungsten is visibly acted upon until the clear orange-coloured ferric chloride blackens again, showing that some ferrous chloride has been reformed. By further addition of nitric acid as required, but so as to demand a total consumption of that acid very slightly greater than would transform the iron wholly to the ferric condition, the sample passes completely into solution in a short time. To attain this end it is essential to use sufficient hydrochloric acid to keep the tungstic oxide in solution until decomposition is complete, to maintain the strength of the acid during the decomposition (that is why it should not be boiled) and lastly to use not more nitric acid than is necessary for the oxidation. When all the alloy has dissolved the solution is evaporated to pastiness, diluted with about twice its volume of hydrochloric acid (1 part conc. acid to 4 parts water) and boiled. The tungstic acid so obtained is easily filtered and washed. It is ignited in a weighed platinum crucible, thoroughly wetted with hydrofluoric acid, evaporated so as to prevent spurting, and re-ignited, in order to remove silica, derived partly from silicon present in the alloy, partly from the vessels used in the analysis. The purified WO_3 is weighed, but it still contains traces of ferric oxide ; these are estimated by fusing the WO_3 with about four times its weight of sodium carbonate, extracting with water, filtering off the ferric oxide, igniting and weighing.

[1] After preliminary crushing in a mortar of hardened steel.

If the tungsten alloy contained any chromium the aqueous filtrate from the traces of ferric oxide may have a faint yellow colour due to sodium chromate. This may be allowed for by acidifying and titrating with ferrous sulphate and potassium permanganate ; the amount of equivalent chromic oxide being deducted along with the ferric oxide from the weight of impure WO_3. The above method can be used for iron alloys containing up to 70 per cent of tungsten. Chromium, if present to the extent of only a few per cent, passes into solution and so does all the molybdenum if present. Both remain in the filtrate from the tungstic acid with exception of a trace of chromic oxide adsorbed by the tungstic acid.

The filtrate from the tungstic acid may still contain a trace of tungstic acid, though generally the amount is negligible. If necessary, it can be recovered by evaporating the filtrate as in the analogous case of silica.

Tungstic acid resembles stannic acid in many respects. Thus it is amphoteric, its acid character being much more pronounced than its basic character. Under suitable conditions it forms several crystalline hydrates, but usually it is obtained in the amorphous condition during analytical operations. It is for that reason very liable to be contaminated with small quantities of other substances by adsorption, and can be readily peptized either by acid or alkali and pass into solution in the first place as a sol, which may readily change into a true crystalloidal solution. Less is known, however, about the colloidal behaviour of tungstic acid than of stannic acid.

The solution in strong hydrochloric acid obtained in the above analytical method is doubtless a crystalloidal one of a tungstic oxychloride. During the evaporation to pastiness this is practically completely hydrolysed with simultaneous coagulation and precipitation of the colloidal tungstic acid. Some dehydration also of the separated acid probably occurs, and it becomes less reactive in consequence.

Presumably this dehydration involves the amphoteric forms of the tungstic oxide and also small amounts of ferric and other hydroxides. These processes are completed during the boiling with dilute hydrochloric acid which keeps the gel in the coagulated condition without being strong enough to dissolve more than the merest trace either as sol or crystalloidal compound.

CHAPTER IX

HYDROLYSIS

ALL aqueous solutions contain both $H^{\cdot}$ and OH' ions in such amounts that the product $[H^{\cdot}][OH'] = K_w$. At 20° the value of K_w is about 1×10^{-14}.

It follows that all substances dissolved in water come under the influence of both hydrogen and hydroxyl ions and in the case of salts this has important consequences. The precise effects observed depend essentially upon whether the acid and base from which the salt is derived are strong or weak, soluble or insoluble.

The salt, which may be represented by MX,[1] will be partially ionized, ions and un-ionized salt being in equilibrium—

$$M^{\cdot} + X' \rightleftarrows MX,$$

while the other equilibria in the solution which have to be considered are—

$$M^{\cdot} + OH' \rightleftarrows MOH$$
$$X' + H^{\cdot} \rightleftarrows HX$$
$$H^{\cdot} + OH' \rightleftarrows HOH$$

The positive and negative ions of the salt combine to some extent with OH' and $H^{\cdot}$ ions derived from the water to form a certain amount of un-ionized MOH and HX respectively.

Expressing the reaction somewhat differently, it may be said that the salt is to some extent decomposed by the water into free base and free acid. Thus—

$$MX + HOH \rightleftarrows MOH + HX$$

Such decomposition is called hydrolysis, but a non-ionic equation like the last gives but an inadequate and sometimes incorrect picture of the process, which is essentially ionic.

The fundamental mechanism of the hydrolysis is as above, whether the salt is derived from strong or weak base or acid, but four important cases need special consideration.

[1] Similar equations could, of course, be derived for salts of polyvalent ions.

(1) *The salt is derived from a strong base and a strong acid.*

Such a salt, as also the base and acid, will be almost entirely ionized in dilute solutions (0·1 N. and less). If the ionization is not quite complete it will occur to practically the same extent in the case of salt, base, and acid. As a result of this, only very small, and equal, amounts of $H^{\cdot}$ and OH' ions are removed as un-ionized acid and base, and these are replaced by ionization of more HOH. The concentration of $H^{\cdot}$ and OH' ions in the solution remains the same as in pure water, and the solution is strictly neutral. There is actually very slight hydrolysis, but the minute amounts of strong acid and strong base formed exactly balance each other.

(2) *The salt is derived from a strong base and a weak acid.*

The ionic reactions involved are the same as in the previous case, but as the acid HX formed by interaction between $H^{\cdot}$ and X' ions is weak a considerable amount of un-ionized HX will be formed. The quantity of un-ionized MOH formed, since it is a strong base, will be very small. The process of hydrolysis results, therefore, in the removal of considerable amounts of $H^{\cdot}$ ion as un-ionized HX and the accumulation of OH' ions in the solution, which consequently becomes alkaline. This process goes on until the ionic concentrations in the solution are such as to satisfy the mass action equations

$$\frac{[H^{\cdot}][X']}{[HX]} = K_{HX} \qquad [H^{\cdot}][OH'] = K_w$$

Dividing one equation by the other we get—

$$\frac{[HX][OH']}{[X']} = \frac{K_w}{K_{HX}} = K$$

In a case such as this the X' ion is derived almost entirely from the salt and the OH' ion from the base, the proportions of each derived from HX and HOH being negligible in comparison. If α_1 and α_2 are the degrees of ionization of MX and MOH and [salt] and [base] their total concentration (both ionized and non-ionized) at equilibrium we can substitute α_1[salt] and α_2[base] for [X'] and [OH'] respectively and obtain—

$$\frac{[HX]\ \alpha_2[base]}{\alpha_1[salt]} = \frac{K_w}{K_{HX}} = K$$

If the degrees of ionization α_1 and α_2 are the same, this simplifies to—

$$\frac{[HX]\,[base]}{[salt]} = \frac{K_w}{K_{HX}} = K \text{ or } \frac{[acid]\,[base]}{[salt]} = \frac{K_w}{K_{acid}}$$

for, since the acid is weak, one can substitute for [HX], without serious error, the expression [acid] which represents the total concentration of acid, both ionized and non-ionized. These equations enable the degree of hydrolysis of any salt of a strong base and a weak acid at any concentration to be calculated. As an actual example, the case of a 0·1 N solution of sodium acetate may be taken. Calling x the amount hydrolysed and substituting in the above equation, we have for a temperature of 25°

$$\frac{[H.C_2H_3O_2]\,[NaOH]}{[NaC_2H_3O_2]} = \frac{K_w}{K_{H.C_2H_3O_2}}$$

$$\frac{x^2}{[0\cdot1-x]} = \frac{1\cdot2 \times 10^{-14}}{1\cdot8 \times 10^{-5}}$$

whence x = 0·0000081, which is 0·0081 per cent of 0·1.

Shields [1] found experimentally that the percentage hydrolysis in 0·1 N solution at 25° was 0·008. He also found that in 0·1 N solution the degree of hydrolysis of the salts given was as follows :—

	per cent
KCN	1·12
Na_2CO_3	3·17
Potassium phenoxide .	3·05
Borax (about) . . .	0·5

If the percentage hydrolysis in a normal solution of sodium acetate is calculated as above, it will be found to be only 0·00258 per cent. The form of the equation shows that the percentage of a salt which is hydrolysed must increase with the dilution. Experiment proves that this is correct. It is worth noting that the value of K_w increases markedly with rise of temperature—from $1\cdot2 \times 10^{-14}$ at 25° to 5×10^{-13}

[1] *Phil. Mag.*, 1893, [5], **35**, 365.

at 100°—while the dissociation constant of a weak acid is, in general, little affected by temperature. If follows from this, as inspection of the equations given above will show, that salts such as sodium acetate will be more hydrolysed the higher the temperature. This seems actually to apply to the hydrolysis of all types of salts.

(3) *The salt is derived from a weak base and a strong acid.*

This is very similar to case (2), and proceeding as in that case an analogous equation for the hydrolytic equilibrium can be derived. This has the form—

$$\frac{[\text{acid}]\,[\text{MOH}]}{[\text{salt}]} = \frac{K_w}{K_{\text{MOH}}} \quad \text{or} \quad \frac{[\text{acid}]\,[\text{base}]}{[\text{salt}]} = \frac{K_w}{K_{\text{base}}}$$

(4) *The salt is derived from a weak base and a weak acid.*

Even salts of this type are highly ionized in solution, and extensive ionization will be assumed in considering their hydrolysis. Hydrolysis in this case leads to the conversion of both ions of the salt into non-ionized base and acid. If the base and acid are of the same strength the concentration of $H^{\cdot}$ and OH' ions will remain the same as in pure water. If they are not quite of the same strength there will be a slight excess of either $H^{\cdot}$ or OH' ions, but any acidity or alkalinity so produced can be only slight and not in any way comparable to that found in cases (2) or (3).

When equilibrium has been reached the concentrations of base, acid, and the several ions must be such as to satisfy both of the equations—

$$\frac{[M^{\cdot}][OH']}{[MOH]} = K_{\text{base}}; \quad \frac{[H^{\cdot}][X']}{[HX]} = K_{\text{acid}}, \text{ and}$$

since both K_{base} and K_{acid} are very small, it is clear that very extensive hydrolysis must occur.

Multiplying together these two equations we obtain—

$$\frac{[HX]\,[MOH]}{[M^{\cdot}]\,[X']} = \frac{K_w}{K_{\text{base}}\,K_{\text{acid}}} \quad \text{or} \quad \frac{[\text{acid}]\,[\text{base}]}{a^2\,[\text{salt}]^2} = K,$$

assuming that practically all the $M^{\cdot}$ and X' ions come from the ionization of salt molecules and that the degree of

ionization of the salt is α. In most cases complete ionization can be assumed, and in this case α^2 becomes unity.

In the case of salts of this type the percentage hydrolysed is independent of the dilution. This is readily shown as follows :—

Let S be the total concentration of dissolved salt and x that of the portion hydrolysed, then

$$\frac{[S - x]^2}{x^2} = K \text{ whence } x = \frac{S}{1 + \sqrt{K}}$$

The percentage hydrolysed $= \frac{100x}{S} = \frac{100}{1 + \sqrt{K}}$ which is independent of the dilution.

When the weak base or acid from which a salt is derived is very sparingly soluble, the amount of hydrolytic decomposition is greater than it would be otherwise.

If both base and acid are weak and sparingly soluble it is evident that both will separate out in the solid state as soon as the values of $[M^{\cdot}][OH']$ and $[H^{\cdot}][X']$ reach the values of their solubility products. If these are very small, then practically no base or acid, or their ions, can remain in solution, and the salt will be almost completely hydrolysed. Such salts cannot be formed in presence of water or, if prepared by dry methods and then added to water, they are decomposed by it.

Where a salt is derived from a strong base and a weak insoluble acid, or a weak insoluble base and a strong acid, the conditions are rather peculiar. Here also the sparingly soluble base or acid would separate as soon as its solubility product was reached. It does not follow that it will be reached, however, unless it has a very small value, for in this particular case the one product of hydrolysis being strong and highly ionized sets a limit to the accumulation of either $H^{\cdot}$ or OH' ion, as the case may be. Other factors, however, may modify this state of affairs, as, for example, in the case of ferric chloride, which is instructive and typical.

A freshly prepared solution of ferric chloride is perfectly clear and fairly strongly acid owing to hydrolysis. No separation of ferric hydroxide occurs because the value of

its solubility product is not reached. Doubtless a condition of equilibrium with respect to $FeCl_3$, HCl, $Fe(OH)_3$, and their respective ions is established comparatively rapidly. This equilibrium is a false one, however. The simple molecules of $Fe(OH)_3$ gradually coalesce or polymerize. This enables more $FeCl_3$ to be hydrolysed to simple $Fe(OH)_3$ molecules, and the solution gets still more acid. The polymerized $Fe(OH)_3$ can still ionize to some extent, and gives rise to a few OH' ions and positively charged particles which soon become large enough to rank as positively charged colloidal particles rather than ions, and impart a dark colour to the solution. The solubility product for these polymerized hydroxide particles is presumably smaller than that of the simple $Fe(OH)_3$ molecules, but owing to the increased acidity of the solution it is still not reached and no precipitation occurs. The same process of polymerization continues slowly until the colloidal particles have become so large and the corresponding solubility product so small that the value of the latter is finally reached and precipitation occurs in spite of the now very considerable acidity of the solution. A very large proportion of the original ferric iron content of the solution is finally deposited at the bottom of the solution. The precipitate may, it is true, be partly chloride. In such colloidal precipitates some interchange of acid radicles may occur in the manner described in Chapter VII. The precipitate is essentially hydroxide, though it may be, and frequently is, regarded as a basic chloride. Its exact composition is liable to vary very much, according to the conditions under which it has separated.

Solutions of salts derived from strong bases and weak sparingly soluble acids, such as sodium aluminate or stannate, show a very similar behaviour. They are essentially unstable, and in time deposit the greater amount of aluminium or stannic hydroxide.

Hydrolysis in Quantitative Analysis

There are many occasions during quantitative analysis where complications may arise owing to hydrolysis. Two may be specially mentioned.

1. It is frequently necessary, during the course of an analysis, to evaporate to dryness in order to remove excess of a volatile acid, such as nitric or hydrochloric, or for some other purpose (e.g. to render silica insoluble). It is important to remember that some of the salts present in the solution may be considerably hydrolysed and that the evaporated residue may, in consequence, contain a proportion of the free bases or basic salts. When taking up the residue with water after the evaporation it is therefore necessary to add a small amount of acid and possibly to warm for some time with the acid. This has already been referred to (see page 138) in connexion with the estimation of silica.

2. It is frequently recommended to precipitate aluminium as hydroxide by adding excess of ammonia to the hot solution and then boiling off all but a very slight excess of the ammonia. If this method is employed the solution must be tested occasionally with litmus paper to see if it still remains alkaline. The boiling must not be continued until ammonia no longer comes off with the steam, for if that is done the solution may become acid. Ammonium salts, including NH_4Cl, are slightly hydrolysed in solution, and on boiling such solutions the ammonia, being more volatile than the acid, escapes more readily and finally leaves an acid liquid.

The hydrolytic decomposition of a salt is often made the basis of a quantitative estimation or separation. The most important case is the following.

The Separation of Iron and Manganese (Nickel, Cobalt or Zinc) by the Basic Acetate Method

All the iron must be present in the ferric condition. The acid solution should be diluted to about 150 c.c. for every 0·1 gram iron present. It is then treated carefully with a solution of ammonia in the cold until a drop of ammonia just gives a slight precipitate which does not dissolve again on vigorous stirring. This is then redissolved by adding a few drops of dilute hydrochloric acid. The success of the basic acetate separation is largely dependent on the careful carrying out of this partial neutralization with ammonia. If the solution is strongly acid to start with the ammonia

can be added fairly quickly at first and need not be very dilute. When the precipitate obtained on addition of ammonia disappears slowly on stirring it is necessary to proceed more cautiously. The neutralization should be continued with ammonia which is not more than twice normal (3·4 per cent). It should be added one drop at a time with vigorous stirring, and as soon as the precipitate persists twice normal hydrochloric acid should at once be added, drop by drop, with vigorous stirring, until a clear solution is obtained. If the addition of hydrochloric acid is unduly delayed, more is required to redissolve the precipitate than if it is added at once, owing to the precipitate becoming less readily soluble on standing in the way characteristic of colloidal precipitates. One gram of ammonium acetate for every 0·1 gram iron, dissolved in a small amount of water, is now added. The solution, which becomes dark reddish brown in colour, is heated and kept just short of actual boiling for two or three minutes. The whole of the iron is then precipitated in a reddish brown flocculent condition, and, on removing the flame, settles well, leaving a colourless[1] solution containing all the manganese (nickel, cobalt, or zinc). When the precipitate has settled, it is filtered hot, washed once or twice by decantation with hot water, and finally on the filter paper. It is ignited and weighed as ferric oxide.

The basic acetate process will usually give a good separation in one operation, but if large quantities of manganese, etc., are present it may be necessary to carry out the precipitation twice. When cobalt or nickel is present this is nearly always necessary. In this case the first ferric precipitate is filtered off, washed once, redissolved by warming with hydrochloric acid, and reprecipitated as before.

Manganese (zinc, cobalt) is estimated in the filtrate from the ferric precipitate, and is conveniently precipitated as manganese (zinc, cobalt) ammonium phosphate (see page 86). As the solution contains free acetic acid it should be neutralized with respect to litmus (not methyl orange), before adding the $(NH_4)_2HPO_4$.

[1] If nickel and cobalt are absent.

If iron is being separated from nickel it is best to effect the preliminary neutralization with sodium carbonate instead of ammonia and to use sodium, not ammonium, acetate. The nickel is then precipitated in the filtrate from the ferric precipitate by means of caustic potash and bromine water (see page 124). If ammonium salts are present no precipitate is obtained until these have been destroyed by the hypobromite.

There are several points of theoretical interest involved in the process described above. As already pointed out on page 122, a good quantitative separation of ferric iron from Mn, Zn, etc., cannot be obtained by precipitation with ammonia in presence of ammonium salts. The basic acetate method depends on the fact that ferric hydroxide is a far weaker base than the hydroxides of manganese, zinc, etc., and because of this, ferric salts are much more hydrolysed in aqueous solution than salts of these metals.

It is because of the large hydrolysis of ferric salts that their solutions cannot be neutralized. Complete neutralization would not occur until all the iron had been precipitated as hydroxide (or possibly basic salt). The solution neutralized up to the point when a precipitate is just not present, in the manner described above, would not be permanently stable. On long standing it would slowly deposit a precipitate as explained on page 122. The solution may be regarded as containing $Fe(OH)_3$, HCl, and $FeCl_3$ in quasi-equilibrium :— $FeCl_3 + 3HOH \rightleftarrows Fe(OH)_3 + 3HCl$, the HCl being almost entirely ionized, the $FeCl_3$ mostly so.

On addition of ammonium (or sodium) acetate most of the hydrogen ions in the solution unite with acetate ions to form feebly ionized acetic acid. The equilibrium between water, $FeCl_3$, and the products of hydrolysis of the latter is thereby quite upset. The $H^{\cdot}$ ion concentration is enormously reduced, and the condition of the ferric hydroxide becomes entirely unstable. At the same time the solution becomes deep reddish brown in colour. This might be due to the formation of large amounts of ferric hydroxide in colloidal solution, but according to Lowry [1] the colour is due

[1] *J. Chem. Soc.*, 1923, **123**, 830.

to non-ionized ferric acetate to which he ascribes the formula $[(CH_3 . C\overset{O\cdots}{\underset{O\cdots}{}})_3Fe]$.

The iron in this compound is fully co-ordinated and in a similar condition to the iron in the red non-ionized ferric thiocyanate [1] or in the red compounds formed when ferric chloride acts upon enolic compounds. The red ferric acetate is unstable, and on boiling hydrolysis occurs with coagulation and precipitation of ferric hydroxide which is analytically complete. The solution contains a considerable number of acetate ions (as well as chloride or other anions) for in order to remove practically all $H^{\cdot}$ ions as un-ionized acetic acid it is necessary to add a considerable excess of ammonium (or sodium) acetate. This excess will be mostly present in the ionized condition. These acetate ions (and possibly to a minor extent other anions) take some part in the neutralization and coagulation of the colloidal ferric hydroxide solution. The precipitate is therefore partly acetate, and is generally referred to as " basic ferric acetate ". The precipitate, however, is essentially hydroxide, but the acetate content, though variable, is nevertheless of importance. If the solution with the suspended " basic ferric acetate " is boiled for a long time the acetate groups tend to be replaced by OH groups and the precipitate becomes much more slimy and difficult to filter. Long boiling should therefore be avoided.

It need hardly be pointed out that even the salts of manganese, zinc, cobalt, or nickel will be slightly hydrolysed. Since, however, the hydroxides of these metals are much stronger bases than ferric hydroxide, and also considerably more soluble, the hydrolysis is very slight. Even in the acetic acid solution the extent of hydrolysis is not sufficient for precipitation of the hydroxides to occur. Only if large quantities of these metals are present is there any danger of partial precipitation occurring, and even then it is due rather to the oxide of the divalent metal entering into combination with the ferric hydroxide than to its actual separation as such.

[1] See p. 24.

Separation of Aluminium from Iron by means of Sodium Thiosulphate

This method is due to Chancel.[1] For numerous other references bearing on the method see Mellor's *Treatise on Quantitative Inorganic Analysis*, p. 495. The method is not to be recommended, though it is one of the very few by which an approximately correct separation of these two metals is possible. The method is of interest, however, partly because it is well known, and partly because it depends on principles essentially similar to those involved in the basic acetate method of separating iron and manganese. The solution is neutralized, as far as possible without getting a permanent precipitate, with sodium carbonate and diluted to about 250 c.c. for every 0·2 gram of the metals present. An excess of sodium thiosulphate (about 5 grams $Na_2S_2O_3 . 5H_20$ for every 0·2 gram metal) is then added, and the solution is boiled until no smell of sulphur dioxide is perceptible; this will take probably two hours or more. The precipitate is a mixture of aluminium hydroxide and sulphur, while the iron remains in the solution in the ferrous condition. The solid is filtered off, washed, ignited, and weighed as Al_2O_3. The filtrate is acidified with HCl to decompose excess of thiosulphate, the SO_2 is boiled off, and nitric acid is then added to oxidize the iron. After digesting for some time to complete the oxidation and cause the sulphur to coagulate the ferric iron is precipitated with ammonia (there is no need to remove the sulphur first). The ferric hydroxide is filtered off, washed, ignited, and weighed as Fe_2O_3.

Thiosulphuric acid is probably a considerably stronger acid than acetic, hence mere addition of sodium thiosulphate to the slightly acid solution containing iron and aluminium is not alone sufficient to lead to precipitation of either aluminium or ferric hydroxide. Some $H_2S_2O_3$ is, however, formed by union of $H^{\cdot}$ and S_2O_3'' ions, and, as it is unstable, it breaks up into water, sulphur dioxide, and free sulphur. This process is accelerated by boiling, as also is the hydrolysis of the aluminium salt present. The two processes go on

[1] *Compt. rend.*, 1858, **46**, 987.

concurrently until all the aluminium has separated from solution as hydroxide, and the final result can be represented by the usual equation $2AlCl_3 + 3Na_2S_2O_3 + 3H_2O = 2Al(OH)_3 + 6NaCl + 3S + 3SO_2$. Thiosulphate or the SO_2 formed in the reaction reduces the iron to the ferrous condition if it is not already present in that form. Since ferrous hydroxide is a relatively strong base and much more soluble than $Al(OH)_3$, its salts are not sufficiently hydrolysed under the prevailing conditions for any iron compound to be precipitated.

Separation of Titanium and Iron

Titanium can be separated from iron, just as can aluminium, by the thiosulphate method. The method of operating is precisely the same. For full details of the estimation of titanium in steel or ferro-titanium see Brearley and Ibbotson.[1]

[1] *The Analysis of Steel-Works Materials* (1902), pp. 96, 171.

CHAPTER X

QUANTITATIVE PRECIPITATIONS BY MEANS OF HYDROGEN SULPHIDE

HYDROGEN sulphide is one of the most important analytical reagents which we possess, and the principles underlying the various reactions in which it takes part are most instructive. This is largely because the law of mass action can be accurately applied to the precipitation of the various metals as sulphides.

In the precipitation of the sulphide of a divalent metal, M, the equilibria and mass action equations involved are as follows :—

$$\begin{array}{lll} M^{\cdot\cdot} + S'' \rightleftarrows MS \rightleftarrows MS & & [M^{\cdot\cdot}][S''] = K_1[MS] \\ \quad\text{(dissolved)}\quad\text{(solid)} & & \\ H^{\cdot} + HS' \rightleftarrows H_2S & & [H^{\cdot}][HS'] = K_2[H_2S] \\ H^{\cdot} + S'' \rightleftarrows HS' & & [H^{\cdot}][S''] = K_3[HS'] \\ 2H^{\cdot} + S'' \rightleftarrows H_2S & & \end{array}$$

$$[S''] = K_2K_3 \frac{[H_2S]}{[H^{\cdot}]^2}$$

$$K_1[MS] = K_2K_3[M^{\cdot\cdot}] \frac{[H_2S]}{[H^{\cdot}]^2}$$

$$\text{whence} \quad \frac{[M^{\cdot\cdot}][H_2S]}{[H^{\cdot}]^2} = \frac{K_1}{K_2K_3}[MS] = K$$

(for [MS] is constant so long as the solid sulphide is present).

This equation shows that the concentration of the metal ion left in solution is directly proportional to the square of the hydrogen ion concentration, and inversely proportional to the H_2S concentration, or to the partial pressure of the gas above the solution, for the latter will, by Henry's law, be practically proportional to the concentration in the liquid. These deductions have been confirmed by several workers—more especially by Bruner and Zawadzki.[1]

[1] *Bull. de l'acad. des Sciences de Cracovie*, 1909, pp. 267–312.

Owing to the extremely small value of the second dissociation constant of hydrogen sulphide (see table on page 40), it is evident that the concentration of S'' ions will be very small in pure aqueous solution, and will be very greatly diminished by even small amounts of a strong acid.

On the other hand, by the addition of alkali—that is to say, hydroxyl ions—the equilibrium $2H^{\cdot} + S'' \rightleftarrows H_2S$ is shifted from right to left owing to removal of $H^{\cdot}$ ions as un-ionized water. It is thus possible to obtain a relatively high concentration of S'' ions in alkaline solution. The following values of K and L, the solubility product, are given, for the sulphides indicated, by Bruner.[1] L has the form $[M^{\cdot}]^2[S'']$, $[M^{\cdot\cdot}][S'']$ or $[M^{\cdot\cdot\cdot}]^2[S'']^3$, according as the metal is mono-, di-, or tri-valent, while K is correspondingly either

$$\frac{[M^{\cdot}]^2[H_2S]}{[H^{\cdot}]^2}, \quad \frac{[M^{\cdot\cdot}][H_2S]}{[H^{\cdot}]^2}, \text{ or } \frac{[M^{\cdot\cdot\cdot}]^2[H_2S]^3}{[H^{\cdot}]^6}$$

In the last column of the table are given the metal ion concentrations in equilibrium solutions which are normal with respect to $H^{\cdot}$ ion and are saturated with H_2S at about 25°. The H_2S concentration would be about 0·1 molar.

Sulphide	K	L	Metal ion concentration when $[H^{\cdot}]=1$ $[H_2S]=0{\cdot}1$
MnS	$6{\cdot}3 \times 10^{6}$	7×10^{-16}	—
FeS	$3{\cdot}4 \times 10^{3}$	$3{\cdot}7 \times 10^{-19}$	—
Tl_2S	$6{\cdot}37 \times 10^{-1}$	7×10^{-23}	2·5
α ZnS (from acid solutions)	$7{\cdot}3 \times 10^{-4}$	8×10^{-24}	$7{\cdot}3 \times 10^{-2}$
β ZnS (from alkaline solutions)	about 1×10^{-2}	about $1{\cdot}1 \times 10^{-24}$	10^{-1}
CdS	$6{\cdot}5 \times 10^{-6}$	$7{\cdot}1 \times 10^{-28}$	$6{\cdot}5 \times 10^{-5}$
PbS	$3{\cdot}1 \times 10^{-6}$	$3{\cdot}4 \times 10^{-28}$	$3{\cdot}1 \times 10^{-5}$
CuS	$5{\cdot}3 \times 10^{-20}$	$5{\cdot}9 \times 10^{-42}$	$5{\cdot}3 \times 10^{-19}$
HgS	7×10^{-26}	$7{\cdot}7 \times 10^{-48}$	7×10^{-25}
Ag_2S	$4{\cdot}4 \times 10^{-31}$	$4{\cdot}78 \times 10^{-53}$	$2{\cdot}1 \times 10^{-15}$
Bi_2S_3	$2{\cdot}5 \times 10^{-25}$	$3{\cdot}2 \times 10^{-91}$	$1{\cdot}58 \times 10^{-11}$

Unless a sulphide has an extremely small solubility product it cannot be precipitated by H_2S under ordinary conditions

[1] *Loc. cit.*, p. 301.

owing to the S'' ion concentration being too low. The metals in analytical groups I and II are those which can be precipitated by H_2S at atmospheric pressure in presence of moderate amounts of acid. The metals placed in analytical group IV on the contrary are readily precipitated as sulphides only in alkaline solutions. There is not really any sharp line of demarcation between the two groups, however, and this must always be remembered.

Under usual conditions of working the position is that if a sulphide (of a divalent metal) has a solubility product smaller than about 1×10^{-27}, it will be precipitated by H_2S at atmospheric pressure from solutions which are decinormal or even half normal with respect to acid. If the solubility product is greater than the above figure no precipitation will occur until the solution is made alkaline. Thus, cadmium is placed in analytical group II and zinc in group IV. It does not, however, require much acid to prevent the precipitation of cadmium sulphide, while zinc sulphide can be precipitated completely from acetic acid solution. The precipitation of sulphides from acid solution is, moreover, often delayed owing to the persistence of unstable conditions of supersaturation. If plenty of time is allowed, zinc sulphide can be separated from relatively very acid solutions. The last column in the above table gives an idea of the minimum concentrations of metal ion which must be present for a precipitate of the corresponding sulphide to form on passing H_2S through the solution, if the latter is normal with respect to $H^{\cdot}$ ion.

Kinetically, there are certain difficulties in interpreting the precipitation of very insoluble sulphides from acid solution by means of hydrogen sulphide. Attention has been drawn to this, recently, by G. M. Smith.[1] There are so few S'' ions present in acid solutions of H_2S that it would be impossible for equilibrium to be established in the short time in which it is, if these ions were directly involved in the precipitation of metallic sulphides. The ions would have to move with very much greater velocities than they actually do. According to Smith, 5 c.c. of a 0·2 N solution of hydro-

[1] *J. Amer. Chem. Soc.*, 1922, **44**, 1500.

chloric acid which is also 0·2 N with respect to hydrogen sulphide contain 3×10^{20} non-ionized molecules of H_2S, 15×10^{13} SH' ions and only one S'' ion.

If the precipitation of sulphides is an ionic process—which there is no reason to doubt—it is consequently far more probable that the SH' ions are involved rather than the S'' ions, at any rate in acid solutions. In this case the primary product of the ionic reaction would be a hydrosulphide, and the sulphide which actually separates in the solid state would result from this by secondary loss of H_2S. Such loss of H_2S could occur either from individual molecules of hydrosulphide or during or after the process of electrolytic coagulation of a hydrosulphide sol formed in the first instance. This would be perfectly analogous to what is observed in some cases with hydroxide precipitations. Thus, $As(OH)_3$ is not known in the solid state, though there is every reason to think that it exists in aqueous solution. On separating from solution, As_2O_3 is formed by elimination of water, and in this case the loss of water probably occurs between individual molecules of $As(OH)_3$. In the precipitation of cupric oxide from hot alkaline solutions the intermediate formation of the hydroxide can be seen. The loss of water in this case occurs during or after coagulation of the sol. There is no reason to think that oxides are ever directly precipitated through the medium of O'' ions.

Even if the SH' ions and not the S'' ions are involved in the primary precipitation of sulphides the values of the constants K and L would not be affected: precipitation would only be a slightly more complex process than was assumed by Bruner and Zawadzki. The equilibria involved would now be, for a sulphide MS :—

$$\underset{\text{dissolved}}{MS} \rightleftarrows \underset{\text{solid}}{MS}; \quad H^{\cdot} + SH' \rightleftarrows H_2S; \quad H^{\cdot} + S'' \rightleftarrows SH'$$

$$M^{\cdot\cdot} + 2SH' \rightleftarrows M(SH)_2 \rightleftarrows \underset{\text{dissolved}}{MS} + H_2S$$

Applying the law of mass action, we have :—

$$[H^{\cdot}][SH'] = K_2[H_2S] \text{ or } [SH'] = \frac{K_2[H_2S]}{[H^{\cdot}]}$$

$$[M(SH)_2] = K''[MS][H_2S]$$

$$[M^{\cdot\cdot}][SH']^2 = K'[M(SH)_2] = K'K''[MS][H_2S]$$

By substituting for [SH'] this gives :

$$\frac{[M^{\cdot\cdot}][H_2S]}{[H^{\cdot}]^2} = \frac{K'K''}{K_2^2}[MS] = K$$

which is precisely the same expression that was deduced on the assumption that S'' ions were involved in the precipitation. Similar results are obtained for the cases of sulphides M_2S or M_2S_3. The values of K have the same form whether precipitation is supposed to involve SH' or S'' ions.

In the following pages it has been assumed that sulphides are precipitated directly by means of S'' ions. No very drastic alterations would be needed if precipitation is regarded as being due to SH' ions followed by loss of H_2S from the hydrosulphide.

The sulphides of analytical groups II and IV and silver sulphide present several features which recall those found among hydroxide precipitates. They are so insoluble that their precipitation is essentially a colloidal process and they adsorb large quantities of water. This tends to result in bulky gels built up of aggregates of very small particles. The water content of the precipitates is variable and loosely held, which accounts for the difference in views as to whether they are hydrated sulphides or hydrosulphides, or even partly hydroxides and hydrosulphides. Possibly all these compounds may be present in different cases and under different circumstances. The tendency to lose water—and perhaps H_2S too—seems to be even more marked among the sulphides than among the hydroxides, and with this is connected the remarkable difficulty with which the sulphides of cobalt, nickel, and, to a less extent, zinc and other metals dissolve in acids although very little acid will prevent their formation in the first instance. Amphoteric neutralization similar to that discussed in the case of the hydroxides may well take place with the sulphides too and be partly responsible for the readiness with which some of the group II sulphides, notably that of copper, carry down from acid solution sulphides of group IV metals such as zinc.

It is to be noted that zinc sulphide occupies much the same position among the sulphides as aluminium hydroxide among

the hydroxides, with regard to the trouble it gives in filtering and washing. The reason is likewise that the individual particles of the gel are ordinarily very small and highly hydrated. The trouble can be overcome by precipitation from slightly acid solutions, when the slightly greater solubility permits the formation of a coarser, denser precipitate. The acidity must not be too great, otherwise precipitation would be incomplete. These difficulties have been overcome in several ways, as, for instance, in the very good method of Riban,[1] where precipitation is effected from a dithionic acid solution. According to Fales and Ware [2] $[H^+]$ should be between 10^{-2} and 10^{-3} for the formation of a satisfactory precipitate.

Bornemann [3] states that the precipitation of zinc sulphide in a dense form is greatly facilitated by co-precipitation with another colloid, especially sulphur. This is carried out by passing a brisk current of H_2S through an acetic or chloracetic acid solution in presence of $NaHSO_3$. The dense precipitate obtained is washed on the filter with 0·5–1·0 per cent NH_4NO_3.

Perhaps it need scarcely be mentioned that just as many hydroxides and sulphides become less soluble and less reactive in course of time, so their tendency to be readily peptized also diminishes. The tendency of some sulphide precipitates to pass through the filter paper during washing, which is usually ascribed to atmospheric oxidation and is prevented by washing with H_2S water, seems to be partly a colloidal phenomenon and can be largely overcome by the use of ammonium nitrate instead of the weak electrolyte H_2S.

It must be mentioned, however, that dissolved hydrogen sulphide has a marked stabilizing effect on pure sulphide sols both in aqueous and non-aqueous media.[4] In the presence of electrolytes such a protective effect is not always observed.[5] Thus, H_2S renders arsenious or mercuric sulphide

[1] *Compt. rend.*, 1888, **107**, 341; *Chem. News*, 1888, **58**, 90.
[2] *J. Amer. Chem. Soc.*, 1919, **41**, 487.
[3] *Z. anorg. Chem.*, 1913, **82**, 216.
[4] Lottermoser, *J. pr. Chem.*, 1907 (2), **75**, 293.
[5] Mukherjee and Sen, *J. Chem. Soc.*, 1919, **115**, 461.

sols more stable against coagulation by salts with univalent cations, but less stable towards salts with cations of higher valency. Cupric sulphide sols, on the other hand, are more easily coagulated by salts in presence of H_2S, no matter what the valency of the cation. Solutions of alkali sulphides tend to stabilize all three of the above-mentioned sulphides against precipitation by salts of mono-, di-, or tri-valent cations, but, as alkali hydroxides do the same, the effect may be mainly due to the hydroxyl ions present owing to hydrolysis.

Another important point to bear in mind with regard to the metallic sulphides (or of the more or less imaginary hydrosulphides) is that they are amphoteric in character just as are many oxides and hydroxides. The behaviour of metallic sulphides with acid or alkali sulphides is perfectly analogous to that of metallic oxides with acid or alkali. Thus :—

$Sb_2S_3 + 6HCl \rightleftarrows 2SbCl_3 + 3H_2S$; $Sb_2O_3 + 6HCl \rightleftarrows 2SbCl_3 + 3H_2O$
$Sb_2S_3 + 6NaHS \rightleftarrows 2Na_3SbS_3 + 3H_2S$; $Sb_2O_3 + 6NaHO \rightleftarrows 2Na_3SbO_3 + 3H_2O$

When antimony sulphide dissolves in sodium hydroxide we should have :—

$$Sb_2S_3 + 6NaOH \rightleftarrows Na_3SbS_3 + Na_3SbO_3 + 3H_2O$$

The reactions certainly take place through the medium of $Sb(OH)_3$ and $Sb(SH)_3$ which can ionize in either of the following ways according as hydrogen ions or hydroxyl (or SH′) ions predominate under the experimental conditions—

$$Sb(OH)_3 \begin{cases} \swarrow 3H^{\cdot} + SbO_3''' \\ \searrow Sb^{\cdots} + 3OH' \end{cases} \qquad Sb(SH)_3 \begin{cases} \swarrow 3H^{\cdot} + SbS_3''' \\ \searrow Sb^{\cdots} + 3SH' \end{cases}$$

The precise nature of the compounds formed in either case will depend on the relative excess and the concentration of alkali or alkali sulphide used. Only with large excesses could either Na_3SbS_3 or Na_3SbO_3 be formed : otherwise $NaSbS_2$ or $NaSbO_2$ are more probable.

In the case of the sulphur compounds H_2S and HS′ take the place of the H_2O and HO′ which are involved in the equilibria of amphoteric hydroxides. Many metallic sulphides dissolve in solutions containing sulphides of the alkali metals or ammonium owing to the formation of compounds such as

those mentioned above, which are the sulphur analogues of the compounds formed on solution of the corresponding metallic oxide in caustic alkali.

Hydrogen sulphide is readily oxidized by atmospheric oxygen in presence of moisture, and for this reason, even in absence of other oxidizing agents, small amounts of free sulphur are generally present in sulphide precipitates. This fact must sometimes be taken into account when such a precipitate has to be weighed after drying at a comparatively low temperature. In alkaline solutions a similar oxidation occurs, possibly of H_2S present owing to hydrolysis, or of HS' or S'' ions (some thiosulphate is always formed in such cases also). The liberated sulphur does not separate as such, as it does in neutral or acid solution, but attaches itself to HS' or S'' ions, forming the complex ions of the so-called polysulphides. These are generally yellow or orange in colour. Some of them have been obtained in definite crystalline form,[1] but in most cases the precise formulæ of the compounds produced are uncertain, as is also the mode of attachment of the additional sulphur atoms. The various polysulphides are derived from acids H_2S_x, where x in different cases may apparently have values up to 7.[2] Solutions of ammonium or alkali sulphides freshly prepared by passage of H_2S through solutions of ammonia or alkali hydroxide are colourless, but rapidly become yellow owing to oxidation. On acidification the unstable H_2S_x breaks up into H_2S and free sulphur. Metallic sulphides precipitated by acidification of polysulphide solutions are therefore always mixed with free sulphur.

Estimation of Copper as Cuprous Sulphide

This is probably the most accurate method of estimating copper. The copper can be precipitated directly either as cuprous sulphide with sodium thiosulphate in acid solution

[1] Some are natural substances, e.g. iron pyrites FeS_2, which is ferrous disulphide.

[2] For a study of the polysulphides of Na, K, and NH_4 see Rule and Thomas, *J. Chem. Soc.*, 1914, **105**, 177, 2819; 1917, **111**, 1063, and Thomas and Riding, *J. Chem. Soc.*, 1923, **123**, 1726.

(considered on page 224), or as cupric sulphide by the action of H_2S as follows :—

The strongly acid solution of the cupric salt is heated to boiling and a current of H_2S passed through until it has cooled to room temperature. The beaker containing the solution should be covered and only a slow current of gas is needed. Sulphuric is the best acid to use, though other strong acids can be employed. The amount needed depends to some extent upon the concentration of electrolytes present. Apart from its use to prevent group IV metals from being precipitated, its main function is to coagulate the colloidal cupric sulphide. If plenty of salts are present less acid is needed and vice versa. The desirable limits of acidity may be placed between, say, half and twice normal.

The black precipitate should settle out in a coarse flocculent state. It is filtered when cold and thoroughly washed with cold water saturated with hydrogen sulphide. Filtering and washing should be carried out as expeditiously as possible for the moist sulphide has some tendency to oxidize, forming soluble compounds such as sulphate and thiosulphate. The H_2S in the washing solution helps to prevent this and also, being an electrolyte, tends to stop any tendency of the precipitate to become peptized and pass through the filter in colloidal form as the washing proceeds.

After drying, the filter paper is ignited separately, care being taken to burn off all carbon. Precipitate and filter ash are then ignited gently in a Rose crucible in a current of dry hydrogen. A pinch of ash-free sulphur may be added to the precipitate before ignition, though this may not be needed, for, during the heating, the cupric sulphide gives up half its sulphur yielding cuprous sulphide—

$$2CuS = Cu_2S + S$$

The hydrogen takes no part in this decomposition which occurs equally well in nitrogen or other inert gas. If the crucible is heated too strongly, however, then the Cu_2S may be reduced to metal by the hydrogen so that excessive heating must be avoided.

The heating is begun with quite a small flame, the size

of which is gradually increased until the crucible is red hot about three-quarters of the way up. The sulphur burns with the hydrogen round the lid, and when sulphur dioxide can no longer be smelt the flame is removed and the crucible is allowed to cool in the current of hydrogen. The ignition in hydrogen should take from 10 to 15 minutes, and the Cu_2S obtained should be black and crystalline. The current of hydrogen should be at the rate of about four bubbles per second through the sulphuric acid bubbler during the heating stage. This rate is doubled during the cooling.

The Estimation of Arsenic as As_2S_3

In most cases arsenic can be estimated by more rapid methods, but owing to the interest attaching to arsenic sulphide its estimation in that form will be considered. This is quite a good method. It is well known that when H_2S is passed into a solution of arsenious oxide in water no precipitate is obtained, but a yellow opalescent colloidal solution of arsenious sulphide. Only after the addition of electrolytes is the sulphide coagulated and precipitated.

This is one of the classical examples of a colloidal solution of a simple inorganic compound and has been the object of a large amount of experimental work.[1] The particles in this colloidal solution are negatively charged owing to adsorption of HS′ or S″ ions, and can be regarded chemically as representing a highly condensed form of sulpharsenious acid H_3AsS_3, which, in its simple form, is too unstable to isolate, just as is arsenious acid H_3AsO_3 itself.

For quantitative estimation as As_2S_3 the arsenic must be present either as arsenious acid or as an arsenite. To produce a pure precipitate of As_2S_3 which can be weighed directly the solution should be placed in a conical flask [2] provided with a doubly perforated rubber bung for inlet and outlet tubes. Through the solution, acidified strongly with hydrochloric acid, carbon dioxide is passed until all the dissolved

[1] For a summary of this by Lottermoser see Abegg and Auerbach's *Handbuch der anorg. Chem.*, 1907, vol. **3**, pt. 3, p. 528.

[2] This must be of such a form that all precipitate can be readily removed with the help of a rubber-tipped glass rod.

air can be presumed to be expelled. This is to prevent contamination of the As_2S_3 with free sulphur formed by oxidation of H_2S. The solution is then saturated with H_2S in the cold, and when all the arsenic has been precipitated the excess of H_2S is displaced by means of a current of carbon dioxide. The object of this is partly to prevent liberation of free sulphur owing to oxidation of H_2S during the filtration, but partly because there seems to be a real tendency for excess of H_2S to retain traces of As_2S_3 in solution as sulph-arsenious acid or as a stabilized sol. The precipitated As_2S_3 is filtered on a Gooch crucible, washed with hot water and weighed after drying at 100° or 105°.

Estimation of Antimony as Sb_2S_3

The best method of estimating antimony gravimetrically is as the trisulphide, but some care is required in carrying out the estimation.

Antimony sulphide begins to be appreciably soluble in hydrochloric acid containing more than 15 per cent HCl. Hence, when precipitating antimony quantitatively as sulphide excess of acid must be avoided. If too little acid is present, however, antimony oxychloride will separate :—

$$SbCl_3 + H_2O \rightleftarrows SbOCl + 2HCl$$

It is therefore best to work with a solution containing more than enough hydrochloric acid to prevent precipitation of the oxychloride, but, after saturating this solution with hydrogen sulphide, it is diluted with an equal volume of water and again saturated with the gas.

At low temperatures, and particularly with rapid streams of hydrogen sulphide, Sb_2S_5 is precipitated from antimonic solutions. When the solution contains more than 10 per cent HCl, the greater the amount of HCl, the greater the proportion of Sb_2S_5 precipitated. The higher the temperature and the slower the stream of gas the greater the proportion of Sb_2S_3 and sulphur mixed with the Sb_2S_5. (Compare the case of arsenate solutions on page 180.)

The acid solution containing the antimony either in the -ous or -ic condition is first saturated with H_2S at the ordinary temperature, then diluted with an equal volume of water

and heated to boiling for about a quarter of an hour while the passage of gas is continued. The flame is then removed and the precipitate, which has become dense under this treatment, is allowed to settle and is then filtered through a Gooch crucible. The precipitate is washed first by decantation, and then in the crucible with hot dilute acetic acid which has been saturated with H_2S: the H_2S counteracts any tendency of the moist sulphide to oxidize owing to absorption of oxygen from the air. As soon as the precipitate is thoroughly washed it will be noticed that the filtrate, which has been clear hitherto, begins to show a faint orange opalescence. The washing is then stopped. So long as any of the strong electrolyte, HCl, is present the Sb_2S_3 remains coagulated, the acetic acid also helping to prevent it going into colloidal solution. The acetic acid alone cannot quite prevent it, however, especially in the presence of the H_2S, which, owing to the marked acidic character of Sb_2S_3, causes its peptization. This peptization results from adsorption of HS′ or S″ ions by the Sb_2S_3, and the opalescence so caused is a sign of sufficient washing. It corresponds to a quite unweighable loss of material.

The precipitate has now to be completely dried and any excess of sulphur present, either as such or as Sb_2S_5, removed so that pure Sb_2S_3 can be weighed. A temperature of 280°–300° is required to decompose any Sb_2S_5 and volatize the excess of sulphur, but at this temperature the sulphide would oxidize rapidly, so the substance must be heated in a current of inert gas, CO_2 (which must be quite free from air) being the most convenient. The Gooch crucible is placed in a wide glass tube which can pass through holes in the sides of a small hot air oven. After all air has been removed by the current of CO_2 the temperature is gradually raised and finally kept at 280°–300° for two hours, at the end of which time the sulphide should be entirely converted into the black modification. At the commencement of the heating care should be taken that no moisture condenses in the glass tube, but is all removed with the current of CO_2. The crucible and contents are left to cool in the current of gas and then weighed.

Determination of Zinc as Sulphide

In the ordinary course of qualitative analysis zinc sulphide is precipitated from ammoniacal solution, but the precipitate so obtained is of a slimy nature and difficult to filter and wash. Zinc sulphide is sufficiently insoluble to be precipitated in solutions of marked acidity and coming down more slowly under such conditions it filters much better. From solutions which are slightly acid with hydrochloric acid, it is deposited in a satisfactory condition, but precipitation is not complete. It is complete from acetic acid solution, but the precipitate does not filter very well. The happy mean is attained by precipitation in presence of dithionic acid, which is stronger than acetic, but permits complete precipitation of the zinc.[1]

The zinc solution, which should be as free as possible from nitric acid, is treated with ammonia until only faintly acid. For every 0·1 gram of zinc present a solution of 0·7 gram of $Na_2S_2O_6 . 2H_2O$ in a small quantity of cold water is added. The solution is then diluted so as to occupy about 150 c.c. for each 0·1 gram of zinc present, and is saturated with H_2S in the cold. The ZnS separates as a very dense, granular precipitate which is readily washed with warm water containing H_2S. It may, with advantage, be left to stand several hours before filtration. After drying, the filter paper is burned completely, apart from the precipitate, which is then ignited in a current of hydrogen and weighed as ZnS. The procedure is the same as in the case of copper.

The effect of adding sodium dithionate to the solution, which is acid owing to the presence of free hydrochloric acid, is to reduce its acidity considerably.

If an amount of $Na_2S_2O_6$ equivalent to the HCl were added, then the reaction

$$Na_2S_2O_6 + 2HCl \rightleftarrows 2NaCl + H_2S_2O_6$$

would proceed until the sodium was distributed between the hydrochloric and the dithionic acids approximately in the ratio of their strengths as acids. Actually more $Na_2S_2O_6$ should be used than is equivalent to the free HCl present,

[1] Riban, *Compt. rend.*, 1888, **107**, 341 ; *Chem. News*, 1888, **58**, 90.

so that the majority of this is replaced by free $H_2S_2O_6$. The latter is, of course, stoicheiometrically equivalent to the former, but it is a considerably weaker acid, so that the effective acidity, that is, the hydrogen ion concentration, of the solution is much reduced.

During the separation of the zinc as sulphide an equivalent amount of acid is liberated, but this, in so far as it is a stronger acid than dithionic acid, is kept from accumulating (and so increasing the acidity of the solution) by reacting as above with the excess of $Na_2S_2O_6$ present. This device for partially neutralizing an acid solution by addition of an alkali or ammonium salt of a weak acid is frequently of value in analytical chemistry, and has already been considered in Chapter IX in connexion with the separation of iron and manganese by the basic acetate method.

The different properties of zinc sulphide precipitated from acid and alkaline solutions respectively, and the marked ageing effects shown by it (see pp. 160, 163) have led to the impression that there are two isomeric forms of the precipitated sulphide. It is probable, however, that the position is very similar to the analogous one of the stannic acids, and that the varying properties of ZnS precipitates formed under different conditions and of different ages are simply the result of gradual dehydration and condensation so characteristic of colloids.[1] The slow course of these processes makes it almost impossible to attain equilibrium in the reaction between zinc sulphide and acid, or zinc salts and H_2S, and to obtain satisfactory values for the constant $\frac{[Zn^{\cdot\cdot}][H_2S]}{[H^{\cdot}]^2}$. False equilibria of a sort may be set up, and the possibility of separating zinc from cobalt and nickel in acid solution by means of H_2S is due to the fact that these false equilibria persist longer with CoS and NiS than with ZnS. It is not because ZnS is less soluble than CoS or NiS ; in all probability it is more soluble.

Precipitation of Manganese as Sulphide

Since manganese sulphide is readily soluble even in weak acids such as acetic acid it has to be precipitated in alkaline solution—usually by means of ammonium sulphide.

[1] Glixelli, *Z. anorg. Chem.*, 1907, **55**, 297.

It is stated by Fresenius[1] and others that ammonium sulphide alone precipitates manganese, zinc, nickel, and cobalt sulphides but incompletely, although if ammonium chloride is present, precipitation is complete. Free ammonia if present in large amounts also interferes with the precipitation. These effects are clearly colloidal in nature. The ammonium chloride coagulates the manganese sulphide sol, which is first formed, but if the amount of the salt is insufficient a small portion of the sulphide remains peptized in the alkaline sulphide solutions. As the precipitate ages, however, the amount so remaining in colloidal solution will diminish. There is evidently a considerable lag in such changes with MnS just as with ZnS, NiS, and CoS. In this connexion it is of interest to note that according to V. M. Fischer,[2] manganese sulphide may be precipitated from a faintly acid solution of a manganese salt by means of H_2S if the passage of the gas is sufficiently protracted. So obtained it is red or orange red and sometimes crystalline.

When precipitated from alkaline solutions manganese sulphide is either pale pink or dull green in colour. The pink variety always comes down in presence of large amounts of ammonium salts and having been coagulated very suddenly is invariably in a fine state of division and readily passes through filter papers in colloidal suspension. Sooner or later the pink variety changes into the green variety which is always much denser and often crystalline, and therefore much more desirable analytically. This change, however, may be enormously delayed. High concentrations of ammonium salts are unfavourable to it, while excess of ammonium sulphide in hot solutions is favourable. It might be thought that the difference between the pink and green sulphides depended simply on the colloidal state, and that the suddenly flocculated finely divided form was pink and the denser form green. It seems pretty certain, however, that there are two allotropic forms of manganese sulphide, and the pink colloidal substance precipitated from alkaline solutions probably corresponds to the red crystalline

[1] *J. pr. Chem.*, 1861, **82**, 265.
[2] *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1481.

sulphide obtained by Fischer[1] from acid solutions. The pink or red form is evidently unstable with respect to the green, and changes into the latter when given a chance. Too much ammonium chloride prevents the change or delays it because the sulphide is kept so severely coagulated. If little ammonium chloride and plenty of sulphide is present slight peptization of the pink sulphide occurs, and a very minute amount probably changes to crystalloidal sulpho-manganite (derived from the weak acid Mn $(SH)_2$), which by hydrolysis gives rise to the stable green form of manganese sulphide. Since this conversion of the pink to the green form occurs slowly the green form is dense and compact or even crystalline.

(This change would be perfectly analogous to the conversion of black HgS into vermilion HgS in presence of alkaline sulphides.)

According to Fischer[1] both red and green sulphides may be anhydrous or contain one molecule of water, according to the precise conditions of precipitation.

Manganese is best separated from alkaline earths and magnesium as sulphide. The solution, which should contain a small amount of ammonium salts to prevent precipitation of $Mn(OH)_2$ by the ammonia, is treated with a good deal of ammonia solution, heated to boiling, and precipitated by slow addition of freshly prepared colourless ammonium sulphide, with thorough stirring. Heating is continued until the precipitate is dirty green in colour. After settling, the precipitate is filtered off, washed with water to which a little ammonium sulphide has been added, dried, ignited in hydrogen in a Rose crucible, and weighed as MnS.

Suitable quantities of reagents to use in the above precipitation are somewhat as follows for 0·25 gram Mn in 25–50 c.c. of solution:—About 0·5 gram of NH_4Cl may be added if enough ammonium salts are not already present, about 10 c.c. of ·880 ammonia, and 10 c.c. of 2·5 per cent ammonia freshly saturated with H_2S.

The above method will generally give satisfactory results even in presence of large amounts of alkaline earth metals.

[1] *Loc. cit.*

There is, however, some possibility of sparingly soluble alkaline earth salts (hydroxide, carbonate, thiosulphate) separating with the manganese sulphide. In such cases, therefore, Treadwell [1] recommends precipitation in the cold in presence of large amounts of ammonium chloride. Under these conditions the troublesome pink form of the manganese sulphide is obtained, and it is probable that double precipitation of the green form would be a preferable procedure where one precipitation does not give a good separation.

The Estimation of Mercury as Mercuric Sulphide

This is one of the best forms in which to separate and weigh mercury. The mercury must be present in the mercuric condition, but it should be noted that solutions containing mercuric chlorides should not be boiled since this compound is appreciably volatile in steam.

In the absence of other metals of analytical group II, the precipitation of mercuric sulphide by means of H_2S is a simple matter. Oxidizing agents such as ferric salts or much nitric acid should be absent as they would lead to co-precipitation of free sulphur. Owing to the insolubility of mercuric sulphide, even considerable amounts of hydrochloric acid do not interfere with the precipitation. It is better, however, to avoid large excess of acid or neutral salt, for mercuric sulphide when precipitated from acid solutions by H_2S comes out so suddenly owing to its insolubility that the primary particles of which the coagulated flocks consist are very fine; in consequence, the precipitate is not particularly easy to filter or wash, and if formed in presence of much electrolyte is apt to be still worse, because coagulated more suddenly.

Volhard's method of precipitating mercuric sulphide [2] is specially designed to give a dense precipitate which filters well by causing it to form slowly. This process is much to be preferred to simple precipitation by means of H_2S in acid solution.

[1] *Analytical Chemistry*, 1919, vol. **2**, p. 122.
[2] *Annalen*, 1889, **255**, 255.

Volhard's procedure is as follows :—

The acid mercuric solution is nearly neutralized with sodium carbonate and a small excess of freshly prepared colourless ammonium sulphide added. Then pure caustic soda solution (free from Al_2O_3, SiO_2, etc.) is added with stirring until the dark liquid begins to brighten up. The mixture is then heated to boiling and further caustic soda is added until the solution has become quite clear. The mercury is then all in solution as the sodium salt of the very weak acid $Hg(SH)_2$.

Excess of ammonium nitrate is then added, and the solution boiled until practically no more ammonia is given off. The precipitated mercuric sulphide settles well and is filtered through a Gooch crucible and washed (first by decantation) with hot water. It is dried at 110° and weighed. The results may be a few tenths of a per cent too high from the presence of a little free sulphur.

Free sulphur can be very conveniently removed from this and other sulphide precipitates by extraction with carbon disulphide in a simple manner due to Vortmann.[1] After washing with hot water, the sulphide is washed several times with alcohol, and the crucible then placed on a glass triangle standing in a beaker containing some CS_2. The beaker stands on a hot water bath and is covered with a round bottomed flask filled with cold water. This acts as a reflux condenser, and the CS_2 condensed on it drips on to the sulphide in the crucible standing just below. All free sulphur will have been removed after about an hour's extraction in this way. The precipitate is freed from CS_2 by washing with a little alcohol, and it is then dried at 110° and weighed.

Mercuric sulphide is distinctly amphoteric though less clearly so than the sulphides of arsenic, antimony, and tin.

In strongly alkaline solutions containing sufficient soluble sulphide it gives rise to salts of the very unstable, feeble acid $Hg(SH)_2$. The equilibria between the HgS and the alkaline sulphide solution can be formulated as follows :—

[1] *Uebungsbeispiele aus der quantitativen chemischen Analyse*, Leipzig, 1910, p. 33.

$$\begin{array}{l} Hg(SH)_2 + 2NaOH \rightleftarrows Hg(SNa)_2 + 2H_2O \\ \quad\quad\quad\

The solubility of mercuric sulphide in strongly alkaline solutions of sodium or potassium sulphides and its insolubility in ammonium sulphide may be made use of in analysing complex mixtures containing several metals in analytical group II.[1]

Estimation of Arsenic as As_2S_5 [2]

All the arsenic must be present in solution as arsenic acid. Suppose there is about 0·2 gram As_2O_5 in 50 c.c. of solution or less. To this amount of solution, which must be cooled in ice, 100 c.c. of ice-cooled, concentrated hydrochloric acid is added slowly. The strongly acid solution, contained in a 400 c.c. conical flask, is treated with a rapid current of hydrogen sulphide for about an hour.

The flask is then corked up and left to stand for two hours. The precipitated As_2S_5 is then filtered through a Gooch crucible which has been dried at 105°, thoroughly washed with water, and finally several times with alcohol in order to facilitate subsequent drying. It is dried at 105° and weighed as As_2S_5.

The above method, which gives excellent results when carried out exactly as above, has been given, not so much because it is a method which would often be used, as because it throws an interesting light on the nature of a solution of arsenic acid. Under the above conditions of precipitation bismuth, lead, cadmium, and antimony remain unprecipitated, so that in some cases the method might well be valuable.[3] It is very necessary to keep the solution quite cold during the addition of the hydrochloric acid, otherwise there is liberation of chlorine, and formation of a corresponding amount of arsenious compound. The resulting sulphide precipitate would then contain some As_2S_3, and low results would be obtained.

Arsenic acid is a fairly strong acid, rather weaker than

[1] See Mellor, *A Treatise on Quantitative Inorganic Analysis*, 1913, p. 341.

[2] Neher, *Z. anal. Chem.*, 1893, **32**, 45.

[3] If arsenic is being separated in this way from bismuth, etc., the As_2S_5 must be washed first with strong hydrochloric acid until the other metals are removed and then with water.

phosphoric acid, though very similar to it. It ionizes in solution almost entirely in such a way as to yield the three ions H_2AsO_4', $HAsO_4''$, and AsO_4''' and, of course, hydrogen ions. But arsenic acid must be looked upon as an amphoteric substance, possessing very feeble basic properties in addition to its much more marked acidic ones. It is much more acidic and correspondingly less basic than arsenious acid, in agreement with the common rule that where an element forms several oxides the higher ones are the most acidic and the lower the most basic.

It must be supposed, then, that there is a very minute concentration of positive arsenic ions in a solution of arsenic acid in virtue of the basic ionization of the very weak base $As(OH)_5$:— $As(OH)_5 \rightleftarrows As^{\cdots\cdots} + 5OH'$. Addition of hydrochloric acid to a solution of arsenic acid would favour the formation of $As^{\cdots\cdots}$ ions first by increasing the proportion of un-ionized H_3AsO_4 and then by encouraging the ionization of the latter in the basic $As(OH)_5$ form by removing OH' ions as water.

The precipitation of As_2S_5 must be regarded as due to the union of $As^{\cdots\cdots}$ and S'' ions. The fact that it can separate from such strongly acid solutions shows that it must have an extremely small solubility product.

It is not surprising, then, that H_2S precipitates pure As_2S_5 even from weak (0·37 per cent As_2O_5) solutions of arsenic acid containing only a few per cents of HCl.[1] The trouble is that in weakly acid solutions the formation of the As_2S_5 precipitate occurs with extreme slowness owing to unstable conditions of false equilibrium persisting. It is probable that the main function of the large excess of hydrochloric acid required for satisfactory quantitative precipitation of As_2S_5 is to cause rapid coagulation and separation of the colloidal sulphide. A large amount of HCl might be expected to favour formation of $As^{\cdots\cdots}$ ions, and so promote the precipitation of As_2S_5 but, as pointed out by Stieglitz,[2] it would at the same time diminish the concentration of S'' ions. This removal of S'' ions by

[1] Usher and Travers, *J. Chem. Soc.*, 1905, **87**, 1370.

[2] *Loc. cit.*, vol. **1**, p. 249.

disturbance of the equilibrium $2H^{\cdot} + S'' \rightleftarrows H_2S$ would be unfavourable to precipitation of As_2S_5. The favourable and unfavourable effects of the acid probably balance one another. This can be seen from the following considerations, on the assumption that the law of mass action can be applied, which is certainly not correct for the strong solutions in the quantitative precipitations, but which might well be approximately true for the dilute solutions in Usher and Travers' experiment.

If $As(OH)_5$ is a very weak base and very slightly ionized, while its chloride $AsCl_5$ is largely ionized, we should have

$$As(OH)_5 + 5H^{\cdot} + 5Cl' \rightleftarrows As^{\cdot\cdot\cdot\cdot\cdot} + 5Cl' + 5H_2O$$

$$\text{whence} \quad [As^{\cdot\cdot\cdot\cdot\cdot}] = K_1[As(OH)_5][H^{\cdot}]^5$$

$$\text{But} \quad 2H^{\cdot} + S'' \rightleftarrows H_2S$$

$$\text{so that} \quad [S''] = \frac{K_2\,[H_2S]}{[H^{\cdot}]^2}$$

Precipitation of As_2S_5 will occur only when the value of the product $[As^{\cdot\cdot\cdot\cdot\cdot}]^2[S'']^5$ exceeds the value of the solubility product. By substituting the above values for $[As^{\cdot\cdot\cdot\cdot\cdot}]$ and $[S'']$ in the expression it is seen to be independent of the hydrogen ion concentration. There may actually be a slight favourable effect of the added acid on account of its first action in diminishing the acidic ionization of the H_3AsO_4.

The action of the H_2S on solutions of arsenic acid is complicated by another possibility. This is reduction of arsenic to arsenious acid by some such reaction as :—$H_3AsO_4 + H_2S = H_3AsO_3 + S + H_2O$, perhaps, however, best represented as follows :— $As^{\cdot\cdot\cdot\cdot\cdot} + S'' = As^{\cdot\cdot\cdot} + S$. In dilute solutions at low temperature this reduction of arsenic acid is very slow. It is hastened by rise of temperature.

As is well known, great difficulty is found in precipitating arsenate solutions with H_2S in ordinary qualitative analysis if they have not previously been reduced by SO_2. This is because precipitation of As_2S_5 and the reduction of H_3AsO_4 with subsequent precipitation of a mixture of As_2S_3 and sulphur both occur so slowly.

CHAPTER XI

QUANTITATIVE SEPARATIONS BY MEANS OF HYDROGEN SULPHIDE IN ACID SOLUTION

THE following separations have been selected not because they are necessarily the best or most convenient methods for separating the metals concerned in all cases, but because they illustrate the influence of two important peculiarities of sulphide precipitates on analytical procedure.

On the one hand, the tendency for more soluble sulphides such as CdS or ZnS to take part in the amphoteric neutralization and condensation of less soluble sulphides such as CuS may make a perfect separation difficult in such cases, even in presence of considerably more acid than would normally suffice to prevent precipitation of the more soluble sulphide. An alternative way of looking at this co-precipitation, which really amounts to much the same thing in the end, is to suppose that the more soluble sulphide is always tending to condense into a much more complex and less soluble form, but that this is so slow that a condition of false equilibrium persists. Precipitation of a less soluble sulphide partially breaks down this false equilibrium.

On the other hand, the persistence of false equilibria may enable separations to be effected somewhat unexpectedly. Thus, the false equilibria persist much longer with NiS and CoS than with ZnS, though the true solubility of the latter may be greater. This enables zinc to be separated as sulphide in weakly acid solution from nickel and cobalt.

The Separation of Copper and Cadmium [1]

Owing to the fact that CuS is much less soluble in acids than is CdS it is possible to get an excellent separation by precipitating the copper as CuS from a strongly acid solution.

To the sulphate solution of the metals concentrated

[1] Treadwell, *Analytical Chemistry*, 1919, vol. **2**, p. 200.

sulphuric acid is added until there is one part of the acid to four parts of the aqueous solution. The solution is then heated to boiling and H_2S passed through the boiling liquid for 20 minutes : the heating is continued for another quarter of an hour after the current of H_2S has been stopped. The hot liquid is then filtered, the funnel being kept filled with CO_2 to prevent oxidation of the moist sulphide, which is thoroughly washed with hot boiled-out water. The precipitate washes splendidly but always contains a little cadmium sulphide ; hence, it has to be dissolved and precipitated a second time.

The precipitate is rinsed into a porcelain dish, dissolved in nitric acid, treated with some sulphuric acid and evaporated as far as possible on the water bath to drive off the nitric acid. The contents of the dish, including any sulphur which has separated, are rinsed into a roomy beaker with as little water as possible, treated with about 50 c.c. of sulphuric acid (1 to 4) for every 0·1 gram of copper and the precipitation of the latter is then carried out as above. The CuS, on ignition in hydrogen, is converted into Cu_2S, which is weighed.

The cadmium is precipitated as sulphide in the filtrate from the copper, but the greater part of the acid present must be neutralized with ammonia until there are only about 5 c.c. of concentrated acid to every 100 c.c. of solution. The precipitation is carried out by saturating the cold solution with hydrogen sulphide. The precipitate is filtered off (it filters well) and washed with water containing a little HCl and H_2S. Unfortunately, one cannot obtain good results by weighing cadmium as CdS, as has often been recommended, for it is not possible to obtain the precipitate free from $CdSO_4$ (or $CdCl_2$ if a chloride solution is used) and CdS is too volatile to ignite with sulphur in a current of hydrogen as in the case of zinc. The CdS is accordingly converted into $CdSO_4$ as follows :—

The greater part of the cadmium sulphide precipitate[1] is transferred by means of a spatula to a porcelain dish

[1] It need not be washed if it has been precipitated from a solution containing only ammonium salts.

and covered with hydrochloric acid (1 : 3). The dish is covered with a clock glass and heated on the water bath until all the precipitate has dissolved. The dish is then placed beneath the funnel, and the CdS still adhering to the filter is dissolved by means of a little hot hydrochloric acid (1 : 3), the filter being subsequently well washed with hot water. The contents of the dish are evaporated to dryness, the residue dissolved in a little dilute sulphuric acid and rinsed into a weighed porcelain crucible. One c.c. of concentrated nitric acid (to oxidize fibres from the filter paper, which otherwise cause slight reduction of the $CdSO_4$) and a small excess of sulphuric acid are added. The contents of the crucible are evaporated as far as possible on the water bath, and the excess of sulphuric acid is then driven off by cautiously heating the crucible in a small air bath formed by a large crucible containing an asbestos ring into which the smaller crucible fits. The temperature is raised gradually until no more H_2SO_4 fumes are given off. The $CdSO_4$ finally obtained should be quite white and completely soluble in water. The method gives excellent results.

The carrying down of sulphate or chloride by CdS precipitates is of some interest : the cause is the same as that which leads to the carrying down of iron, chromium, etc., by $BaSO_4$ (see p. 113). Cadmium salt solutions are well known to be peculiar owing to a considerable proportion of the cadmium being present in the form of complex anions such as $Cd(SO_4)_2''$ or $CdCl_4''$. These ions take part in the electrolytic neutralization and coagulation of the CdS sol which is first formed. The consequence is that the ratio of cadmium to sulphur in the precipitate is not quite what it should be for pure CdS, and the precipitate can be regarded as containing small amounts of $CdSO_4$ or $CdCl_2$.

Separation of Cu from Zn, Ni, or Co

Even when CuS is precipitated from strongly acid solution it carries down some ZnS, NiS, or CoS if any one of these metals is present. By double precipitation of the copper, as in the case of Cu and Cd, a perfect separation can be

obtained. According to Treadwell, copper and zinc can be separated perfectly by one precipitation if 20 to 30 c.c. of 2N HCl or H_2SO_4 are present in every 100 c.c. of solution.

It is, however, generally best to precipitate copper as Cu_2S by the thiosulphate method if Zn, Ni, or Co is present. A perfect separation is then obtained in one operation (see page 224).

Separation of Mn from Ni or Co

These separations depend on the insolubility of NiS and CoS in acetic acid.

The chloride or sulphate solution is treated with a small excess of Na_2CO_3, then acidified strongly with acetic acid, and 0·5 gram ammonium acetate is added for every 0·1 gram of Ni or Co. The solution, which should occupy from 10 to 20 c.c., is heated to 70°–80° and saturated with H_2S. The precipitated NiS or CoS is filtered and washed with hot water.

The filtrate is evaporated to at least half its bulk, made alkaline with ammonia, and colourless ammonium sulphide is added to the cold solution. This precipitates the MnS which, however, almost always contains some NiS or CoS. A small excess of acetic acid is, therefore, added, and the mixture warmed. All the MnS dissolves easily but the small amount of NiS or CoS remains insoluble and is filtered off on a separate small filter paper.

From what has been said previously it will be realized that the small amount of nickel or cobalt sulphide recovered from the manganese sulphide precipitate had been kept in solution not so much owing to its true solubility in the acid as owing to the partial persistence of a condition of false equilibrium.

The manganese is precipitated as MnS from hot ammoniacal solution, and after ignition in hydrogen weighed as MnS.

Estimation of the Nickel or Cobalt

The washed NiS or CoS is ignited, dissolved in HCl, and the metal precipitated as hydrated Ni_2O_3 or Co_2O_3 by means of KOH and bromine (see page 124). During ignition of

the sulphide some sulphate is always formed so that the oxides obtained cannot be weighed directly. In the case of cobalt the estimation is more conveniently made by converting the ignited sulphide into sulphate and weighing as $CoSO_4$. The method of doing this is similar to that given for cadmium on p. 183.

Separation of Zinc from Nickel or Cobalt

The separation of these metals depends on the fact that ZnS can be precipitated from a rather more acid solution than can NiS or CoS—not so much because the true solubility is less, as because the conditions of false equilibria and supersaturation persist less readily in the case of ZnS than with NiS or CoS.

The following method is originally due to Zimmermann,[1] and has been modified by Treadwell.

The faintly acid solution containing the metals as chlorides or sulphates is treated with sodium carbonate solution until there is a slight permanent precipitate, which is dissolved by the addition of a few drops of quite weak hydrochloric acid. For every 80 c.c. of the solution—containing from 0·2 to 0·3 gram of the metals—10–15 drops of twice normal hydrochloric acid are added, and then 10 c.c. of a 1 : 5 solution of ammonium thiocyanate, chloride, or sulphate.

The solution is heated to 50°–70°, and is saturated with H_2S. For some time little happens, but after a while pure white ZnS separates in flocks which gradually become more and more compact. When the solution is thoroughly saturated with H_2S, the covered beaker is left to stand in a warm place until the precipitate has settled completely. The zinc sulphide is then filtered and washed, first by decantation, with a 2 per cent solution of NH_4Cl, $(NH_4)_2SO_4$, or NH_4CNS saturated with H_2S. It is finally dried, ignited in hydrogen and weighed as ZnS.

The nickel and cobalt (and manganese, if present) are best precipitated from the filtrate by ammonium sulphide,

[1] *Annalen*, 1879, **199**, 3.

the sulphide precipitate is dissolved in aqua regia, and the metals are then separated and estimated in a suitable manner.

In the above method for separating zinc it is quite necessary to add about the amount of hydrochloric acid indicated, since otherwise the separation is not complete and some nickel or cobalt sulphide is carried down with the zinc—especially if the solution contains much nickel or cobalt and little zinc.

The ammonium salts added are all salts of strong acids, and consequently will have little effect on the acidity of the solution. Their function appears to be simply that of coagulating the colloidal zinc sulphide and accelerating the breakdown of the condition of false equilibrium. In the proportions used they do this for the zinc sulphide but not for the nickel or cobalt sulphide. They do it partially for the latter also, however, if much nickel or cobalt is present, and there is insufficient hydrochloric acid.

The method of separating zinc from cobalt or nickel which has just been described is given mainly because of the peculiar effects of false equilibrium which are involved. The present writer's experience is that it is very difficult to precipitate the zinc completely, and he does not consider the method a good one. From the results given by Treadwell, however, it would seem that it can effect a good separation under certain conditions. It is probably better to separate cobalt from zinc by means of α-nitroso-β-naphthol, and nickel from zinc by means of α-dimethylglyoxime (see Chapter XII).

CHAPTER XII

CO-ORDINATION AND SOLUBILITY

IT is well known that the majority of simple compounds are not fully saturated. In terms of the ordinary simple valencies the molecules of such compounds may appear to be saturated, but they are, nevertheless, still capable of forming numerous more complex compounds by combination with other molecules. Such compounds have been very fully investigated, especially by Werner, who has, as a result, developed his theory of " Co-ordination ".[1]

Werner has shown that the numerous complex salts are best conceived as originating by the addition of electrically neutral molecules to positive ions. The molecules so added may be of the most varied nature, H_2O, NH_3, various organic amines, etc. Positive complex ions result in this way, which carry the same number of charges as the original simple ions. By suitable methods, however, one or all of the associated negative ions may take the place of one or more of the neutral molecules in the complex ion, and when all the original negative ions are so attached a complex compound results which is a non-electrolyte. The process can go further, however, and more of the neutral molecules can be replaced by negative ions derived from other salts. Negatively charged complex ions then result, which are balanced by the positive ions originally associated with the additional negative ions. As an example of these different stages the following may be given :—

$CrCl_3$; $[Cr(NH_3)_6]Cl_3$; $[Cr(NH_3)_3Cl_3]$; $K_3[CrCl_6]$;
$(Cr''' + 3Cl')$; $([Cr(NH_3)_6]''' + 3Cl')$; (non-electrolyte) ; $(3K' + [CrCl_6]''')$.

The various complex negative ions of complex salts can be derived in this way.

[1] See his *New Ideas on Inorganic Chemistry*, English edition, published by Longmans, Green, and Co. (1911).

Abegg and Bodländer[1] approach the matter rather differently, considering that complex ions originate by the addition of neutral molecules (H_2O, NH_3, various neutral salts or salt-like compounds such as SiF_4) to ions, either positive or negative. The two methods of looking at the matter are, however, essentially the same.

The groups or atoms associated in this way with the central atom are said to be co-ordinated with it. In the great majority of cases the maximum number of groups or atoms which can be thus co-ordinated is six. Werner concludes from this that spatial considerations are in some way involved, and sees confirmation of this view in the fact that where the central atom is one of small atomic volume (such as boron, carbon, nitrogen), the maximum number is only four, whilst it is sometimes as high as eight with atoms of large atomic volume such as calcium.

As examples of such co-ordinated compounds the following may be given :—

$[Cu(NH_3)_4](NO_3)_2$; $[CuH_2O(NH_3)_4]SO_4$; $[Cu(NH_3)_6]Cl_2$; $K[BF_4]$; $[NH_4]Cl$; $[N(CH_3)_4]I$; $[Ca(NH_3)_8]Cl_2$; $K_3[Fe(CN)_6]$; $K_4[Fe(CN)_6]$.

The co-ordinated complex is enclosed in square brackets.

The connexion between maximum co-ordination number and atomic volume may be partly accidental. In any case, the maximum co-ordination number of the halogens appears to be only four in spite of the fact that their atomic volumes are comparatively large.

There can be little question that the formation of co-ordination compounds is connected with the production of electron shells of maximum stability just as with simple compounds, but the conditions are more complex, and not so easily interpreted. It is worth noting, however, that in the case of the complex cobaltic salts, which are among the most stable and best investigated of all co-ordination compounds, the cobalt atom appears to be surrounded by an outer shell of 18 electrons. This is the number present in the outer shell of the krypton atom, and is the number towards which the elements in the series of elements which begins with potassium and contains cobalt are trending.

[1] *Z. anorg. Chem.*, 1899, **20**, 453.

The atomic number of cobalt is 27, and its outermost electron shell contains nine electrons (on the Langmuir system). The cobaltic ion having lost three electrons only contains six electrons in its outer shell. If six molecules of NH_3, H_2O, or other compounds having two unshared electrons available attach themselves to the cobaltic ion, so that two electrons of each NH_3, etc., are shared between the cobalt and nitrogen (or oxygen, etc.), a complex is formed in which there is a cobalt nucleus with an outer shell of 18 electrons. The remarkable stability of compounds such as $[Co(NH_3)_6]Cl_3$ is intelligible on this basis.

Where the addition is that of neutral molecules to the cobaltic ion, as in the case just considered, the resulting complex carries the same number of positive charges as a simple cobaltic ion. But the necessary additional electrons required to build up the shell of 18 need not all be obtained in this way. Thus in $Co(NH_3)_3Cl_3$ six electrons are contributed by the three nitrogen atoms while each chlorine atom supplies only one. In such compounds there are no electrovalencies and the compound is a non-electrolyte, but the cobalt nucleus is surrounded by an 18 electron shell.

In the compounds $[Co(NH_3)_4Cl_2]Cl$ and $[Co(NH_3)_5Cl]Cl_2$ one and two, respectively, of the chlorine atoms are attached by electrovalencies and are ionizable, but the cobalt nucleus has still the 18 electron shell.

There is still another method of building up the 18 electron shell. Three additional electrons may be obtained by means of co-valencies, as in $Co(NH_3)_3Cl_3$, while six others are contributed by negative ions instead of by neutral molecules such as NH_3. Compounds such as $[CoCl_6]K_3$ or $[Co(NO_2)_6]K_3$ are formed in this way, and the complex carries as many negative charges as the ions which have been added.

It is to be noted that although in the complex compounds just considered the attachment of neutral molecules such as NH_3 to the central atom of the complex has originated in a different manner from the co-valency attachment of a chlorine or similar atom or group, yet the final attachment is electronically identical. In each case it is by means of two shared electrons, and the two modes of attachment can

be regarded as somewhat different types of co-valencies. Werner has shown quite clearly that, structurally, the two types of attachment are identical, though he refers one to "subsidiary" valency and the other to "principal" valency.

When dealing with chemical combination and reactivity in terms of atomic structure Langmuir's fixed electron system is much more convenient than any system of rotating electrons. All attempted explanations in this direction have so far been based on the fixed electron system. Usually, too, electron shells of the Langmuir size and order have been assumed rather than those of the Bohr type. Which size and order of electron shells will eventually prove to be best remains to be seen. It must be remembered that the connexion between atomic structure and chemical reactivity is only just beginning to be traced, and views expressed are liable to be quickly altered or modified.[1]

Crystal Formation and Co-ordination

Modern work by the Braggs and others on crystal structure as revealed by X-rays shows that in crystals of simple substances such as sodium chloride the simple chemical molecules have but a doubtful existence. In these cases there seem to be indications that each atom in the crystal edifice is combined in a further sense than it is in an isolated simple molecule. It appears to be more or less fully co-ordinated in that each positive atom is equally related to and surrounded by a number of negative ones, and conversely for each negative atom. The connexion, however, between the structure of such crystals and the distribution of electrons in the constituent atoms is still obscure. It appears, for example, that in a crystal of sodium chloride neither the sodium nor the chlorine atom has an eight electron sheath,[2]

[1] The following references may be found useful. Lewis, *J. Amer. Chem. Soc.*, 1916, **38,** 762 ; Langmuir, *ibid.*, 1919, **41,** 868, 1543 ; 1920, **42,** 274 ; Bohr, *The Theory of Spectra and Atomic Constitution* (Cambridge University Press, 1922) ; Lowry, *Chemistry and Industry*, 1923, pp. 316, 412, 462, 711 ; Sidgwick, *J. Chem. Soc.*, 1923, **123,** 725.

[2] W. L. Bragg, James and Bosanquet, *Phil. Mag.*, 1922, [5], **44,** 433.

as seems to be the case with sodium and chlorine ions. In the crystals of more complex compounds the simple chemical molecules do not lose their identity as in crystals of very simple compounds. They are still distinguishable, but are grouped together in small numbers (generally 2, 3, or 4) to form the units of which the crystals are constructed.[1] This difference, if it is a real one, is possibly due to the fact that most of the atoms within a complex molecule are already more or less fully co-ordinated within the chemical molecule itself, so that the additional co-ordination occurring on crystallization is of a much less profound character.

Solution and Co-ordination

Whilst it is almost impossible to prove it, there are reasons for thinking that solubility in water depends, among other things, upon a capacity for combination with water, or hydration. That hydration can occur in many cases is shown by the separation of crystalline hydrates, though the existence of these does not necessarily show that they are present to any extent in the aqueous solution from which they separate. Conversely, the fact that only the anhydrous salt separates from solution does not prove that hydrates of the salt are not present in the solution. The degree of hydration of the dissolved substance need not correspond to any simple molecular ratio, but should be regarded rather as representing a definite attraction or affinity between molecules of solute and molecules of water. If no such attraction existed between a substance and water, the attraction between the water molecules would prevent solution of the substance. The more nearly the attraction between the molecules of solute and water approximates to that between the water molecules themselves the greater is the solubility to be expected. A substance will dissolve in water until a condition of equilibrium is reached where these several attractions are satisfactorily balanced.

Perfectly definite solubilities under any specified set of conditions originate in this way. The type of combination

[1] W. H. Bragg, *J. Chem. Soc.*, 1922, **121**, 2766.

thus postulated in solution would necessarily be somewhat indefinite as it would depend to some extent on the concentration of the dissolved substance, on the temperature, and on other factors. The compounds present are perhaps best considered as analagous to the adsorption complexes formed by colloidal particles rather than to the definite co-ordination compounds which it is possible to obtain in the crystalline condition. The attraction between water and a compound containing definite water of crystallization would probably be more like the attraction between water molecules themselves than would the attraction between water and a compound which could not form compounds with water of crystallization. It is not surprising, therefore, to find that in a series of salts the more highly hydrated ones are generally the more soluble, though the converse does not of necessity follow. The diminishing solubility of the chlorides and nitrates of the alkali or alkaline earth metals with increasing atomic weights may be connected with their diminishing capacity for co-ordination with water. The effect of combined water in increasing solubility is shown rather well by the following pair of compounds. Luteocobaltic chloride $[Co(NH_3)_6]Cl_3$ is soluble at 0° to the extent of 4·26 grams of the salt in 100 grams of water, while roseocobaltic chloride $[Co(NH_3)_5H_2O]Cl_3$ dissolves at 0° to the extent of 16·12 grams per 100 grams water. At higher temperatures also the roseo compound is much more soluble.

Many of the peculiarities of solubility in water are probably to be interpreted in terms of varying capacity for hydration in the dissolved state. The greater this is the greater is the solubility to be expected. The average organic compound is insoluble in water unless it contains an adequate proportion of $-OH$, $=CO$, $-NH_2$, or other similar groups containing atoms which are not fully saturated from the co-ordination point of view. It may be hydration of these groups which causes solution.

The capacity for hydration in the dissolved state is commonly indicated by the tendency to form crystalline hydrates, though there seem to be exceptions. Thus $AgNO_3$ is known only in the anhydrous state, though its great solubility

suggests considerable hydration in the dissolved state. It is an unfortunate fact that we know comparatively little about the structural nature of salt hydrates. In a good number of cases there is every reason to suppose that the water of hydration is associated with the positive constituent of the salt (e.g. $[Co(H_2O)_6]Cl_2$), but in other cases some, or all, of it may be associated with the negative constituent. The electronic structure of the salt and its constituent atoms is doubtless the determining factor in hydration as in all other chemical relationships. The H_2O molecule, owing to the unshared electrons of the oxygen atom, is particularly ready to help to build up incomplete electron shells round other atoms. This is doubtless what occurs when solid hydrates are formed and also in a modified form when substances dissolve in water.

The formation of hydrates, as also of other complex compounds, is dependent in some way upon spatial factors, and so is solubility in water. If a molecule is derived from ions of very unequal size, the smaller ion—whether this is the cation or anion—will tend to expand, when opportunity occurs, by addition of water or other compounds. Hydrated ions or other complex ions result. Many very soluble electrolytes are actually derived from ions of very unequal size, while sparing solubility is found with salts having spatially similar anion and cation.[1]

Where a simple compound has resulted from the union of two atoms which both have a high capacity for co-ordination it is not improbable that this capacity may be satisfied either within the molecule itself or by co-ordination with molecules of its own kind in preference to molecules of water.

This would account for the great insolubility of compounds formed by the union of two ions of low electro-affinity, such as oxides, hydroxides, and sulphides of the heavy metals.

From the point of view of co-ordination and hydration one thus comes to the conclusion that there should be two types of salt-like compounds which are very sparingly soluble in water. These are (1) compounds formed by the union

[1] Ephraim, *Ber.*, 1921, **54** B, 379.

of two atoms or groups having a small capacity for co-ordination with water or other molecules or atoms; examples are CsCl, $BaSO_4$, $KClO_4$. (2) Compounds formed by the union of two atoms or groups having a great capacity for co-ordination with water or other molecules or atoms; examples are CuS, AgCNS, $Fe(OH)_3$, possibly CaF_2.

As a class the compounds of type (1) would tend to be more soluble than those of type (2), for most of the constituent ions have some capacity for hydration.

The most soluble compounds should be those formed by the union of an atom or group having a high capacity for co-ordination with another having only a very small capacity. Examples of such compounds are the strong mineral acids, the oxides and sulphides of the alkali metals, $AgNO_3$, $FeCl_3$. Many, but not all, compounds of this type are soluble in alcohol, ether, and other organic solvents owing to co-ordination with them. Other compounds would naturally occupy intermediate positions. It will be seen that the conclusions with regard to solubility reached by this method are precisely the same as those reached when considering the matter from the standpoint of the theory of electro-affinity (see page 57).

If the constituent molecules in a crystalline anhydrous salt are more or less saturated by co-ordination among themselves, this condition has to be broken down before solution in water can occur. If, on the other hand, the salt is hydrated this breaking down process has already begun so that solution of the hydrated salt in water may be expected to occur more readily than in the case of the corresponding anhydrous salt. The final solubility reached, however, need not necessarily be greater.

Anhydrous crystalline salts (e.g. $FeCl_3$, $CoCl_2$, $CaSO_4$) do frequently dissolve more slowly than the hydrated compounds, even though, in cases where a solution saturated with respect to the anhydrous salt can be finally obtained, it may actually be supersaturated with respect to the hydrated salt at the same temperature. The remarkable insolubility of sublimed $CrCl_3$ as compared with the hydrated compound is a striking instance of this behaviour.

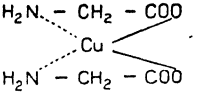
There seems no doubt from vapour density determinations that anhydrous ferric chloride is Fe_2Cl_6 at 400°, though at higher temperatures it dissociates into simple $FeCl_3$ molecules.[1] At 1200°–1300° anhydrous chromic chloride has a vapour density corresponding to $CrCl_3$, but with this compound also there are indications of Cr_2Cl_6 molecules at lower temperatures.[2] Other anhydrous chlorides (e.g. ferrous, chromous) also have double molecules at lower temperatures, which dissociate as the temperature is raised.[2] Molecules such as Fe_2Cl_6 or Cr_2Cl_6 may be regarded as being of the non-electrolyte type and containing two fully co-ordinated metallic atoms and representable by the co-ordination formulæ $[Cl_3Fe : FeCl_3]$ and $[Cl_3Cr : CrCl_3]$. Such formulæ would agree well with the insolubility of sublimed anhydrous chromic chloride and the comparatively slow rate at which anhydrous sublimed ferric chloride dissolves.

It is to be noted that though on the above method of formulation both the iron and chromium atoms would be fully co-ordinated in Werner's sense, they would not be surrounded by shells of 18 electrons. Each iron or chromium atom is sharing six electrons with the second atom of iron or chromium and two electrons with each chlorine atom. This would give a 14 electron shell round each iron atom and a 12 electron shell round each chromium atom. Judging by the greater insolubility of the chromic chloride the 12 electron shell is more stable than that of 14 electrons. The compounds could be formulated also as $[FeCl_6]Fe$ and $[CrCl_6]Cr$, in which only one of the two metallic atoms is fully co-ordinated in Werner's sense. Even then the fully co-ordinated chromium atom would only have a shell of 15 electrons surrounding it, as in most ordinary co-ordinated chromic compounds, while the fully co-ordinated ferric atom would have a 17 electron shell. Co-ordination formulæ of the symmetrical non-electrolytic type seem to agree better with the general character of the anhydrous chlorides than do the unsymmetrical formulæ.

[1] Grünewald and V. Meyer, *Ber.*, 1888, **21**, 687.
[2] Nilson and Pettersson, *J. Chem. Soc.*, 1888, **53**, 814.

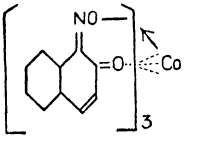
The solubility of salt-like compounds in water is evidently due to a number of causes, of which the capacity for ionization and the capacity for co-ordination with water are two of the most important. If both of these are absent great insolubility should result.

Where a salt-like compound has become co-ordinated within the simplest chemical molecule in such a way as to have at the same time lost the capacity for ionization it should be very sparingly soluble. One of the simplest examples of this type seems to be copper glycocollate, which is almost a non-electrolyte, the copper atom being co-ordinated with the two $-NH_2$ groups as well as with the two $-COO$ groups thus [1]:



There is also a molecule of water of crystallization in the solid salt, the position of which is not clear. The compound is sparingly soluble in water, and it is possible that this solubility is mainly determined by slight co-ordination with solvent water in lieu of the $-NH_2$ groups. The slight conductivity may also depend upon this.

One of the most striking examples of this type of compound and one of the most interesting from the analytical point of view is the cobaltic salt of 1 : 2-naphthaquinone-1-oxime (α-nitroso-β-naphthol). This compound is very stable and insoluble, and is used as a means of quantitatively separating cobalt from nickel and other metals. Morgan and Smith [2] have shown that it has the following structure, the cobalt atom being fully co-ordinated and non-ionizable.



[1] See Abegg and Auerbach's *Handbuch der anorg. Chem.*, 1908, vol. **2**, pt. 1, p. 534.

[2] *J. Chem. Soc.*, 1921, **119**, 704.

Separation of Cobalt from Nickel by means of α-Nitroso-β-Naphthol [1]

As is well known, nickel forms only one series of salts, in which the metal is divalent, while cobalt forms compounds in which it is either di- or tri-valent. Although the compounds of divalent cobalt and nickel do differ greatly in some respects, as, for example, in colour, yet they are chemically so similar that satisfactory quantitative separations are not possible. Trivalent cobalt, however, is so different from divalent nickel that separation is easy enough, and all the usual analytical methods for separating nickel and cobalt are, in fact, methods for separating divalent nickel from trivalent cobalt and make use of the capacity which trivalent cobalt possesses of forming very stable co-ordination compounds.

If excess of a cobalt salt is added to a neutral aqueous solution of sodium α-nitroso-β-naphthol a brownish red precipitate of the cobaltous salt $(C_{10}H_6NO_2)_2Co$ is obtained. By heating with acids it is converted into the cobaltic salt $(C_{10}H_6NO_2)_3Co$. The oxidation involved is brought about in all probability partly by water and partly by atmospheric oxygen. The equations expressing the reactions in the two cases would be :—

$$2(C_{10}H_6NO_2)_2Co + 2C_{10}H_6NO_2Na + 2H_2O = 2(C_{10}H_6NO_2)_3Co + 2NaOH + H_2$$

$$2(C_{10}H_6NO_2)_2Co + 2C_{10}H_6NO_2Na + H_2O + O = 2(C_{10}H_6NO_2)_3Co + 2NaOH$$

This would be analogous to the oxidation of potassium cobalto-cyanide to potassium cobalti-cyanide discussed on page 222.

The nickel compound $(C_{10}H_6NO_2)_2Ni$ is obtained as a brownish yellow precipitate on adding a nickel salt to a solution of α-nitroso-β-naphthol in 50 per cent acetic acid. It is sparingly soluble in water, but hydrochloric and sulphuric acids decompose it readily, dissolving the nickel whilst α-nitroso-β-naphthol separates. These facts are applied

[1] Ilinski and Knorre, *Ber.*, 1885, **18**, 699; Lunge, Keane, *Technical Methods of Chemical Analysis*, 1911, vol. **2**, pt. 1, p. 312.

to the quantitative separation of cobalt from nickel by means of α–nitroso–β–naphthol, as follows :—

The solution of the metals in dilute nitric acid is evaporated down with a slight excess of sulphuric acid, and the nitric acid completely driven off. The residue is dissolved in water, 5 c.c. of dilute (twice normal) hydrochloric acid are added, the solution is warmed, and a freshly prepared hot solution of α–nitroso–β–naphthol in 50 per cent acetic acid added until, when the precipitate has subsided, a fresh addition of the solution produces no further precipitate. After digesting for several hours at a gentle heat, the very bulky precipitate of the cobaltic compound and much α–nitroso–β–naphthol is filtered off, washed first with cold, then with warm, 12 per cent hydrochloric acid, and finally with hot water. The filter is then folded together and placed in a weighed platinum crucible, and the crucible with the lid on is heated over a bunsen burner. When no more combustible gases are evolved, the lid is removed, the crucible placed in a slanting position, and the coke-like carbon, which burns with difficulty, ignited away completely ; this requires from half an hour to an hour.

If care be taken to secure good access of air, the cobalt is left behind as black Co_3O_4. If reducing gases from the burner are allowed to get into the crucible they may cause some reduction to CoO or even metallic cobalt. As there is always some uncertainty in weighing cobalt as oxide, the latter after weighing may be transferred to a weighed porcelain Rose crucible and weighed as metal after ignition in a current of hydrogen.

The above method gives excellent results, but on account of the bulkiness of the cobaltic compound it is best adapted for the estimation of small quantities of the metal. It cannot be used to separate cobalt directly from copper, chromium, and iron, which would be precipitated along with the cobalt. Although few, if any, other metals would be similarly precipitated, it is generally best first to separate cobalt and nickel together from other metals, and then to estimate the cobalt in the mixture.

The Separation and Estimation of Nickel by means of α–Dimethyl Glyoxime

Tschugaeff [1] showed in 1905 that α–dioximes differ from all others in reacting with nickel, cobalt, iron, platinum, palladium, and copper salts to form stable compounds which he called dioximines. Of these dioximines the nickel, platinous, and palladous compounds are of such remarkable stability and so insoluble that they can be used to effect a complete separation of nickel, palladium, and platinum from other metals.

α-dimethyl glyoxime

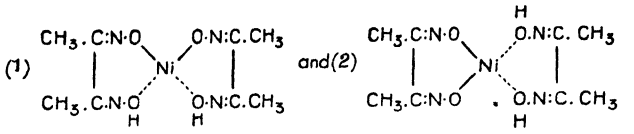
$$\begin{matrix} CH_3.C:NOH \\ | \\ CH_3.C:NOH \end{matrix}$$

has come into general use as a reagent for the detection and estimation of nickel [2] as it enables nickel to be rapidly and quantitatively separated by precipitation from iron, aluminium, chromium, cobalt, manganese, zinc, and probably copper and other metals. It is a white crystalline powder, insoluble in water but soluble in warm alcohol. A 1 per cent alcoholic solution is used for the precipitation; this produces a bright red precipitate of the nickel compound $Ni(O.N:C.CH_3:C.CH_3:N.OH)_2$. This compound, which can be sublimed unchanged at 250°, is very insoluble in water, and Tschugaeff states [3] that dimethyl glyoxime will give a definite reaction for nickel in a solution which contains only 1 part of nickel in 400,000 parts of water. It is only very slightly soluble in alcohol, ether, benzene, glacial acetic acid, or pyridine, and is very stable towards most reagents. Alkali hydroxides and ammonia, alkali and ammonium carbonates, and hydrogen sulphide do not attack it, whilst ammonium sulphide acts only slowly. Weak acids do not affect it, but with strong acids there is reversible decomposition into dimethyl glyoxime and the nickel salt of the acid.

The insolubility of the nickel glyoximine is due to the fact that it is a non-electrolyte which is fully co-ordinated within

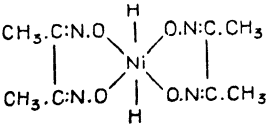
[1] *Z. anorg. Chem.*, 1905, **46**, 144.
[2] Brunck, *Z. angew. Chem.*, 1907, **20**, 834, 1844.
[3] *Ber.*, 1905, **38**, 2520.

the single chemical molecule. Tschugaeff suggested two alternative structural formulæ—



of which the first is possibly to be preferred.

According to both formulæ the nickel has a Werner co-ordination number of four as in many complex nickel compounds. The co-ordination is to oxygen atoms in all cases, and according to both formulæ the oxygen atoms are surrounded by 8 electron shells and the nickel atom by a 16 electron shell. The nickel shares two electrons with each oxygen atom, but in the case of those to which it is joined by full lines in the formulæ one electron is contributed by the nickel and one by the oxygen. These are " principal valencies " of the " co-valency " type. In the case of the two oxygen atoms to which the nickel is represented as attached by dotted lines all the shared electrons belong to the oxygen atoms. These are " subsidiary " valencies in the Werner notation. Lowry[1] suggests quite a different formula—



in which the nickel has a Werner co-ordination number of six, although the electron shell surrounding it still contains only 16 electrons, as the structure is built up by the attachment of two hydrogen ions to the nickel atom. Whether such a formula will be generally accepted remains to be seen.

The 16 electron shell, though two electrons short of the maximum of 18, seems to be of considerable stability. The cobalt glyoximines which have been prepared are cobaltic compounds such as $[Co(O.N : C.CH_3.C.CH_3 : N.OH)_2(NH_3)_2]Cl$

[1] *Chemistry and Industry*, 1923, p. 464.

in which the cobalt atom has its usual co-ordination number of six and is surrounded by an 18 electron shell. These compounds are electrolytes and consequently do not have the insolubility of nickel glyoximine. It is to be noted that theoretically a cobaltic compound

$$[Co(O.N : C.CH_3.C.CH_3 : N.OH)_3]$$

could have been formed which would have been analagous to the cobalt compound of 1 : 2–Naphthaquinone–1–oxime and which would doubtless have been insoluble. For some reason, however, the cobalt atom builds up an 18 electron shell with the help of two molecules of NH_3—or possibly of H_2O in absence of NH_3—rather than with glyoxime alone. It may be for similar reasons that zinc does not form an insoluble glyoximine.

Such facts as these illustrate the specificity of chemical combination and show the care that must be used in drawing conclusions from considerations of electronic structure alone.

Estimation of Nickel in Nickel Steel by means of α–Dimethyl Glyoxime

To illustrate the estimation of nickel by means of α-dimethyl glyoxime details of the direct determination of nickel in nickel steel will be given.[1]

Iron is either completely oxidized to the ferric state, and the solution then treated with tartaric acid to prevent its precipitation by ammonia, or it is reduced by sulphur dioxide to the ferrous condition, and the nickel precipitated in dilute acetic acid solution in presence of sodium acetate ; the former procedure is adopted in presence of chromium. Small quantities of manganese, copper, or vanadium do not influence the results : if considerable quantities of manganese be present the precipitation must be effected in acetic acid solution owing to the danger of atmospheric oxidation and precipitation of some of the manganese as MnO_2 in ammoniacal solution.

About 0·5 gram of nickel steel is dissolved in 10 c.c. of hydrochloric acid, which should not be too concentrated,

[1] Lunge, Keane, *Technical Methods of Chemical Analysis*, 1911 vol. **2**, pt. 1, p. 66.

and the solution is oxidized with nitric acid. If any silica separates, it is dissolved by the cautious addition of hydrofluoric acid. From 2 to 3 grams of tartaric acid are then introduced, the whole is diluted to 300 c.c., and a small excess of ammonia is added to make sure that no precipitation occurs. The solution is then just acidified with hydrochloric acid and heated to boiling. The nickel is precipitated by the addition of 20 c.c. of a 1 per cent alcoholic solution of dimethyl glyoxime,[1] ammonia being subsequently added drop by drop until the solution is alkaline, to ensure complete precipitation. The precipitate can be filtered at once, though, in the case of specially accurate determinations, it is preferable to allow it to stand for twenty-four hours. The precipitate is collected in a Gooch crucible, washed with cold water, and dried at 110° to 120° to constant weight. It contains 20·3 per cent of nickel.

Alternatively, the precipitate may be collected on a filter paper and weighed as NiO after careful ignition. To avoid sublimation of the glyoxime compound the precipitate is rolled up in the moist filter paper and then wrapped in a second wet filter paper before ignition. The filter and precipitate are first gently heated in the crucible until completely charred, without flame; the temperature is then gradually raised until the filter is incinerated and the residue then very strongly heated.

According to Bogoluboff,[2] it is best to remove most of the iron by shaking with ether, in which ferric chloride is soluble, before the addition of tartaric acid. He states that in presence of a large excess of iron the nickel precipitate is always contaminated with iron which it is impossible to wash out. The subsequent procedure is as given above.

In regard to the use of tartaric acid to prevent the precipitation of iron and chromium by ammonia, it is to be noted that in solutions containing sufficient tartaric acid, the iron and chromium are not present as ferric and chromic ions. The nature of the compounds formed is obscure, but the ferric iron or the chromium appears to be present

[1] The solution does not keep well and should be freshly made.

[2] *Stahl u. Eisen*, 1910, **30**, 458.

entirely in the form of a complex negative ion. This is shown by the fact that on electrolysis the colour travels towards the anode.[1] From the work of Packer and Wark [2] on cupri-tartrates and Wark on cupri-lactates and -malates,[3] it would appear that the metal in such complexes either replaces the hydrogen of alcoholic -OH groups or else partly the hydrogen of alcoholic -OH groups and partly that of -COOH groups. It is possible that, in addition, the metal atom is united by subsidiary valencies, that is, co-ordinated, with other parts of the tartrate molecule, but there is no evidence to show whether such is the case or no.

Separation of Nickel and Cobalt by means of α-Dimethyl Glyoxime

If only a small proportion of cobalt is present the separation and estimation are carried out exactly as described above for the case of nickel steel. In the absence of iron the tartaric acid need not be added. Precipitation should be carried out from a volume of solution such that 100 c.c. does not contain more than 0·1 gram of cobalt. If, however, more cobalt than nickel is present it is better to precipitate from acetic acid solution as follows :—[4]

0·5 gram of the sample is dissolved in hydrochloric acid and the solution evaporated nearly to dryness. To the hot liquid, diluted to 400 c.c., there are added 0·2 gram of α-dimethyl glyoxime (or 20 c.c. of the 1 per cent alcoholic solution) and 2 grams of sodium acetate. The precipitate is filtered off after half an hour and treated as described above.

According to Tschugaeff α-diphenyl glyoxime (α-benzil dioxime)

$$\begin{matrix} C_6H_5.C : NOH \\ | \\ C_6H_5.C : NOH \end{matrix}$$

is about ten times as sensitive a reagent for nickel as the dimethyl glyoxime, enabling 1 part of nickel to be detected in 5,000,000 parts of water or in 5,000 parts of cobalt. The

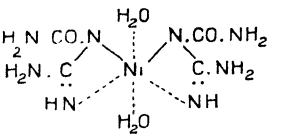
[1] Pickering, *J. Chem. Soc.*, 1913, **103**, 1358.
[2] *J. Chem. Soc.*, 1921, **119**, 1348.
[3] *J. Chem. Soc.*, 1923, **123**, 1815, 1826.
[4] Brunck, *Z. angew. Chem.*, 1907, **20**, 1844.

dimethyl compound suffices for ordinary requirements, however, and is the glyoxime reagent commonly used.

Use of Dicyanodiamidine and Nitrosophenylhydroxylamine in Quantitative Analysis

Of recent years two other organic compounds have found important analytical uses. These are dicyanodiamidine (guanyl urea), $NH_2.NH:C.NH.CO.NH_2$, and nitrosophenylhydroxylamine, $C_6H_5.N(NO)OH$, which is generally used in the form of its ammonium salt called " Cupferron ", the name given by Baudisch,[1] who first employed it in analysis. The value of these compounds lies in the fact that with certain metals they form very insoluble and stable compounds, and that the capacity to form such compounds is highly specific.

Dicyanodiamidine is essentially a reagent for nickel, with which in alkaline solutions it forms the yellow crystalline compound $Ni(C_2H_5N_4O)_2.2H_2O$; this becomes flesh coloured when dehydrated. Cobalt and zinc do not form analogous compounds, so that conditions are very similar to those holding in the case of the glyoximines, and, in fact, dicyanodiamidine can be used for estimating nickel in all the cases where α-dimethyl glyoxime can be used. Dicyanodiamidine is said by Grossmann and Schück,[2] who first used it as a reagent, to be capable of detecting 1 part of nickel in 200,000 parts of water, so that it is about half as sensitive as α-dimethyl glyoxime. As the nickel compound is not decomposed by boiling with potassium hydroxide, there can be little question that it is a co-ordinated compound of the non-electrolyte type—similar to nickel glyoximine. The following structural formula may be suggested, though it is not easy to say to which parts of the dicyanodiamidine molecule the nickel is



[1] *Chem. Zeit.*, 1909, **33**, 1298.
[2] *Chem. Zeit.*, 1907, **31**, 535; *Ber.*, 1906, **39**, 3356.

attached. According to this formula the nickel would have a co-ordination number 6 as in compounds like $[Ni(NH_3)_6]Cl_2$, but it would be surrounded by a shell of 20, not 18, electrons. Possibly it is for this reason that the two molecules of water are lost comparatively easily. After their removal the outer shell would contain only 16 electrons, which in the case of nickel seems to be a more stable arrangement than that in which there are 20 electrons.

Separation of Nickel from Cobalt by means of Dicyanodiamidine

If iron or chromium is present tartaric acid has to be used to prevent precipitation by ammonia as in the glyoxime method already described. For the procedure in such cases consult Lunge, Keane, *loc. cit.*, p. 67. In the procedure described below iron and chromium are assumed to be absent. It is essential to oxidize all the cobalt to the cobaltic condition, otherwise there is some danger of cobalt being precipitated along with the nickel.

0·5 gram of the sample is dissolved in hydrochloric acid and ammonia is added until any precipitate formed is redissolved, and the liquid has a perceptible ammoniacal odour. A few c.c. of a 10 per cent solution of hydrogen peroxide are then introduced and the beaker is set aside for half an hour. About two grams of dicyanodiamidine sulphate dissolved in 20 c.c. of water are added in the cold, followed by about 15 c.c. of a 10 per cent solution of sodium hydroxide. The total volume of solution should not be more than about 70 c.c. After standing for several hours the yellow crystalline precipitate is filtered on a Gooch crucible and washed, not more than five times, with 6 per cent ammonia. It is dried at 120°–130° and weighed as anhydrous $Ni(C_2H_5N_4O)_2$, which contains 22·5 per cent of nickel. The cobalt can be precipitated from the filtrate as sulphide, which is converted into sulphate and weighed (see pages 183, 185).

Separation of Nickel from Zinc

The method is the same as for the separation from cobalt, with the exception that the addition of hydrogen peroxide is not necessary.

Estimation of Copper and Iron by means of "Cupferron"

"Cupferron" has been used chiefly for separating copper and iron (thence the name) from other metals. The precipitation is carried out in acid solution, and the chief value of the method is due to the fact that iron can be thus separated directly from aluminium, chromium, cobalt, zinc, manganese, nickel, alkaline earths, and phosphates. Copper can also be separated by its means from the same metals, but in the case of copper there are other good methods by which this can be done, so that the need for a new method was not so great.

Cupferron has been recommended also for separating titanium from aluminium,[1] zirconium from aluminium [2] and uranium,[3] and as a precipitant for vanadium.[4]

The precipitated iron and copper salts are only slightly affected by cold 2N HCl, though they are decomposed by hot acid. Cold dilute sodium carbonate has no appreciable action, but alkaline hydroxides decompose the precipitates rapidly. Ammonia does not affect the iron salt, but it quickly dissolves the copper salt.

It is probable that in the insoluble compounds formed by cupferron with copper, iron, titanium, zirconium, and vanadium the metal is co-ordinated both with the oxygen of the -OH group (by principal valencies) and the oxygen of the -NO group (by subsidiary valencies). On this basis the ferric salt would be a non-ionizable compound represented by the co-ordination formula $\left[(C_6H_5N.\overset{O}{\overset{|}{\underset{|}{NO}}})_3Fe\right]$. Again it will be noticed that there is some specific effect at work which allows only certain metals to form such compounds, as with α-dimethyl glyoxime, etc.

Analysis of Brown Iron Ore [5]

Five grams of the ore are dissolved in 60 c.c. of strong hydrochloric acid; the iron is fully oxidized by boiling

[1] Bellucci and Grassi, *Atti R. Accad. Lincei*, 1913, [5], **22**, i, 30.
[2] Thornton and Hayden, *Amer. J. Sci.*, 1914, [4], **38**, 137.
[3] Angeletti, *Gazzetta*, 1921, **51**, i, 285.
[4] Turner, *Amer. J. Sci.*, 1916, **41**, 339.
[5] Baudisch, *loc. cit.*

with potassium chlorate, and, when cold, the whole is diluted to 500 c.c. Twenty-five c.c. of the diluted solution are placed in a beaker and 20 c.c. of strong hydrochloric acid and 100 c.c. of cold distilled water added. During stirring, a solution of 3 grams of cupferron in 50 c.c. of water is added. A reddish-brown flocculent precipitate of the iron compound separates and the precipitation is complete when a white precipitate of nitrosophenylhydroxylamine begins to form. When this point is reached more of the cupferron solution, say about a quarter of that already used, should be added, for it is advisable to have a good excess. After about 15 minutes the precipitate is collected on a filter paper and washed with cold water until the washings are no longer acid. The filtrate can be used for the estimation of manganese. The iron precipitate is then washed with dilute ammonia (1 : 1) to remove the excess of nitrosophenylhydroxylamine and then once with water. The precipitate is ignited slowly, without previous drying, and weighed as Fe_2O_3.

The solution of cupferron is best made fresh for each determination. It can be kept in the dark for about a week, but slowly decomposes with separation of nitrobenzene. Turbid solutions should be filtered before use.

Analysis of Nickel Ore [1]

The iron and copper present are precipitated jointly as above with "cupferron" and the nickel in the filtrate is estimated by a suitable method. After washing the mixed copper + iron precipitate with cold water the copper is extracted with strong ammonia. The ammoniacal solution containing the copper is evaporated to dryness in a weighed porcelain dish or large crucible, the residue ignited and weighed as CuO. The precipitate insoluble in ammonia is ignited and weighed as Fe_2O_3.

In precipitating copper by cupferron a large excess of mineral acid should be avoided; hence, in the nickel ore analysis it is best to add ammonia carefully to the solution until there is only just enough acid left to prevent precipita-

[1] Baudisch, *loc. cit.*

tion of iron. The cupferron reagent is then added (in about twice the theoretical amount) followed by two grams of sodium acetate dissolved in a small amount of water—on the assumption that 0·5 gram ore has been used. The precipitation thus occurs from an acetic acid solution. This method of separating copper and iron gives good results according to Biltz and Hödtke,[1] although in a general way co-precipitation of two metals followed by solution of one of them is not to be recommended. If copper alone is being precipitated by means of cupferron it is done similarly from acetic acid solution, and after treating the greyish white precipitate with cold water the excess of nitrosophenylhydroxylamine is washed out with 1 per cent sodium carbonate solution. Finally, the precipitate is washed with water, ignited, and weighed as CuO.

Two examples will now be given of the application in quantitative analysis of the sparing solubility of complex compounds of the kind classified as type (1) on page 193. These are the estimation of potassium as K_2PtCl_6 and the separation of cobalt from nickel as $K_3Co(NO_2)_6$.

Estimation of Potassium as K_2PtCl_6

All metals other than magnesium, alkaline earth metals, sodium, and ammonium must have been previously separated. Platinic chloride forms double salts with the chlorides of Na, K, Mg, Ca, Sr, Ba, and NH_4 (all derived from the acid H_2PtCl_6). Of these only K_2PtCl_6 and $(NH_4)_2PtCl_6$ are insoluble in alcohol. (Rb_2PtCl_6 and Cs_2PtCl_6 also are insoluble in alcohol, so their presence would make modifications necessary.) The first step in the analysis is to free the aqueous solution from sulphuric and phosphoric acids if these are present, for the sulphates and phosphates of sodium, magnesium, etc., are insoluble in alcohol. The amount of material to be used in the analysis and the precise mode of operating naturally depends on the character of the material. If it is a crude potassium mineral such as carnallite or kainite it is better to weigh out a large amount, so as to get a more representative sample, and subdivide it as the analysis

[1] *Z. anorg. Chem.*, 1910, **66**, 426.

proceeds. If it is homogeneous and rich in potassium a small amount, say 0·3 gram, can be weighed out and all used for the estimation.

Details will be given for the case of such a crude soluble potassium mineral.

From 30–35 grams of the well-ground crude salt are dissolved in a 500 c.c. graduated flask by boiling with 300 c.c. of water and 15 c.c. of concentrated hydrochloric acid, and after cooling the solution is made up to the mark. 50 c.c. of the solution, filtered if necessary, are transferred to a 200 c.c. graduated flask and heated to boiling ; any sulphate present is then precipitated by cautious addition of barium chloride solution from a burette. Not more than a slight excess should be added.

When precipitated thus from a hot, fairly strongly acid solution, $BaSO_4$ carries down practically no potassium with it, as it is liable to do if precipitated from a neutral solution. That is the main reason for adding hydrochloric acid when dissolving the potassium salt in the first instance.

If any phosphate is present, which will not normally be the case when dealing with ordinary potassium salts, it is now precipitated by adding a slight excess of ferric chloride solution. After the iron and the barium have been removed by ammonia and ammonium carbonate (in slight excess) the solution is allowed to cool, diluted to the mark, and allowed to settle. 20 c.c. of the solution (filtered if need be) are now taken for the actual potassium estimation. Although $BaPtCl_6$ is moderately soluble in alcohol it is decomposed by it to a considerable extent with formation of insoluble $BaCl_2$. It is, therefore, advisable to separate any excess of barium by means of ammonium carbonate, as above, before proceeding further with the analysis.

The 20 c.c. of solution are evaporated to dryness in a platinum dish (porcelain can be used but platinum is better), and the residue is heated over a wire gauze, at first gently to avoid spitting, then more strongly, and finally to a dull red heat, so as to volatilize all ammonium salts. The temperature must be kept as low as is consistent with this in order to avoid volatilization of potassium chloride. The

residue is weighed in the dish, taken up with a little hot water, the solution filtered through a small filter into a porcelain dish, the filter and platinum dish thoroughly washed out, and a few drops of pure hydrochloric acid added to the filtrate, which is then evaporated to dryness on the water-bath. Two or three c.c. of water are added and then platinum chloride solution (of such a strength that 1 gram platinum is present in 20 c.c.) to the amount of 3·5 c.c. for every 0·1 gram of salt obtained as residue in the platinum dish. Should the residue consist mainly of NaCl with very little KCl, it is better to use rather more platinum chloride solution, say 4 c.c. for every 0·1 gram salt, for a moderate excess of $PtCl_4$ facilitates removal of sodium salts during the washing with alcohol by preventing a slight tendency of the Na_2PtCl_6 to decompose into NaCl and $PtCl_4$. The use of pure platinic chloride is of the utmost importance. It must be free from platinous chloride and oxides of nitrogen, and contain at most only a small quantity of free hydrochloric acid. For full details of how to prepare it the reader is referred to Lunge-Keane.[1]

After addition of the platinic chloride solution to that of the mixed chlorides the resulting liquid is evaporated on the water-bath in an ammonia-free atmosphere. Should much magnesium be present, this evaporation is carried only to the stage of a syrup and cessation of hydrochloric acid fumes, otherwise it is continued to dryness. During cooling the syrup should be stirred to prevent formation of large crystals of sodium salt, which consist of the orange-coloured hexahydrate $Na_2PtCl_6.6H_2O$, and which are more difficult to wash out with alcohol than are the small crystals. The dehydrated Na_2PtCl_6 dissolves more readily in alcohol than the hexahydrate doubtless because it can better enter into co-ordination with the alcohol. For this reason it is best to carry the evaporation to complete dryness unless much magnesium is present. In the latter case, since the magnesium compound seems to be more readily removed when not dehydrated, less complete evaporation, as described above,

[1] *Technical Methods of Chemical Analysis*, 1908, vol. **1**, pt. 2, p. 521.

is better. The cold solid mixture is crushed with a flat-headed glass rod, then thoroughly ground with 20 c.c. of absolute alcohol, and the washings filtered through a weighed Gooch crucible. This process is repeated until the solution running through is quite colourless and the residue of K_2PtCl_6 is pure golden yellow in colour with no specks of orange-coloured $Na_2PtCl_6.6H_2O$. All the K_2PtCl_6 is transferred to the crucible and weighed after drying at 100°–110°.

The weight of K_2PtCl_6 obtained multiplied by the factor 0·1931 gives the weight of K_2O in the amount of substance used in the estimation. This is a rather smaller factor than the theoretical one (which is 0·1938 if Pt is taken as 195·2). The platinic chloride reagent in the potassium estimation is really a solution of H_2PtCl_6. During the estimation slight hydrolysis of this occurs with formation of $H_2Pt(OH)_6$, a white solid, which fairly readily loses one molecule of water and becomes yellow. Further loss of water does not occur readily. The K_2PtCl_6 weighed in the platinum estimation always contains traces of these hydroxy platinic acids and hence has a smaller proportion of KCl than if it were pure K_2PtCl_6. Hence the use of the smaller factor which experience has shown to give correct results.[1]

The platinic chloride reagent has to be free from platinous chloride because that also forms a double chloride K_2PtCl_4 with potassium chloride. Oxides of nitrogen should be absent because of the possibility of the formation of compounds containing one or more NO_2 groups in place of chlorine.

Separation of Cobalt from Nickel as $K_3Co(NO_2)_6$

If a complex alloy or ore is being analysed the cobalt with the nickel must first be separated from other metals by appropriate methods. They are finally obtained together either electrolytically as metals, or as the sulphides or as the black peroxides. The metals are dissolved in hot dilute (2N) nitric acid, the oxides in hot, fairly strong hydrochloric acid, and the sulphides in aqua regia—filter papers being

[1] See Dittmar and M'Arthur, *J. Soc. Chem. Ind.*, 1887, **6**, 799.

ignited and the ash added to the acid which was used to dissolve the precipitates.

About 0·2 to 0·3 gram of nickel plus cobalt—or less, according to circumstances—would generally be a convenient quantity for the actual separation of the two metals. The acid solution is evaporated to dryness on the water-bath in a porcelain dish. The residue is taken up in a few c.c. of water, 5 grams of potassium nitrite are added (in cold, saturated aqueous solution), and then acetic acid until nitrous acid is evolved. Yellow $K_3Co(NO_2)_6$ separates, but as its formation involves oxidation of the cobaltous compound originally present in the solution, precipitation is not complete till after some hours, and it should be left for 24 hours in a warm place before filtration. If there is any doubt about precipitation being complete, some of the clear solution is pipetted out, more KNO_2 added to it, and the mixture left to stand for 12 hours. Should more precipitate form, more nitrite must be added to the main solution and the whole left another 24 hours before filtration. The precipitate is in due course filtered off and washed with a 5 per cent solution of KNO_2 which has been made faintly acid with acetic acid. It is rinsed from the filter into a porcelain dish and dissolved in hot 2N hydrochloric acid, which is poured through the filter paper. If any silica, derived from the KNO_2, should separate, this is filtered off and the cobalt is precipitated in a porcelain dish as black cobaltic oxide with potash and bromine water.

The filtrate from the $K_3Co(NO_2)_6$ is heated with excess of 2N hydrochloric acid, and the nickel is precipitated, after dilution, as black peroxide with potassium hydroxide and bromine water.

The cobalt is weighed as metal, the nickel as NiO (see page 125).

There seems to be some doubt about the precise formula of the potassium cobalti-nitrite. Sometimes it appears to be anhydrous, at others to contain several molecules of water of crystallization, whilst it may contain also hydrated cobaltic oxide.[1] For these reasons it cannot be weighed

[1] Rây, *J. Chem. Soc.*, 1906, **89**, 551.

directly. The corresponding sodium salt is readily soluble in water, and in acetic acid solutions gives a yellow precipitate with potassium salts. This is a very useful qualitative test for potassium, but as the composition of the precipitate is variable it cannot be used satisfactorily for estimating potassium.

When applied under carefully controlled conditions the precipitation of potassium by means of sodium cobalti-nitrite is said to lead to the precipitation of dipotassium sodium cobalti-nitrite, which, after drying at 120°, has the formula $K_2NaCo(NO_2)_6.H_2O$. A method for estimating potassium gravimetrically has been based upon this precipitation.[1]

[1] See Clerfeyt, *Bull. Soc. Chim. Belg.*, 1922, **31**, 417.

CHAPTER XIII

OTHER ANALYTICAL ASPECTS OF COMPLEX-ION FORMATION

THE connexion between complex formation and solubility has been considered in the last chapter, but complex ions are of the greatest analytical importance in many other ways. There are probably far more complex ions than simple ones, and if all ions are hydrated (or, more generally, solvated), as seems possible, then there are no simple ions.

Complex ions are frequently used to prevent precipitation [1] or to delay it. Differences in their stability may be the basis of separations which are impossible without their intervention. Indeed, the uses to which they can be put almost defy classification; this is not surprising when it is remembered that even ions like SO_4'', PO_4''', NH_4^+ are in reality complex ions though for most purposes conveniently regarded as simple.

For the present purpose it will be convenient to regard complex ions as originating by the addition of neutral molecules or atoms to a simple ion, or by the partial neutralization of a polyvalent ion by oppositely charged simple ions. In the first case the complex ion has the same charge as the simple ion from which it has been formed, in the second case the charge is the algebraic sum of the charges carried by the constituent ions. Examples of the first type are $[Cr(H_2O)_6]^{\cdots}$, $[Cu(NH_3)_4]^{\cdot\cdot}$, $[Co(CN)_6]'''$, $[SiF_6]''$, formed from $Cr^{\cdots}$, $Cu^{\cdot\cdot}$, CN', and F' by addition of H_2O, NH_3, $Co(CN)_3$, and SiF_4 molecules respectively, while examples of the second type are OH' (formed from $O'' + H^+$), BiO^+ (formed from $Bi^{\cdots} + O''$), HPO_4'' (formed from $PO_4''' + H^+$). Ions like SO_4'' and PO_4''' can be placed in the first of the above groups and regarded as S'' or P''' ions strengthened

[1] The use of tartaric acid to prevent precipitation of iron or chromium is an example of this, and has been referred to on pp. 201, 202.

by the addition or co-ordination of four neutral atoms of oxygen. Or they may be derived from hypothetical positive sulphur and phosphorus ions (carrying six and five charges respectively) by addition of four oxygen ions, each of which carries two negative charges. But this is a less satisfactory method of derivation.

It was shown by Abegg and Bodländer [1] that the weaker an ion, that is to say, the smaller its tendency to retain its charge, the greater its tendency to form complex ions. The complex ion holds its charge much more firmly than the original simple ion. By the addition of one or more neutral molecules very strong ions can be formed from very weak ones. Thus $NH_4^{\cdot}$, $[Co(NH_3)_6]^{\cdot\cdot\cdot}$, SO_4'', $Fe(CN)_6'''$ are very strong ions, though the parent ions ($H^{\cdot}$, $Co^{\cdot\cdot\cdot}$, S'', and CN') are very weak indeed.

Weak ions can add on neutral molecules of the most varied character, but, as would be expected, the nature of the resultant complex depends on the nature of the added molecule. If the molecule added has a considerable tendency to ionize itself the complex will not be so stable as in the opposite case.

Thus the complex ion $[FeCl_4]'$ formed from $FeCl_3$ and Cl' is not nearly so stable as $[PtCl_6]''$ owing to the fact that $FeCl_3$ has a marked tendency to ionize while $PtCl_4$ has practically none. When a complex ion has resulted from the union of a simple ion and a neutral salt molecule, the complex will always be in equilibrium with the simple ions of the salt. Complex ion $\rightleftarrows$ simple ion + neutral molecule $\rightleftarrows$ ions.

This is of the greatest analytical importance.

All types of complex ions are met with in analytical work, but among the most important are complex anions such as $[Co(NO_2)_6]'''$; $[Ag(CN)_2]'$; $[PtCl_6]''$ formed by addition of several weak or comparatively weak simple negative ions to a molecule of a simple salt derived from weak positive and negative ions.

If a neutral molecule has a marked positive character

[1] *Z. anorg. Chem.*, 1899, **20**, 453.

it does not, as a rule, form complex ions by union with negative ions and vice versa. Thus NH_3 forms complex cations only, by union with simple positive ions, while acidic oxides such as CrO_3 form complex anions (such as Cr_2O_7'') only, by union with negative ions (in this case CrO_4'').

Water owing to its completely neutral character is equally ready to build up complex cations or anions : examples are $[Cr(H_2O)_6]'''$; $[Co(NH_3)_5H_2O]'''$; $[Fe(CN)_5H_2O]''$. This must always be remembered when dealing with aqueous solutions, for water molecules may displace other molecules from the complex. They are very liable to do this, for the concentration of water molecules in a weak aqueous solution is very great in comparison with that of the molecules of dissolved substance.

The ions of the alkali metals are very strong, and in consequence they do not appear to form complex ions. It is very possible, however, that in aqueous solution they exist as complex hydrated ions. The large mass effect of the water molecules may well cause this although in its presence no other neutral molecule has a chance of remaining associated with such strong ions. That the alkali metals have some tendency to form complex cations with water and even other molecules is shown by the existence of numerous solid hydrates and by a few compounds such as $NaCl.5NH_3$ obtained by Joannis [1] as crystals decomposing above—24°.

The whole character of the complex compounds which yield the complex ions is referable to the one cause, namely, that the strength of the simple ion has been greatly increased by its conversion into a complex ion although it does not follow that this is a strong one. Thus, the acid or base corresponding to the complex ion will be much stronger than that corresponding to the simple ion. (Compare $H_4Fe(CN)_6$ with HCN, and H_2SO_4 with H_2S, or $Ag(NH_3)_2OH$ with AgOH.) The strong complex ions will give rise to readily soluble compounds when combined with other ions that are not too strong—though the corresponding compound derived from the weaker simple ion may be insoluble. (Compare

[1] *Compt. rend.*, 1891, **112**, 393.

the soluble $Ag(NH_3)_2Cl$ with the insoluble AgCl, or soluble $CuSO_4$ with insoluble CuS.)

With very strong ions of the opposite sign the complex ions may give salts which are less soluble than the simple ones. Thus, K_2PtCl_6 is less soluble than KCl, $BaSO_4$ than BaS. If the opposite ion is very weak complex ions can yield insoluble salts. Thus, the ferro-, ferri-, and cobalti-cyanides of the heavy metals are very insoluble. This may well be due to intra molecular co-ordination or complex formation.

It will be realized that the character of the neutral molecule or molecules which form part of a complex ion is profoundly modified by such inclusion. In particular such molecules become stable towards water if previously unstable, and in many cases soluble, though previously insoluble. Thus, SiF_4 itself is decomposed by water but the complex ion $[SiF_6]''$ is stable towards water. AgCN is insoluble in water, but compounds such as $KAg(CN)_2$ derived from the $[Ag(CN)_2]'$ ion are soluble.

Quantitative Methods Involving Complex Ions.
Titration of a Soluble Cyanide by means of Standard Silver Nitrate (Liebig's Method)

An amount of the solid or solution equivalent to about 25 c.c. of decinormal silver nitrate is placed in a beaker or flask standing on a sheet of black paper. If not already alkaline it is rendered moderately so by the addition of a suitable amount of caustic soda solution. The solution is diluted to 80–100 c.c. and the standard silver nitrate run in slowly from the burette with constant stirring. A white precipitate of AgCN forms at the point where the silver solution enters the other, but this at once disappears on stirring owing to formation of the complex ion $[Ag(CN)_2]'$. The alkali salt corresponding to this is soluble in water, but as soon as all the cyanide originally present has been converted into the complex salt further addition of silver nitrate produces a permanent precipitate of silver cyanide. The end point is that where the first slight permanent

turbidity appears. One molecule of silver nitrate has then been added for every two molecules of NaCN or KCN originally present.

The following are the ionic equilibria involved in these reactions :—

$$K^{\cdot} + CN' \rightleftarrows KCN \qquad Ag^{\cdot} + NO_3' \rightleftarrows AgNO_3$$

$$Ag^{\cdot} + CN' \rightleftarrows AgCN \qquad AgCN + CN' \rightleftarrows Ag(CN)_2'$$

$$Ag^{\cdot} + 2CN' \rightleftarrows Ag(CN)_2'$$

$$Ag^{\cdot} + Ag(CN)_2' \rightleftarrows Ag.Ag(CN)_2$$

The mass-action equation expressing the equilibrium between the complex ion and its simple constituent ions is the following :—

$$\frac{[Ag^{\cdot}]\,[CN']^2}{[Ag(CN)_2']} = K$$

The value of the constant K was found by Bodländer and Eberlein[1] to be $9{\cdot}1 \times 10^{-22}$, which shows how very stable the complex ion is. Hardly any of it is broken down into its simple ionic constituents.

Solid silver cyanide is to be regarded as $Ag.Ag(CN)_2$ rather than as AgCN.

Denigès' Modification of Liebig's Process

The silver cyanide which separates at the point where the silver nitrate solution enters that of the cyanide does not dissolve at all readily towards the end of the titration. This makes it rather difficult to determine the end point exactly.

Denigès[2] has accordingly modified the process in such a way that the titration is carried out in ammoniacal solution with potassium iodide as indicator.

To 100 c.c. of solution containing about 0·15 gram KCN are added 10 c.c. of ammonia (2 normal) and about 10 drops of a 20 per cent solution of potassium iodide. The liquid is then titrated with decinormal silver nitrate solution until there is a faint permanent turbidity of silver iodide. This point corresponds, as in the Liebig method, to the addition of one molecule of silver nitrate to two of cyanide, and is

[1] *Z. anorg. Chem.*, 1904, **39**, 222.
[2] *Ann. Chim. Phys.*, 1895, [7], **6**, 381.

much sharper because the silver cyanide formed as the silver nitrate is added dissolves readily even when practically all the CN′ ions have been converted into $Ag(CN)_2'$ ions. The concentration of ammonia remains then practically as great as at the beginning of the titration so that, even though the AgCN dissolves only very slowly because of the small CN′ ion concentration, it still dissolves readily enough owing to formation of the complex cation $Ag(NH_3)_2^{\cdot}$.

Once the silver cyanide has gone into solution any $Ag(NH_3)_2^{\cdot}$ ions thus first formed will be converted into $Ag(CN)_2'$ ions so long as any CN′ ions remain,

$$Ag(NH_3)_2^{\cdot} + 2CN' \rightleftarrows Ag(CN)_2' + 2NH_3$$

for the $Ag(CN)_2'$ ion is far more stable than the $Ag(NH_3)_2^{\cdot}$ ion. This is readily seen from the mass-action constants for the two complex ions which have the values (at 25°) :—

$$\frac{[Ag^{\cdot}][CN']^2}{[Ag(CN)_2']} = 9{\cdot}1 \times 10^{-22}; \quad \frac{[Ag^{\cdot}][NH_3]^2}{[Ag(NH_3)_2^{\cdot}]} = 6{\cdot}8 \times 10^{-8}$$

The value of the solubility product $[Ag^{\cdot}][Ag(CN)_2']$ is $2{\cdot}25 \times 10^{-12}$, while that of $[Ag^{\cdot}][I']$ is 3×10^{-16}, so it is clear that the turbidity produced at the end point will be due to silver iodide and not silver cyanide.

With the quantities suggested for the titration about 10 c.c. of the 0·1N $AgNO_3$ would be used, and the total volume of solution at the end point would be about 120 c.c. As 0·5 c.c. (=10 drops) of 20% KI had been added, the molar concentration of iodine ions—[I′]—would then be approximately 4×10^{-3} assuming complete ionization of the KI. Similarly, assuming complete ionization of the $KAg(CN)_2$, the molar concentration of the negative ions—$[Ag(CN)_2']$—at the end point would be approximately $8{\cdot}3 \times 10^{-3}$. From the above values of the solubility products it follows that in order to produce a precipitate of silver iodide, sufficient excess of silver nitrate must be added to make the molar concentration of silver ion—$[Ag^{\cdot}]$—equal to $7{\cdot}5 \times 10^{-14}$, while to produce a precipitate of silver cyanide a molar concentration of $2{\cdot}7 \times 10^{-10}$ would be needed, that is to say 3,600 times as great.

Now, most of the excess of silver nitrate added after conversion of all the cyanide into $KAg(CN)_2$ gives rise to $Ag(NH_3)_2^{\cdot}$ ions, only very little remaining in the form of $Ag^{\cdot}$ ions. The total molar concentration of silver—x—which is required to give $[Ag^{\cdot}] = 7 \cdot 5 \times 10^{-14}$ is obtained from the mass-action equation for the $Ag(NH_3)_2^{\cdot}$ ion. With the 10 c.c. of 2N ammonia used in the experiment and a final volume of 120 c.c. the molar concentration of NH_3 is approximately 0 ·17.

Substituting these values we get :—

$$\frac{[Ag^{\cdot}]\ [NH_3]^2}{[Ag(NH_3)_2^{\cdot}]} = \frac{(7 \cdot 5 \times 10^{-14})\ (0 \cdot 17)^2}{x - 7 \cdot 5 \times 10^{-14}} = 6 \cdot 8 \times 10^{-8}$$

from which x is found to be $3 \cdot 19 \times 10^{-8}$. In order, therefore, to obtain the end point, an excess of silver nitrate solution must be added sufficient to produce a $3 \cdot 19 \times 10^{-8}$ molar solution of silver (as $[Ag^{\cdot} + Ag(NH_3)_2^{\cdot}]$).

To produce 120 c.c. of such a solution (the volume at the end point) only 0·038 c.c. of 0·1 normal silver nitrate would be required—that is to say rather less than 1 drop. With the amount suggested for the titration the end point is thus quite satisfactory, but it is clear that if too little potassium iodide or too much ammonia were used an undue excess of silver nitrate would be required to produce a permanent turbidity.

Liebig's Cyanide Method for Separating Nickel and Cobalt

In applying this excellent method no metals other than nickel, cobalt, and alkalis should be present. To the neutral solution in a porcelain dish and occupying, say, 100 c.c. for 0·2 gram Ni + Co, there is added a solution of pure KCN (about 2N) until the precipitate ($Ni(CN)_2 + Co(CN)_2$) first formed has just dissolved. An additional 1 c.c. is added after this. The solution is then made strongly alkaline by the addition of about 3 grams of pure KOH, and bromine water is slowly added with stirring until no further precipitate of black nickelic oxide is produced. When this point is reached the solution should still be strongly alkaline. The mixture is diluted with about 50 c.c. of cold water, and the

nickel precipitate filtered, washed with hot water, ignited and weighed as NiO, or as metal after reduction in hydrogen. Any silica present must be estimated and allowed for (see page 125).

It is sometimes sufficiently accurate and in any case much quicker to obtain the cobalt by difference. For this purpose another portion of the nickel-cobalt mixture is precipitated as black peroxides with KOH and bromine water and the mixed oxides filtered, washed, and ignited. The ignited oxides are then washed to remove adsorbed alkali, again ignited, reduced in hydrogen, and the mixture of metallic nickel and cobalt weighed.

If, however, the cobalt is to be determined directly, the filtrate from the original nickel precipitate is just acidified with sulphuric acid and evaporated to dryness in a porcelain dish. To the residue are added 10 c.c. of water and 10 c.c. of concentrated sulphuric acid. The mixture is heated on the sand bath until all effervescence has ceased and fumes of sulphuric acid begin to be evolved. The cobalti-cyanide is completely decomposed by this operation, the reaction being in accordance with the equation :—

$$2K_3Co(CN)_6 + 11H_2SO_4 + 13H_2O = 2CoSO_4 + 3K_2SO_4 + 6(NH_4)_2SO_4 + 11\ CO + CO_2$$

The residue in the basin is transferred to a beaker with hot water and diluted to about 200 c.c. Owing to the ammonium salts present it is not satisfactory to precipitate the cobalt directly with KOH and bromine, since the latter simply oxidizes ammonia with liberation of nitrogen. It is better to make the solution alkaline with ammonia, and to precipitate cobalt as sulphide from the hot solution with sulphuretted hydrogen. The CoS is allowed to settle, filtered, washed twice with water saturated with H_2S, and then rinsed off the funnel into the beaker with the minimum quantity of water. The filter paper is dried and ignited, and the ash added to the precipitate in the beaker. When the precipitate has been dissolved in sufficient aqua regia, the separated sulphur is filtered off and the cobalt is precipitated with KOH and bromine and weighed as metal (see page 125). Alternatively the sulphide can be converted into sulphate and weighed in that form (see pages 183, 185).

The chief points of interest in connexion with the above method for separating nickel and cobalt are as follows: The $Ni(CN)_2$ and $Co(CN)_2$ first formed on adding the KCN solution dissolve in excess of the latter owing to formation of the complex anions $Ni(CN)_4''$ and $Co(CN)_6''''$ corresponding to the salts $K_2Ni(CN)_4$ and $K_4Co(CN)_6$. The nickel compound is of the same type as that formed by zinc while the cobalt compound corresponds to $K_4Fe(CN)_6$. There are so few $Ni^{\cdot\cdot}$ or $Co^{\cdot\cdot}$ ions in solutions of these compounds that the hydroxides are not precipitated on addition of KOH.

$K_2Ni(CN)_4$ is not capable of oxidation to a nickelic double salt, none of which are known, but $K_4Co(CN)_6$ oxidizes with the greatest ease to $K_3Co(CN)_6$, which is a remarkably stable compound. The oxidation occurs so readily that on boiling its aqueous solution the water oxidizes it with liberation of hydrogen :—

$$2K_4Co(CN)_6 + 2H_2O = 2K_3Co(CN)_6 + 2KOH + H_2$$

Oxidation occurs more quickly with atmospheric oxygen. If a rapid current of air is used only half the oxygen absorbed goes to form $K_3Co(CN)_6$, the other half going to form hydrogen peroxide :—

$$2K_4Co(CN)_6 + 2H_2O + O_2 = 2K_3Co(CN)_6 + 2KOH + H_2O_2$$

As H_2O_2 also oxidizes $K_4Co(CN)_6$ slowly it is found that when a slow air current is used practically all the oxygen absorbed is used in forming $K_3Co(CN)_6$.[1] The production of H_2O_2 during oxidations by gaseous oxygen is frequently observed.

In the analytical procedure described the oxidation of the $K_4Co(CN)_6$ is mainly due to potassium hypobromite.

$$2K_4Co(CN)_6 + KBrO + H_2O = 2K_3Co(CN)_6 + KBr + 2KOH$$

Ionically this can be represented as follows :—

$$2Co(CN)_6'''' + BrO' + H_2O = 2Co(CN)_6''' + Br' + 2OH'$$

or it can be supposed that the oxidation occurs through the medium of the few $Co^{\cdot\cdot}$ ions which are in equilibrium with the complex $Co(CN)_6''''$ ($Co(CN)_6'''' \rightleftarrows Co^{\cdot\cdot} + 6CN'$) thus :—

$$2Co^{\cdot\cdot} + BrO' + H_2O \rightleftarrows 2Co^{\cdot\cdot\cdot} + Br' + 2OH'$$

[1] Manchot and Herzog, *Ber.*, 1900, **33**, 1742.

This equilibrium is shifted from left to right owing to almost quantitative conversion of the $Co^{\cdot\cdot\cdot}$ ion into the complex $Co(CN)_6'''$ ($Co^{\cdot\cdot\cdot} + 6CN' \rightleftarrows Co(CN)_6'''$).

Although the black hydroxide corresponding to the $Co^{\cdot\cdot\cdot}$ ion is very insoluble it is not precipitated even in the strongly alkaline solution, as the stability of the $Co(CN)_6'''$ complex is too great. In the case of the nickel compound, however, the position is different. A few of the $Ni^{\cdot\cdot}$ ions in equilibrium with the $Ni(CN)_4''$ complex are oxidized :—

$$2Ni^{\cdot\cdot} + BrO' + H_2O \rightleftarrows 2Ni^{\cdot\cdot\cdot} + Br' + 2OH'$$

and as there is no stable complex cyanide ion corresponding to the $Ni^{\cdot\cdot\cdot}$ ions the latter are simultaneously precipitated by the OH′ ions present as the very insoluble black hydroxide. (It makes little difference to the theoretical aspect of the precipitation whether this hydroxide corresponds to an oxide Ni_2O_3 or NiO_2. In the latter case, presumably a $Ni^{\cdot\cdot\cdot\cdot}$ ion would be first formed.)

In the case of the nickel oxidation equilibrium, however, the $Ni^{\cdot\cdot}$ ion is favoured rather than the $Ni^{\cdot\cdot\cdot}$ ion. The concentration of the latter at any time is very small so that in order for all the nickel to be precipitated a high concentration of OH′ ion is required. Hence, the need for a strongly alkaline solution. For the same reason much excess of cyanide should be avoided, for otherwise the amount of $Ni^{\cdot\cdot}$ ion in equilibrium with the $Ni(CN)_4''$ complex becomes too small for complete (or in extreme cases, any) precipitation of $Ni(OH)_3$.

$$Ni(CN)_4'' \overset{KCN}{\leftrightarrows} Ni^{\cdot\cdot} \overset{BrO'}{\rightleftarrows} Ni^{\cdot\cdot\cdot} \overset{OH'}{\rightleftarrows} Ni(OH)_3$$

The cobalto- and cobalti-cyanides are of considerable interest in connexion with the view that co-ordination compounds result from the building up of electron shells approximating to those of maximum stability—that is, shells containing the number of electrons characteristic of the inert gases. In potassium cobalto-cyanide the cobaltous atom is surrounded by an electron shell containing 19 electrons. By loss of one of these the much more stable configuration containing only 18 electrons results. This gives a satisfactory explana-

tion of the extreme ease with which $K_4Co(CN)_6$ is oxidized to $K_3Co(CN)_6$ in which the cobaltic atom is surrounded by 18 electrons.

In potassium ferrocyanide the ferrous atom is surrounded by an 18 electron shell; the compound is accordingly stable, and not very readily oxidized to the ferricyanide in which the ferric atom is surrounded by a shell containing only 17 electrons. Potassium ferricyanide is, however, far more stable, and not nearly so readily reduced. It is also much more difficult to reduce $K_3Fe(CN)_6$ than it is to oxidize $K_4Co(CN)_6$. Lowry [1] has pointed out that a deficiency of one or two electrons in such co-ordinated compounds seems to render them less unstable than does a similar excess of electrons.

Precipitation of Copper as Cuprous Sulphide with Sodium Thiosulphate

This method is particularly useful for separating copper from zinc and other metals of analytical group IV, and also from cadmium, in which case it is not easy to get a perfect separation by means of hydrogen sulphide. Metals of group I, and metals of group II other than cadmium should be absent. If the solution contains much nitric acid it should be first evaporated down on the water bath with sulphuric acid until nearly all the nitric acid has been removed. About 2 c.c. of concentrated sulphuric acid should be added for every 0·1 gram copper. After diluting the residue to about 75 c.c. for every 0·1 gram copper and heating the solution to boiling, a strong solution of sodium thiosulphate is slowly added until further addition produces no more black precipitate. For this about one gram of $Na_2S_2O_3.5H_2O$ is required for each 0·1 gram of copper. On first adding the thiosulphate there is a white precipitate of sulphur due to decomposition of free thiosulphuric acid ($H_2S_2O_3 = H_2SO_3 + S$), but almost at once a black precipitate of cuprous sulphide, Cu_2S, begins to form. This settles well, so it is easy to see when further addition of thiosulphate produces only white sulphur and no more black sulphide.

[1] *Chemistry and Industry*, 1923, p. 316.

The mixture is kept hot for a short time, and the precipitate is then filtered off and well washed with hot water. It is a very satisfactory precipitate to handle, as it filters rapidly and, unlike CuS, has no tendency to oxidize or go into colloidal solution. After drying, the precipitate is ignited in hydrogen and weighed as Cu_2S. (see page 167). If zinc or other metals are to be estimated in the filtrate, the latter should be concentrated until its volume is about halved, and concentrated nitric acid is then added cautiously to the hot solution. The beaker should be covered with a clock glass, for there is a vigorous reaction. Tetrathionic and pentathionic acids present in the solution are oxidized with liberation of sulphur, and the nitric acid is added until the reaction is finished, for which about one c.c. may be needed. If enough nitric acid has been added and if the liquid is kept hot, the finely divided sulphur will gradually collect into lumps and can be readily filtered off. Iron, manganese, zinc, etc., can then be estimated by any suitable means. If the thionic acids are not thus removed, the decompositions which may subsequently occur on making the solution alkaline might lead to precipitation of sulphur or sulphides when they were not wanted.

The precipitation of copper by the above method involves three main reactions.[1] In the first place the cupric copper is reduced to cuprous, thiosulphate being simultaneously oxidized to tetrathionate, $2Cu^{\cdot\cdot} + 2S_2O_3'' \rightleftarrows 2Cu^{\cdot} + S_4O_6''$. The $Cu^{\cdot}$ ions are removed by excess S_2O_3'' with the formation of very stable complex cuprous thiosulphate ions, and this causes the above equilibrium to shift completely from left to right:

$$2Cu^{\cdot} + 2S_2O_3'' \rightleftarrows Cu_2(S_2O_3)_2''$$

The precise complex formed depends on the concentration, excess of thiosulphate, etc. The one indicated above corresponds to the white crystalline salt $Na_2Cu_2(S_2O_3)_2 \cdot H_2O$.

Under other conditions the yellow crystalline salt $Na_4Cu_6(S_2O_3)_5 \cdot 6H_2O$ is precipitated. Although these complex thiosulphates are very stable in absence of acid, and com-

[1] Bassett and Durrant, *J. Chem. Soc.*, 1923, **123**, 1279.

paratively so, in the cold, in its presence, they are immediately decomposed in hot acid solutions. Consequently they have only a transitory existence when copper is precipitated as cuprous sulphide in the manner described above.

The decomposition of the complex thiosulphates, with precipitation of a mixture of cuprous sulphide and sulphur, is the last stage in the reaction—doubtless a consequence of the instability of $H_2S_2O_3$ and $Cu_2S_2O_3$. In the acid solution small amounts of each will be formed from the complex acid $H_2Cu_2(S_2O_3)_2$, and each will decompose in its characteristic fashion :—

$$Cu_2S_2O_3 + H_2O = Cu_2S + H_2SO_4$$
$$H_2S_2O_3 = H_2SO_3 + S$$

until the complex is completely destroyed.

It is worth noting that it is not at all easy to precipitate copper completely by this method in hydrochloric acid solution. This is owing to the readiness with which complex cuprous chlorides are formed such as $Na_2Cu_2Cl_4$ or $H_2Cu_2Cl_4$. The first stage of the reaction, namely, reduction to the cuprous condition, occurs normally in hydrochloric acid solution, but in the second stage a part of the cuprous copper forms complex chlorides instead of complex thiosulphates. Of course, by further addition of sodium thiosulphate, a large proportion of the complex cuprous chloride remaining in solution would be converted into complex thiosulphate and then hydrolysed to Cu_2S. In practice, however, some copper, possibly only a small amount, will be left in solution. In presence of sulphuric acid, however, complete precipitation of the copper can be obtained without difficulty, though under certain conditions complex cuprous sulphates can be formed.[1] A variable amount of pentathionic acid is usually found in the filtrate from the Cu_2S. It results from secondary changes which may involve the thiosulphate, tetrathionate, and sulphurous acid. For an account of these complex reactions the reader is referred to a long paper by Foerster and Hornig.[2]

[1] Bassett and Durrant, *loc. cit.*

[2] *Z. anorg. Chem.*, 1922, **125**, 86.

Titration of Boric Acid with Standard NaOH in presence of Glycerol or Mannitol

This method, due to Thomson,[1] is an interesting analytical application of the strengthening of a weak ion by its conversion into a complex ion.

Boric acid is a very weak acid, its dissociation constant being little greater than that of phenolphthalein (see pages 39, 40). Consequently, it cannot be directly titrated with NaOH in presence of this indicator. If this is attempted the first pink colour appears long before one molecule of NaOH has been added for each molecule of H_3BO_3, and the colour gradually gets deeper as more alkali is added.

If, however, a considerable quantity of glycerol or mannitol is added to the boric acid solution, then on titration with caustic alkali and phenolphthalein a perfectly sharp change from colourless to red is obtained when one molecule of NaOH has been added for every molecule of H_3BO_3.

This behaviour is due to the strengthening of the boric ion by addition of a molecule of glycerol or mannitol. Crystalline mannito-boric acid $H[BO_2.C_6H_8(OH)_6]$ and several of its salts have been prepared by Fox and Gauge.[2] Other mannitol-boric complexes appear to exist also, but none of them are very stable, and on dilution they tend to dissociate. In aqueous solution boric acid is present essentially as either H_3BO_3 or HBO_2.[3] The above mannito-boric acid could result by direct addition of a molecule of mannitol to the BO_2' ion, or it may be that addition to the H_2BO_3' ion of orthoboric acid occurs followed by loss of a molecule of water from the complex $H_2BO_3.C_6H_8(OH)_6'$ thus formed.

Wohl and Neuberg[4] prepared a crystalline potassium salt of glycero-boric acid to which they give the formula $KO.B[O.CH(CH_2OH)_2]_2$.

A great many organic compounds containing -OH groups

[1] *J. Soc. Chem. Ind.*, 1893, **12**, 432.

[2] *J. Chem. Soc.*, 1911, **99**, 1075.

[3] See Abegg and Auerbach, *Handbuch der anorg. Chem.*, 1906, vol. **3**, pt. 1, 34.

[4] *Ber.*, 1899, **32**, 3491.

form similar complexes with boric acid.[1] Other weak acids such as molybdic also form complexes with, and are strengthened by the addition of, organic compounds containing OH groups. That there is an actual increase in the hydrogen ion concentration of boric or molybdic acid solutions after addition of mannitol, etc., has been shown by direct measurement.[2]

According to Fox and Gauge's results [3] only one molecule of water is lost when one molecule of boric acid and one of mannitol react to give the crystalline mannito-boric acid which they isolated.

The method of titrating boric acid will be seen from the following analysis of an alkali borate. 5 grams of the borate are dissolved and made up to 250 c.c. with CO_2—free water. 50 c.c. of the solution are titrated with approximately half normal hydrochloric acid, methyl orange being used as indicator. To another 50 c.c. of the borate solution there is added the same amount of $\frac{N}{2}$ hydrochloric acid that was taken in the methyl orange titration, so that all the boric acid is present in the free state. One adds now 50 c.c. of glycerol or a gram of mannitol, as well as two or three drops of phenolphthalein solution, and the boric acid is titrated with $\frac{N}{2}$ caustic soda free from carbonate. When the pink colour appears it is desirable to add 10 c.c. of glycerol or another gram of mannitol, and if the pink colour disappears the titration with the sodium hydroxide must be continued. This procedure must be repeated until the pink colour persists, when more mannitol or glycerol is added.

If the borate under analysis contains carbonate the solution after the addition of HCl must be boiled for some time to expel CO_2 before proceeding with the titration of the boric acid. This boiling must be carried out in a flask with reflux

[1] See Böeseken, *Rec. trav. chim.*, 1921, **40**, 553; Gilmour, *J. Chem. Soc.*, 1922, **121**, 1333.

[2] Rimbach and Ley, *Z. physikal. Chem.*, 1922, **100**, 393; see also Magnanini, *ibid.*, 1890, **6**, 58.

[3] *Loc. cit.*

condenser attached, as otherwise some boric acid would be lost with the steam.

Glycerol is frequently slightly acid. If so it must be carefully neutralized with decinormal caustic soda before use. Owing to the comparative instability of the glycerol-boric complex, sufficient glycerol should be used to make the solution at the end of the titration about 30 per cent with respect to glycerol. No great excess of mannitol, however, is needed.

Heteropolyacids and Polyacids

There is a group of remarkable complex compounds of great interest and importance on which recent investigations have thrown considerable light. These are the complex acids which result from the interaction of the metallic acids (chromic, molybdic, tungstic) belonging to group six of the periodic classification with other acidic oxides (boric, silicic, phosphoric, vanadic, etc.). Complex acids of this sort derived from more than one acidic oxide have been termed "Heteropolyacids" by Rosenheim, who is responsible for a great deal of recent systematic work upon them.

These acids and their salts are numerous, and have certain characteristics in common. The acids themselves are very soluble and very strong. They crystallize well, however, as do their salts, some of which are very sparingly soluble in water. They are stable only in acid or neutral solution. Their formulæ are highly complex, and many peculiar and, at first sight, unaccountable cases of isomorphism are found amongst these compounds.

They are divisible into several well-marked groups according to the number of atoms of the group six element (Mo, W, etc.) present in the complex for each atom of the other acidic element (B, Si, P, etc.).

The highest number of atoms of Mo, etc., ever found for one atom of the other element is 12. This seems to be the limiting number therefore, and it is independent of the ordinary valency (3, 4, or 5) of the other element.

On the basis of Miolati's [1] extension of Werner's Co-

[1] *J. pr. Chem.*, 1908, **77**, 417.

ordination Theory, Rosenheim [1] has been able to group together and account for in a very satisfactory manner a great number of these compounds which were previously very puzzling. According to Miolati and Rosenheim these complex acids are built up round the acidic atom present in the smaller proportion in the complex (B, Si, P, V, etc.). This is the central atom around which the metallic acid is co-ordinated. The co-ordination, however, is not directly to the central atom but to the oxygen atoms co-ordinated with it. One of the simplest of this type of compound is 3-Molybdoarsenic acid—

$$H_3\left[\begin{matrix}\text{As}\\ \end{matrix}\begin{matrix}\text{O–MoO}_3\\ \text{O–MoO}_3\\ \text{O–MoO}_3\\ \text{O}\end{matrix}\right] \text{ derived from } H_3\left[\begin{matrix}\text{As}\\ \end{matrix}\begin{matrix}\text{O}\\ \text{O}\\ \text{O}\\ \text{O}\end{matrix}\right]$$

Other examples of a similar but simpler type are found among the polyacids such as those of chromium.

$$H_2\left[\begin{matrix}\text{Cr}\\ \end{matrix}\begin{matrix}\text{O}\\ \text{O}\\ \text{O}\\ \text{O}\end{matrix}\right]; \quad H_2\left[\begin{matrix}\text{Cr}\\ \end{matrix}\begin{matrix}\text{O.CrO}_3\\ \text{O}\\ \text{O}\\ \text{O}\end{matrix}\right]; \quad H_2\left[\begin{matrix}\text{Cr}\\ \end{matrix}\begin{matrix}\text{O.CrO}_3\\ \text{O.CrO}_3\\ \text{O}\\ \text{O}\end{matrix}\right]$$

Chromic. *Dichromic.* *Trichromic.*

These simple poly- and heteropoly-acids are derived from acids in which the central atom is co-ordinated with four oxygen atoms. Many such compounds appear to exist, but they are not, as yet, well known. The more complex, and at present more important heteropolyacids, are derived from acids in which the central atom is co-ordinated with six oxygen atoms. Such "parent" acids would be, for example, $H_9[BO_6]$; $H_8[SiO_6]$; $H_7[PO_6]$; but none of them are capable of existence as such, for they lose water until the central atom is co-ordinated with only four or even only three oxygen atoms.

The general formula for all "parent" acids with six co-ordinated oxygen atoms is $H_{12-n}[RO_6]$ where n is the ordinary valency of the central atom R. When all of the

[1] See especially Rosenheim and Jaenicke, *Z. anorg. Chem.*, 1917, **100**, 304. Also Rosenheim in Abegg and Auerbach's *Handbuch der anorg. Chem.*, 1921, vol. **4**, pt. 1, ii, pp. 977–1064.

six oxygen atoms are co-ordinated with one or two molecules of an acidic oxide such as MoO_3, WO_3, the stability of the above hypothetical acids becomes so great that, in many cases, there is no difficulty in isolating the derivative so formed.

If the central atom R is of a very feeble acid character, it would seem that not more than six molecules of MoO_3, etc., can be co-ordinated so that the complex acids with central atoms such as Al, Fe(-ic), Cr, Te, I are all of the type $H_{12-n}[R(MO_4)_6]$ (where M is Cr, Mo, or W). With strongly acidic central atoms such as B, Si, P, As, twelve molecules of MO_3 are co-ordinated and complexes of the type

$$H_{12-n}[R(M_2O_7)_6]$$

result. These are, in both cases, the limiting or saturated types, but compounds with one or more oxygen atoms which have not yet been co-ordinated with MO_3 are theoretically and actually capable of existence.

The analytically important complex acids, such as silico-tungstic, phosphomolybdic, etc., belong to the second of the above types.

Some of the known compounds may be tabulated :—

$H_7[P(Mo_2O_7)_6]$.	$28H_2O$	and	$22H_2O$
$H_7[P(W_2O_7)_6]$.	$28H_2O$	,,	$22H_2O$
$H_8[Si(Mo_2O_7)_6]$.	$28H_2O$		—
$H_8[Si(W_2O_7)_6]$.	$28H_2O$	,,	$22H_2O$
$H_9[B(W_2O_7)_6]$.	$28H_2O$	,,	$22H_2O$

It is worth noting that the stability of the complexes depends on the nature of the constituents which build them up. The less acidic the central atom the weaker the complex, while the tungsten derivates are always more stable than the molybdenum ones. For these reasons a 12-Molybdoboric acid has not yet been obtained.

All the above compounds containing 28 molecules of crystal water are isomorphous in the tetragonal system, while those with 22 molecules of crystal water are isomorphous in the hexagonal system. The small differences due to the varying number of acidic hydrogen atoms are clearly not sufficient to prevent such isomorphism.

From the phosphomolybdic and silicotungstic acids the guanidine salts $(CN_3H_6)_7[P(Mo_2O_7)_6]10H_2O$ and $(CN_3H_6)_8[Si(W_2O_7)_6].6H_2O$ have been obtained, hence there appears no doubt that the acids really do contain 7 and 8 acidic hydrogen atoms respectively.

The formation of heteropolyacids, according to the scheme, metallic acid + metalloid acid $\rightleftarrows$ heteropolyacid, is a reversible process. When excess of the metallic acid (molybdic, tungstic) is used the compounds containing 12 atoms of Mo, etc., in the molecule are formed. With excess of the metalloid acid, however, acids containing only 9 atoms of Mo, etc., for each central acidic atom are obtained. The general formula of these 9-acids seems to be $H_{11-n}\left[R\begin{matrix}(M_2O_7)_4\\ O\end{matrix}M_2O_7\begin{matrix}(M_2O_7)_4\\ O\end{matrix}R\right]H_{11-n}$ and, in agreement with this, the silver 9-molybdo-arsenate and -phosphate contain six atoms of silver for each atom of arsenic or phosphorus.

The Molybdate Method for Separating and Estimating Phosphoric Acid

In view of the fact that many of the complex acids which have just been considered are very strong, it is not surprising to find that while the acids themselves are excessively soluble, their salts with strong bases are often very sparingly so. This is especially the case with the potassium salts and with various amine salts. Sometimes also the ammonium salt is very sparingly soluble. Such sparingly soluble salts are not necessarily those in which all the acidic hydrogen atoms have been replaced; they are frequently acid salts.

The yellow phosphomolybdate precipitate, which is so important in the separation of phosphoric acid, is a triammonium salt of 12-molybdo-phosphoric acid. The precise nature of the yellow precipitate, however, is somewhat obscure, but it is apparently an acid salt. According to Hundeshagen,[1] it has a composition corresponding with the formula $(NH_4)_3PO_4.12MoO_3.2HNO_3.H_2O$ after drying to constant weight in a desiccator over calcium chloride or

[1] *Z. anal. Chem.*, 1889, **28**, 141.

caustic potash. The above formula corresponds to the case where the precipitate has been prepared from nitric acid solution. If obtained from hydrochloric acid solution it contains 2HCl in place of $2HNO_3$. Whether any water of crystallization is lost during the drying in the desiccator is not stated. Hundeshagen states that both the water and the acid (HNO_3 or HCl) are expelled quickly and completely above 130°, the residue being $(NH_4)_3PO_4.12MoO_3$.

The published evidence indicates that the yellow phosphomolybdate precipitate, when first formed, contains considerably more than the one molecule of water given in the above formula. Other investigators say nothing about the combined nitric or hydrochloric acid. The compound is best regarded as a derivative of $(NH_4)_3H_4[P.(Mo_2O_7)_6]$.

The analytical value of the yellow ammonium phosphomolybdate lies in its insolubility in even comparatively strong nitric acid. This enables phosphoric acid to be separated completely from metals such as calcium, which form phosphates insoluble in alkaline solutions. Owing, however, to the existence of other, less known, phosphomolybdates, which are not so insoluble, it is necessary to carry out the precipitation under carefully controlled conditions if reliable results are to be obtained.

For the preparation of the ammonio-nitro-molybdate reagent 100 grams of ammonium molybdate $[(NH_4)_6Mo_7O_{24}.4H_2O]$ (= 81·6 grams MoO_3) are dissolved in 280 c.c. of 7 per cent (0·97 s.g.) ammonia solution, and 30 c.c. of this ammonium molybdate solution are mixed with 70 c.c. of nitric acid of specific gravity 1·21. Since, however, the reagent in course of time slowly deposits yellow molybdic acid $(MoO_3.2H_2O)_x$, it is best made up only just before use by gradually adding the ammonium molybdate solution to the nitric acid, stirring all the while. A white precipitate of H_2MoO_4 is first formed, which redissolves in the excess of nitric acid, owing perhaps to the formation of a complex nitro-molybdic acid. No true heteropoly-acids, however, derived from nitric acid and containing nitrogen as the central atom are known in the solid state, and if any such nitromolybdic acid exists in solution it is

certainly very unstable. To prevent contamination with silica the ammonium molybdate solution is best stored in a wax or wax-lined bottle.

The substance in which P_2O_5 is to be estimated is dissolved in nitric acid (an amount containing about 0·1 gram P_2O_5 is a convenient quantity to work with), and the solution, which should occupy about 25 c.c., is treated with 50 c.c. of the above ammonio-nitro-molybdate reagent. The mixture immediately turns yellow (unless there is a very small amount of P_2O_5 present) and a yellow precipitate begins to form almost at once. The beaker containing the solution is then hung in a water-bath heated to about 50° for 10–15 minutes, and the contents are stirred occasionally. When the beaker has been removed from the water-bath it is placed in a dish of cold water for another 15 minutes.

At the end of this time precipitation of the yellow compound is complete. The precipitate, which is very dense, is allowed to settle, and the supernatant liquid decanted through a filter paper. It is washed by decantation from 8 to 10 times, each time with about 20 c.c. of a solution containing 1 per cent HNO_3 and 5 per cent NH_4NO_3. The precipitate which has accumulated on the filter is then rinsed back into the beaker containing the remainder and the whole is dissolved in 2·5 per cent ammonia solution (using 50 c.c. for each 0·1 gram P_2O_5); the ammonia should be poured through the filter into the beaker in order to dissolve the small amount of precipitate still adhering to the paper. The ammoniacal liquid is heated to incipient boiling, and the phosphoric acid is precipitated as magnesium ammonium phosphate by the addition, drop by drop, of 10 c.c. of magnesium solution (one litre of which should contain 50 grams $MgCl_2.6H_2O$ and 150 grams NH_4Cl). The precipitate is left to stand over night, washed with 2·5 per cent ammonia, ignited and weighed as usual as $Mg_2P_2O_7$.

The best conditions for the quantitative precipitation of phosphoric acid as ammonium phosphomolybdate have been carefully studied by Hundeshagen [1] as well as by a number of other workers.

[1] *Z. anal. Chem.*, 1889, **28**, 141.

The formation of the phosphomolybdic acid from phosphoric and molybdic acids takes time, but occurs more rapidly at higher temperatures. This is one reason for heating the reacting mixture, whilst another reason is that from the hot solution a precipitate is obtained which is very uniform in its grain and consists of distinctly formed octahedra. It settles well, and can be more easily washed and filtered than the precipitate formed in the cold. Heating to too high a temperature or for too long a time is bad, however, as white prismatic crystals of ammonium tetramolybdate, $(NH_4)_2Mo_4O_{13}.2H_2O$, are then liable to be precipitated along with the yellow ammonium phosphomolybdate.

Owing to the reversibility of the phosphomolybdic acid formation a certain excess of molybdic acid is necessary if the precipitation of the phosphoric acid is to be quantitative, and the excess required is greater the greater the dilution of the phosphoric acid. Undue amounts of nitric acid also tend to keep phosphoric acid in solution—owing possibly to formation of nitromolybdic acid—but this effect of nitric acid can be countered by using a larger amount of the ammonium molybdate solution.

Jörgensen [1] recommends the use of the following amounts of ammonium nitromolybdate reagent, prepared as stated above, for the quantitative precipitation of the amounts of P_2O_5 shown in the table at the concentration indicated :—

Amount of P_2O_5	Vol. of phosphate solution.	Amount of nitromolybdate reagent to be used.
0·20 grm.	50 c.c. 25 c.c.	100 c.c. 91 c.c.
0·15 grm.	50 c.c. 25 c.c.	79 c.c. 70 c.c.
0·10 grm.	50 c.c. 25 c.c.	58 c.c. 50 c.c.
0·05 grm.	50 c.c. 25 c.c.	38 c.c. 29 c.c.

The presence of ammonium nitrate is necessary for the precipitation of the ammonium phospho-12-molybdate, but

[1] *Z. anal. Chem.*, 1906, **45**, 306.

other ammonium salts are not nearly so satisfactory. The ammonium nitrate required is already present in the ammonium nitromolybdate reagent prepared as above. There is considerable difference of opinion as to the effect of ammonium nitrate, and indeed of other ammonium salts, in decreasing and increasing the solubility of the phosphomolybdate precipitate, but unless present in excessive amounts it does not seem to have any adverse effect.[1] All phosphoric acid must be present as orthophosphate for precipitation as ammonium phospho-12-molybdate. Silica should be absent, and, if necessary, should be removed in the usual way, as otherwise it is liable to be precipitated as ammonium silico-12-molybdate along with the phosphoric acid compound. Arsenic also should be absent, since, unless present only in very small amount, some of it will come down as ammonium arseno-12-molybdate.

The ammonium phosphomolybdate precipitate is washed with a solution containing nitric acid and ammonium nitrate, because it is slowly decomposed by pure water. Sometimes the addition of ammonium molybdate to the washing solution is recommended, but that does not seem to be really necessary.

Considerable difficulty and uncertainty is still attached to the study of poly- and heteropoly-acids and their salts. This is illustrated by the fact that not only is the exact composition of the yellow phosphomolybdate precipitate uncertain, but the formula even of the ordinary ammonium molybdate is the subject of difference of opinion. It is generally supposed to correspond with the formula $3(NH_4)_2O.7MoO_3.4H_2O$. Rosenheim,[2] however, thinks that the formula is probably $5(NH_4)_2O.12MoO_3.7H_2O$, corresponding with the co-ordination formula $(NH_4)_5H_5[H_2(MoO_4)_6]$. The first formula requires MoO_3, 81·52 per cent; H_2O, 10·20 per cent; NH_3, 8·26 per cent; while the second requires MoO_3, 81·73 per cent; H_2O, 10·22 per cent; NH_3, 8·05 per cent; so that it is not easy to decide between them merely from the analysis.

[1] See Mellor, *A Treatise on Quantitative Inorganic Analysis*, 1913, pp. 591, 594.

[2] *Z. anorg. Chem.*, 1916, **96**, 139.

Considerable use has been made by Rosenheim of such co-ordination formulæ built up around two hydrogen atoms and derived, as it were, from $(H_2O)_6$, $(= H_{10}[H_2O_6])$, in which two hydrogen atoms play the same part as one atom of phosphorus, silicon, etc., in the heteropolyacids. Many polyacids are co-ordinated in this way round the double hydrogen atom, and are therefore to be regarded as a special type of heteropolyacid in which water plays a similar part to, say, phosphoric or silicic acid. This method of formulation, though it may appear rather artificial, accounts in a satisfactory way for the isomorphism of many of the polyacids and their salts.

Thus meta-tungstic acid is formulated as $H_{10}[H_2(WO_7)_6].22H_2O$, and this formula agrees with its isomorphism with the heteropolyacids containing 22 molecules of water of crystallization given on page 231. Ammonium tetra-molybdate, which is generally written as $(NH_4)_2Mo_4O_{13}.2H_2O$, may be regarded as $(NH_4)_6H_4[H_2(Mo_2O_7)_6]3H_2O$, and is thus an acid ammonium salt of meta-molybdic acid. It is formed from the ordinary ammonium molybdate $(NH_4)_5H_5[H_2(MoO_4)_6]$ by the action of acid, and may perhaps be regarded as an intermediate stage of its conversion into the phosphomolybdate $(NH_4)_3H_4[P(Mo_2O_7)_6]$. Owing to the changes in complexity involved, the formation of this and similar compounds requires time. This statement applies also to the formation of the yellow molybdic acid usually written as $MoO_3.2H_2O$, which separates in course of time from a mixed nitromolybdate reagent. With alkali, the yellow molybdic acid gives octomolybdates and therefore it is probably not less complex than is represented by the formula $(H_2Mo_8O_{25})\ (H_2O)_{15}$.

By the action of alkalis 12-molybdophosphoric acid is broken down and yields salts of phosphoric and molybdic acids. There are, however, three intermediate stages before that of complete breakdown. These stages are 9-molybdo-phosphoric acid (luteo-phosphomolybdates), 17-molybdo-2-phosphoric acid and 5-molybdo-2-phosphoric acid (white phosphomolybdates). White, acid ammonium salts of the latter acid can be obtained in a well-crystallized condition

from colourless ammoniacal solutions of the yellow phosphomolybdate. According to Miolati,[1] the white phosphomolybdates are derived from the PO_4''' ion and are acid salts of the acid—

$$H_4\left[P^{(MoO_4)_2}_{O_2}\right] - MoO_4 - \left[P^{(MoO_4)_2}_{O_2}\right]H_4$$

In the ammoniacal solution of the yellow ammonium phosphomolybdate precipitate one probably has some of the above white phosphomolybdate and some simple phosphate and molybdate. Any equilibrium between these which may prevail will be more in favour of the simple phosphate + molybdate the more ammoniacal the solution. Precipitation of the phosphate as magnesium ammonium phosphate shifts the reaction over so that precipitation of the phosphate is complete.

[1] *J. pr. Chem.*, 1908, **77**, 424.

CHAPTER XIV

OXIDATION AND REDUCTION

ALL chemical combination and most, if not all, chemical reactions involve either transference of electrons from one or more atoms to other atoms in the reacting systems or at least re-arrangements of the electrons in some of the atomic electron shells.

Direct transference of electrons gives rise to "electrovalency". A re-arrangement of electrons leading to a new structure in which an even number of electrons is contributed and shared equally by the combining atoms is characteristic of "co-valency", while "subsidiary valency" arises from the sharing of electrons, contributed wholly by one atom, between two combining atoms. Instances of various compounds based on these several types of valency have been considered in Chapters XII and XIII. It is possible that other somewhat modified forms of these three types of valency may also occur.

It must, however, be remembered that probably no sharp line of division exists between the three types. Thus there are grounds for thinking that even a simple compound like H_2O may be constructed partly on the "electrovalency" and partly on the "co-valency" plan, with a definite equilibrium between the electrovalency and co-valency forms of the compound. The position of such an equilibrium would be dependent upon temperature and other factors.

Owing to reasons of this sort, chemical processes can frequently be explained in alternative ways which, although apparently quite different, yet yield equally satisfactory results.

The processes of oxidation and reduction are intimately connected with the transference and re-arrangement of electrons mentioned above.

Although the term oxidation originally implied combination with oxygen while reduction implied its removal, the meaning of the term was soon extended. The terms were broadened so that oxidation could be caused by combination with many other elements chemically equivalent to oxygen, such as sulphur, chlorine, bromine, or iodine, these elements being at the same time reduced. Removal of these same elements was similarly regarded as reduction. Combination with hydrogen or elements equivalent to it (metals) was also reduction. It is true that such cases were often so regarded because the compounds concerned could be derived through the oxides. Thus $CuCl_2$ and CuS were products of oxidation of copper obtainable through CuO—

$$\mathrm{Cu} \xrightarrow{O} \mathrm{CuO} \xrightarrow{HCl} \mathrm{CuCl_2} \xrightarrow{H_2S} \mathrm{CuS}$$

although they could also be obtained by direct union of copper with chlorine or sulphur.

Similarly the hydrogen not only in water but also in HCl or H_2S is regarded as oxidized. On the same basis the hydrogen in H_3N should be regarded as " oxidized ", although it is doubtful if many regard the hydrogen in ammonia in this light. The fact of the matter is that since the introduction of the theory of electrolytic dissociation the meaning of the terms oxidation and reduction has undergone a complete transformation, and since the differentiation of valencies by means of electronic structure has taken an important place in chemical theory a still closer consideration of the real meaning and comprehensiveness of the terms is necessary.

The most striking difference between the hydrogen and chlorine in hydrogen chloride, on the one hand, and in hydrogen gas and chlorine gas on the other, is that the former on solution in water gives rise to hydrogen ions and chlorine ions, while hydrogen gas and chlorine gas do not. The same applies, though to a less obvious extent, to water and H_2S, which give hydrogen, oxygen, and sulphur ions, if only in very small amount. Generally, it may be stated that an element on oxidation becomes converted into a positive ion, which we now know occurs by the loss of one or more electrons.

Reduction on the other hand involves the addition of electrons and formation of negative ions. Obviously this idea can be extended so that any positive ion, however complex, can be regarded as a product of oxidation of the neutral complex, while any negative ion is a product of reduction of the neutral group composing it. Complex ions can be reduced or oxidized by addition or subtraction of electrons as can simple ions.

For this reason " oxidation " has come to be regarded as largely synonymous with loss of electrons, while " reduction " is synonymous with gain of electrons. Thus, the changes indicated by the upper arrows in the following equations represent oxidations, while those indicated by the lower arrows represent reductions, ⊖ standing for an electron.

$$\mathrm{Cu} \underset{+\ominus}{\overset{-\ominus}{\rightleftarrows}} \mathrm{Cu^{\cdot}} \underset{+\ominus}{\overset{-\ominus}{\rightleftarrows}} \mathrm{Cu^{\cdot\cdot}} \qquad \mathrm{2Cl'} \underset{+2\ominus}{\overset{-2\ominus}{\rightleftarrows}} \mathrm{Cl_2}$$

$$\mathrm{[Co(NH_3)_6^{\cdot\cdot}]} \underset{+\ominus}{\overset{-\ominus}{\rightleftarrows}} \mathrm{[Co(NH_3)_6^{\cdot\cdot\cdot}]} \qquad \mathrm{4OH'} \underset{+4\ominus}{\overset{-4\ominus}{\rightleftarrows}} \mathrm{O_2 + 2H_2O}$$

It has to be remembered, however, that in whatever way the change occurs, oxidation must always be accompanied by simultaneous reduction of an equivalent amount of something else which receives the electron or electrons lost by the substance undergoing oxidation. Thus in the reaction $2CuSO_4 + 4KI = 2CuI + I_2 + 2K_2SO_4$, which is represented ionically by the equation—

$$2Cu^{\cdot\cdot} + 2I' = 2Cu^{\cdot} + I_2$$

the two cupric ions are reduced to two cuprous ions while the two iodine ions are simultaneously oxidized to a molecule of free iodine.

An electric current, applied from external sources, causes a flow or transference of electrons and is hence a most potent means of causing either oxidation or reduction. These two changes occur in equivalent amounts at the points (the electrodes) where the current enters and leaves the reacting system. The only difference between oxidation and reduction brought about by a purely chemical reaction and by means of an applied electric current is that in the former

case the oxidation and reduction occur side by side during atomic or molecular collisions while in the latter they may, by suitable experimental arrangements, be separated by considerable distances.

It will be noticed that on the ionic interpretation of oxidation and reduction these two processes are associated with the establishment of electrovalencies. The two processes cannot, however, be restricted to such valencies but must be taken to cover many cases of combination by co-valencies. Thus, in the formation of carbon monoxide and dioxide, and probably many other oxides, by direct union of the elements only co-valencies are involved so far as we know. These are, nevertheless, cases of oxidation. Even water, the product of oxidation of hydrogen, is probably essentially formed by means of co-valencies. In many cases it is convenient and satisfactory for theoretical purposes to suppose that a compound formed essentially by co-valencies is in equilibrium under suitable conditions with some of the form in which the union is by electrovalencies. The oxidation or reduction can be regarded as occurring by means of a mechanism involving electrovalencies, the establishment of co-valencies being a subsequent process. It is easy to understand from what has been said that a certain vagueness attaches to the terms "oxidation" and "reduction". Where a reaction is one definitely involving electrovalency and transfer of electrons, or can be conveniently so regarded, it is commonly considered to be a case of oxidation and reduction. Where a reaction occurs in such a way that only co-valencies come into play, it is considered to be a case of oxidation only if oxygen is added on, and a case of reduction if it is removed.

Thus the union of silicon or carbon with oxygen at high temperature would be called oxidation, but the union of silicon and carbon would not be so termed. Reactions which involve only subsidiary valencies, such as the combination of NH_3 and HCl, or the formation of salt hydrates, are never regarded as oxidation or reduction processes.

The electronic transfer theory of oxidation and reduction has enabled great progress to be made in the study of these

processes. It has been shown that, in common with all other chemical changes, they are reversible and proceed until a condition of equilibrium is established which depends on the temperature, concentrations, etc., of the reacting system. This development has been accomplished mainly by electro-chemical studies of aqueous systems and to a less extent, of non-aqueous ones.

Some of the simplest cases of oxidation and reduction are those in which one metal is displaced by another from a solution of one of its salts. Thus, the precipitations of copper and mercury from solutions of their nitrates by zinc and copper respectively are represented by the ionic equations—

$$Cu^{\cdot\cdot} + Zn \rightarrow Cu + Zn^{\cdot\cdot} \qquad Hg^{\cdot\cdot} + Cu = Hg + Cu^{\cdot\cdot}$$

In the first reaction the copper is reduced and the zinc oxidized, while in the second mercury is reduced and copper oxidized.

The possibility of these two reactions shows that the process expressed by the equation $Cu \rightleftarrows Cu^{\cdot\cdot} + 2\ominus$ must be reversible : a copper atom holds its two valency electrons less firmly than a mercury atom, hence the mercuric ion can remove the two electrons it requires for conversion into a neutral atom of mercury from a neutral atom of copper. The above equilibrium between copper and copper ions is therefore shifted from left to right. Precisely the opposite applies to the case of copper and zinc.

This tendency for copper and other metals to throw off ions when in contact with pure water or aqueous solutions, was first pointed out by Nernst,[1] and called by him " electrolytic solution tension ". By a study of the potential difference between various elements and solutions of their ions it has been possible to express this conception quantitatively.

Thus, applying the law of mass action to the equilibrium $Cu^{\cdot\cdot} + 2\ominus \rightleftarrows Cu$, we obtain the expression $\frac{[Cu^{\cdot\cdot}]}{[Cu]} = a$ constant $= K$.

[1] See his *Theoretical Chemistry*, 1923, p. 859.

Now, for pure dense copper (but not for a very thin film of the metal) the solubility [Cu] of the un-ionized metal may be taken as constant at a given temperature. (It will, of course, be excessively small.) The above expression can therefore be reduced to $[Cu^{\cdot\cdot}] = \text{a constant} = K_{Cu^{\cdot\cdot}}$, which is analogous to the "solubility product" of a salt. The value of $K_{Cu^{\cdot\cdot}}$ at 18° is $8{\cdot}3 \times 10^{-22}$, which means that metallic copper can be directly in equilibrium with a solution containing cupric ions only if the concentration of the latter is $8{\cdot}3 \times 10^{-22}$ gram ion per litre. If the concentration is greater than this, cupric ions will be discharged on the metal more rapidly than they are re-formed from it. The metal will in consequence become positively charged until the accumulated charge is large enough to repel all positive cupric ions from the film of liquid immediately surrounding it, excepting those representing the concentration $8{\cdot}3 \times 10^{-22}$. The greater the original cupric ion concentration the greater the charge which must thus accumulate on the copper and the greater the potential difference which will be established between the metal and the solution. For the equilibrium $Zn^{\cdot\cdot} + 2\ominus \rightleftarrows Zn$ the conditions are rather different, inasmuch as the value of the constant $[Zn^{\cdot\cdot}] = K_{Zn^{\cdot\cdot}}$ is very large—namely, $1{\cdot}4 \times 10^{17}$ at 18°. The consequence is that when metallic zinc is placed in solutions containing zinc ions in any realizable concentrations zinc ions will leave the metal more rapidly than they are discharged upon it. The zinc thereby becomes negatively charged until a potential difference is established between it and the solution sufficient to attract enough positive ions to the immediate neighbourhood of the metal to produce equilibrium. $H^{\cdot}$ ions are so attracted as well as $Zn^{\cdot\cdot}$ ions, and before the impossibly high concentration of the latter, which is theoretically required, is reached, the accumulation of $H^{\cdot}$ ions is such that some are discharged. The equilibrium finally established involves both the reactions $Zn^{\cdot\cdot} + 2\ominus \rightleftarrows Zn$ and $H^{\cdot} + \ominus \rightleftarrows H$. It is essentially a false or unstable equilibrium which is generally attained, however, and one dependent upon the nature of the metallic zinc surface and the condition of the discharged hydrogen. The well-known peculiarities in the rate of evolution of

hydrogen by the action of zinc on acids are connected with this.

The potential $E_{M,\ M\text{-ion}}$ between a metal and a solution of its salts is given [1] by the expression—

$$E_{M,\ M\text{-ion}} = \frac{RT}{nF} \log_e \frac{C}{K}$$

In this formula n is the number of electrons lost when an atom of the metal M becomes an ion, or vice versa; C is the concentration of the metal ion in any given case; and K is the concentration represented by the solution tension constant. F is the faraday, that is to say, 96,500 coulombs.

By substituting the numerical values of R (= 8·32 joules) and F, and multiplying by the factor 2·303 to reduce the logarithm from base e to base 10, one obtains

$$E_{M,\ M\text{-ion}} = \frac{0{\cdot}0002T}{n} \log \frac{C}{K}$$

which is the practical form of the equation and gives the electrode potential in volts. If T is put equal to 290° absolute, the expression becomes

$$E_{M,\ M\text{-ion}} = \frac{0{\cdot}058}{n} \log \frac{C}{K}$$

which is commonly used when working at ordinary temperatures.[2] The subscripts to E are written in such an order that the sign of the expression on the right-hand side of the equation denotes the character of the charge on the first component written in the subscript. When C is greater than K the metal will be positive, when C is less than K it will be negative. For elements such as chlorine, oxygen, etc., which form negative ions the corresponding expression reads

$$E_{Elem,\ ion} = -\frac{0{\cdot}058}{n} \log \frac{C}{K}$$

[1] Nernst, *loc. cit.*

[2] Or $\frac{0{\cdot}058}{n} \log \frac{p}{P}$, where p and P are the osmotic pressures corresponding to the concentrations C and K : P is the "electrolytic solution pressure."

If the electrode reactions are completely reversible and occur at constant temperature E × nF is a measure of the maximum external work which can be obtained from each gram ion during its discharge.

It is the values of E for normal concentration of the respective ion (C = 1) that are given in the table on page 53. All the potentials given in that table and in the present chapter are based on the assumption that the absolute zero of potential is at such a point that the so-called standard normal calomel electrode has a value + 0·56 volt relative to this zero. The normal hydrogen electrode then has a value + 0·277 volt. From the values given 0·277 volt must be subtracted if the hydrogen electrode is taken as zero.

Although the concentrations of the un-ionized metals can be taken as constant, those non-metallic elements which have a measurable solubility dependent upon the external pressure cannot be assumed to have a constant concentration in the un-ionized condition. When dealing with oxygen, hydrogen, or the halogens the equation expressing equilibrium between the element and its ions is—

$$2El' \rightleftarrows El_2 + 2\ominus$$

or for oxygen—

$$2O'' \rightleftarrows O_2 + 4\ominus \text{ or } 4OH' \rightleftarrows O_2 + 2H_2O + 4\ominus.$$

In applying the law of mass action we get the expression—

$$\frac{[El']^2}{[El_2]} = \text{constant, for hydrogen or the halogens,}$$

$$\frac{[O'']^2}{[O_2]} = \text{constant or } \frac{[OH']^4}{[O_2]} = \text{constant, for oxygen.}$$

The concentration of the respective ions will have a definite equilibrium value only when the concentration of the neutral element is specified. For gaseous elements it is customary to specify this in terms of the gaseous pressure, for the solubility is directly proportional to the latter. The molecular concentration of the gas at the particular temperature and pressure can be used in the above expression instead of the molecular concentration of the dissolved un-ionized gas,

although a different numerical value for the constant will be so obtained since

$$\frac{[El']^2}{[El_2]_{\text{solution}}} = \frac{[El']^2}{k[El_2]_{\text{gas}}} = K \text{ or } \frac{[El']^2}{[El_2]_{\text{gas}}} = kK$$

where both k and K are constants.

Since one gram molecule of gas at 0° and 760 mm. occupies 22·4 litres the molecular concentration (per litre) $[El_2]_{\text{gas}}$ at t° and p mm. will be—

$$\frac{1}{22{\cdot}4 \times \frac{(273 + t)}{273} \times \frac{760}{p}}$$

If it is desired to compare the electrode potentials produced by different ionic processes it is clearly necessary to make the comparison under similar conditions. It is customary, so far as possible, for the comparison to be made between the potentials assumed by the electrode in solutions normal with respect to all the soluble reactants taking part in the electrode reaction. Where one of the reactants is for practical purposes insoluble (such as the metals, MnO_2, etc.), the solution is supposed to be saturated with it, while in the case of gaseous reactants the comparison is made with solutions saturated with the gases under a pressure of one atmosphere. Such potentials are called " Normal Potentials ".

If two single electrodes are combined to form an electric cell the difference of potential between them is equal to the algebraic difference of the two individual electrode potentials. Thus for the Daniell cell we should have

$$E_{Cu,\,Zn} = E_{Cu,\,Cu^{\cdot\cdot}} - E_{Zn,\,Zn^{\cdot\cdot}} = \frac{0{\cdot}058}{2}\left(\log\frac{C_{Cu^{\cdot\cdot}}}{K_{Cu^{\cdot\cdot}}} - \log\frac{C_{Zn^{\cdot\cdot}}}{K_{Zn^{\cdot\cdot}}}\right)$$

since n has the value 2 both for copper and zinc. This and corresponding equations are the basis of all electrical work on oxidation and reduction.

It is evident from the above equation that if

$$\frac{C_{Zn^{\cdot\cdot}}}{K_{Zn^{\cdot\cdot}}} = \frac{C_{Cu^{\cdot\cdot}}}{K_{Cu^{\cdot\cdot}}}, \text{ that is } \frac{C_{Zn^{\cdot\cdot}}}{C_{Cu^{\cdot\cdot}}} = \frac{K_{Zn^{\cdot\cdot}}}{K_{Cu^{\cdot\cdot}}},$$

there would be no difference of potential between the two electrodes, no electric current would flow when they were connected, and no oxidation and reduction would occur. Writing the more usual expression for ionic concentrations $[Cu^{\cdot\cdot}]$ and $[Zn^{\cdot\cdot}]$ instead of $C_{Cu^{\cdot\cdot}}$ and $C_{Zn^{\cdot\cdot}}$, we see that the condition for equilibrium is

$$\frac{[Zn^{\cdot\cdot}]}{[Cu^{\cdot\cdot}]} = \frac{K_{Zn^{\cdot\cdot}}}{K_{Cu^{\cdot\cdot}}} = K_{eq.},$$

and the value of this ratio is found to be—

$$\frac{1{\cdot}4 \times 10^{17}}{8{\cdot}3 \times 10^{-22}} = 1{\cdot}7 \times 10^{39}$$

It is obvious from this that excess of metallic zinc will remove cupric ions from solution practically completely. This does not, however, mean that it will remove copper completely from solution. It is well known that if sufficient potassium cyanide is added to a solution of cupric salt, so few cupric (or cuprous) ions are left in the solution that it will not give a precipitate with hydrogen sulphide. This is due to the formation of very stable cupro-cyanide complex ions, $[Cu(CN)_4]'''$:—

$$2Cu^{\cdot\cdot} + 2CN' \rightleftarrows 2Cu^{\cdot} + (CN)_2$$
$$Cu^{\cdot} + 4CN' \rightleftarrows [Cu(CN)_4]'''$$

Zinc also forms complex cyanide ions, but they are not so stable as those of copper, hence addition of cyanide does not affect the zinc ion concentration to the same extent as that of the copper ions. The result is that in presence of sufficient KCN the establishment of equilibrium between zinc and copper may require the removal not of copper but of zinc from solution. In other words, metallic copper can dissolve and displace metallic zinc from cyanide solutions.

It is important to realize that oxidations and reductions can be profoundly modified by the formation of complex ions—or, indeed, by other processes which alter ionic concentrations—just as can precipitations which involve only double decomposition. All oxidations and reductions tend to proceed until a definite condition of equilibrium, dependent upon the experimental conditions, is established. It may

happen, of course, that the position of equilibrium is not reached until the reaction has proceeded practically to completion in one direction. For the purposes of quantitative analysis it is usually necessary that this should be the case.

Quantitative Estimations by means of Standard Solutions of Iodine and Sodium Thiosulphate

There are a number of excellent quantitative methods involving oxidation by iodine. They depend upon the fact that the equilibrium constant of the reaction $2I' \rightleftarrows I_2 + 2\ominus$ is of such a magnitude that the reaction can be readily shifted in one direction or the other.

The value of the constant $\frac{[I']^2}{[I_2]}$ is about $2{\cdot}5 \times 10^{28}$ at 25°. Sodium thiosulphate reduces iodine readily and quantitatively, being itself oxidized to tetrathionate according to the equation $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$, which, however, is best written ionically as

$$2S_2O_3'' + I_2 = S_4O_6'' + 2I'.$$

As is well known, standard solutions of either iodine or sodium thiosulphate are used according to whether one is estimating thiosulphate or free iodine, or standard solutions of both can be used in conjunction for the purpose of other estimations. Decinormal solutions are generally the most suitable. Owing to the somewhat hygroscopic character of sodium thiosulphate and the fact that it contains five molecules of water of crystallization it is not customary to make up the standard thiosulphate solution by direct weighing. It is preferably standardized either by direct titration of a weighed amount of iodine or indirectly with potassium dichromate. Iodine solutions are best made up to approximately the desired strength by weighing, and are then standardized against previously prepared standard thiosulphate solution.

Preparation of $\frac{N}{10}$ Sodium Thiosulphate Solution

One-tenth gram molecule of crystallized $Na_2S_2O_3.5H_2O$ is weighed out and made up to a litre with distilled water.

This is best done about a week before it is to be actually standardized, since the slight decomposition caused by the action of dissolved carbon dioxide increases the effective strength of the solution. The H_2SO_3 formed during this decomposition requires twice as much iodine for oxidation as does the $Na_2S_2O_3$ from which it is produced:

$$Na_2S_2O_3 + 2H_2CO_3 = 2NaHCO_3 + H_2SO_3 + S$$
$$H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI$$

After this small initial change the thiosulphate solution will keep its strength unaltered for months if it is preserved in a well-stoppered bottle.

Preparation of pure dry Iodine for Standardization

In order to remove possible traces of chlorine or bromine, 5 to 6 grams of ordinary pure commercial iodine are ground up with two grams of solid potassium iodide. The mixture is placed in a dry 300 c.c. spoutless beaker. On this beaker rests a glass flask or bulb of slightly greater diameter than the beaker, with a closed piece of tubing about an inch in diameter sealed into the bottom. The flask is thus more or less pear-shaped, and the bottom of the narrow end should reach to within about one and a half inches of the bottom of the beaker. The neck of the flask is closed by a cork carrying inlet and exit tubes for water, the inlet tube reaching to the bottom of the narrow extension of the flask. The flask is filled with water at room temperature, and the beaker is surrounded by a cylinder of asbestos. The beaker is heated on a wire gauze over quite a small flame. In a short time practically all the iodine has sublimed and condensed on the narrow base of the flask. A current of cold water is then passed through the flask and the compact crust of iodine can easily be pressed off on to a watch glass by means of a glass rod. It is once more sublimed at as low a temperature as possible, without addition of any potassium iodide, in order to free it from any traces of the latter which may have been carried along mechanically with the iodine vapour during the first sublimation. The twice-sublimed iodine is crushed up in a mortar, placed on a watch glass,

and left to dry for 24 hours over calcium chloride in a desiccator which has a well-fitting, but ungreased lid.[1]

Standardization of the Thiosulphate Solution

A small weighing bottle with a well-ground stopper, and containing 2–2·5 grams of iodate-free potassium iodide and 0·5 c.c. of water, is weighed accurately. Pure sublimed iodine (0·4–0·5 gram) is quickly introduced, the stopper is replaced, and the bottle is again weighed. The iodine dissolves almost at once in the strong potassium iodide solution.

A conical 500 c.c. flask containing about 200 c.c. of water and 1 gram of potassium iodide is held on the slant and the weighing bottle with contained iodine which has just been weighed is allowed to slide into it. The stopper of the weighing bottle is removed just as the latter slides into the flask and is then dropped after the bottle. In this way no iodine is lost. The solution of the accurately known amount of iodine is now titrated with the sodium thiosulphate solution which is to be standardized. It is run in steadily from the burette with continuous shaking of the flask until only a faint yellow colour remains. 2–3 c.c. of starch solution are then added, and the titration is continued carefully until the blue starch-iodine colour just disappears. In all titrations of iodine with thiosulphate the starch should be added only when almost all the free iodine has been removed. Otherwise it is difficult to get all the iodine in the starch-iodine complex to react with thiosulphate without using excess of the latter.

Preparation of Standard Iodine Solution

For an approximately decinormal solution 20–25 grams of pure potassium iodide are placed in a litre flask and dissolved in a small amount of water. To this solution are added 12·7 grams of ordinary commercial iodine, weighed out roughly on a watch glass. After all the iodine has dissolved in the strong KI solution, the flask is filled to the

[1] Action of iodine vapour on the grease would produce HI, which might lead to contamination of the iodine.

mark with distilled water, the solution is mixed well and standardized against the standard thiosulphate solution.

Free iodine can be titrated by (neutral) sodium thiosulphate either in neutral or acid solution. Alkaline solutions, which would of course contain not free iodine but hypoiodite (or iodate), cannot be used, for thiosulphate is oxidized to sulphate, not tetrathionate, by hypoiodite.

Preparation of the Starch Solution

This can either be made by shaking up a small amount of the commercial " soluble starch " with cold water or it can be prepared as follows from ordinary starch.

Grind up half a gram of starch to a fine powder and mix this with a small amount of cold water to a thin paste. This is then added slowly to 100 c.c. of boiling water. Continue the boiling for one or two minutes until a nearly clear solution is obtained. This solution, after standing overnight, is filtered, and then keeps for several days before moulds begin to develop.

Two matters connected with iodine titrations call for some comment. They are (1) the nature of the solutions of iodine in potassium iodide and (2) the nature of the starch iodine reaction.

Solutions of Iodine in Potassium Iodide
Polyhalogen Compounds [1]

The solubility of iodine in pure water is only slight. At 20° it is 0·296 gram per litre (= 0·00116 gram mol.). Iodine dissolves readily, however, in various organic solvents (alcohol, carbon disulphide, chloroform, benzene, etc.), as also in aqueous solutions of the iodides of the alkali and alkaline earth metals, ammonium iodide and iodides of organic ammonium bases. This solubility in iodide solutions is due to the formation of polyiodides, which in different cases and according to circumstance may contain from three to nine atoms of iodine per equivalent of metal or ammonium base. Organic ammonium polyiodides containing nine atoms

[1] Abegg and Auerbach, *Handbuch der anorg. Chem.*, 1913, vol. **4**, pt. 2, 432–46. Numerous references to work on the subject are given.

of iodine have actually been prepared. No similar inorganic compounds containing more than five atoms of iodine per molecule have been actually isolated, though there are indications that such compounds exist containing up to nine atoms. There seems no doubt that all the iodine in these polyiodides is in the form of complex anions, but their structure is still obscure. They are to be regarded as only special cases of polyhalogen compounds, for numerous analogous compounds are known in which the complex anion contains more than one halogen, although the tendency to form such polyhalogen compounds increases from chlorine to iodine. Analytically, potassium tri-iodide is probably the most important of these, as it is the chief compound concerned in the iodine solutions used in volumetric work.

In common with all the polyhalogen compounds its stability is not of a very high order, and it tends to dissociate in accordance with the scheme :—

$$KI + I_2 \rightleftarrows KI_3$$
$$\text{or } I' + I_2 \rightleftarrows I_3'$$

Hence, a solution in which potassium tri-iodide is present reacts towards thiosulphate and other reducing agents practically like a solution of free iodine. The position of equilibrium is actually such that the concentration of I_3' ions is almost the same as that of the I' ions, when the solution is in equilibrium with solid iodine.

The value of $\frac{[I'][I_2]}{[I_3']}$ at 25° is about 0·00137. The expression should have a constant value at a given temperature but, owing to some obscure complications, it is actually not as steady as might be expected. Now, at 25° a saturated solution of iodine in water contains 0·00134 gram mol. per litre. Hence in the above expression $[I_2] = 0{\cdot}00134$, and it is evident that the value of $[I']$ must be practically the same as that of $[I_3']$.

It follows that the minimum amount of potassium iodide required to dissolve a given amount of iodine will be twice that calculated from the equation $I_2 + KI = KI_3$. This would be 16·6 grams KI per 12·7 grams iodine. Practically 20–25 grams KI is found to be better, since

the iodine then dissolves more rapidly and certainly, and these are the proportions used in preparing iodine solutions for volumetric work.

The Nature of the Starch-Iodine Reaction [1]

Starch can be precipitated quantitatively [2] by means of a strong solution of iodine in potassium iodide, but with small quantities of starch and small amounts of iodine the effect produced is that of a blue solution rather than a precipitate. The blue substance is in colloidal solution and is negatively charged. This well-known reaction for free iodine is an extremely sensitive one under proper conditions, and can detect from 0·1 to 0·3 milligram of free iodine in a litre of solution. The use of starch therefore enables a very delicate end-point to be obtained in titrations with iodine or thiosulphate.

It is well known that not only starch and free iodine, but also salts or acids, especially KI or HI, are involved in the formation of the blue substance. For a ready formation of the blue substance iodide ions appear to be necessary, and substances (such as iodic acid) which destroy them prevent the blue coloration appearing with starch even though plenty of free iodine is present.[3]

There seems no doubt that the reaction is due to adsorption by the colloidal starch, and it should be borne in mind that other colloidal substances, notably basic lanthanum acetate, give a similar blue coloration with iodine. The precise mechanism of the reaction is still obscure, but it would appear that the negatively charged starch particles first take up positive ions (especially $H^{\cdot}$ or $K^{\cdot}$) and that the aggregates so formed adsorb iodine, possibly as the I_3' ions. It is to be noted that the formation of such a starch-iodine complex is of the nature of a distribution of iodine between the starch

[1] See Lottermoser in Abegg and Auerbach's *Handbuch der anorg. Chem.*, 1913, vol. **4,** pt. 2, 592; also Treadwell, *Textbook of Analytical Chemistry*, 1919, vol. **2,** 652; and Barger and Field, *J. Chem. Soc.*, 1912, **101,** 1394.

[2] Reed, *Chem. News*, 1911, **104,** 271; Small, *J. Amer. Chem. Soc.*, 1919, **41,** 107.

[3] Roberts, *Amer. J. Sci.*, 1894, [3], **47,** 422.

particles and the aqueous solution. Rise of temperature and the presence of excessive amounts of KI tend to increase the solubility of the iodine in the aqueous solution. Perhaps for this reason the coloration given by starch and iodine changes from blue, through violet, red, and orange, to yellow when the temperature is raised from 40° to 70°. Addition of large amounts of KI produces a similar colour change.

Under ordinary conditions, in work with decinormal solutions of iodine, there is usually enough potassium iodide present for the reaction with starch to be sufficiently sensitive. With centinormal solutions, however, it may be necessary to put in additional potassium iodide, especially if only small amounts of the 0·01 N iodine solution are being added to large volumes of other solutions. In such cases it is important to standardize the iodine solution under similar conditions as regards KI concentrations, etc., to those prevailing in the actual determination.

Estimation of Sulphurous Acid or of Sulphites by means of Standard Iodine and Sodium Thiosulphate Solutions

This is the only reliable method. The two things to guard against are loss of SO_2 and atmospheric oxidation. The only trustworthy procedure therefore is to run a measured amount of the sulphurous acid solution from a pipette into excess of standard iodine solution and then to titrate back with standard thiosulphate. The sulphurous acid is oxidized quantitatively to sulphate. The iodine solution should be in a conical flask, and must be shaken round while the sulphurous acid is being run in. The tip of the pipette is best placed just beneath the surface of the iodine solution, until nearly all the sulphurous acid has run out.

In the case of sulphites the standard iodine is acidified with hydrochloric acid, and either a weighed amount of the solid sulphite or a measured amount of its solution is added to the iodine.

The reaction—

$$H_2SO_3 + I_2 + H_2O \rightleftarrows H_2SO_4 + 2HI$$
$$\text{or} \quad SO_3'' + I_2 + H_2O \rightleftarrows SO_4'' + 2I' + 2H^{\cdot}$$

is reversible but the position of equilibrium is entirely in favour of sulphate unless the concentration of the reacting system is very considerable. For any concentration used in volumetric work, such as normal or less, oxidation of the sulphurous acid is complete.

The Volumetric Estimation of Copper by means of Sodium Thiosulphate [1]

This useful method depends on the liberation of iodine by the action of cupric salts on soluble iodides. A precipitate consisting of a mixture of cuprous iodide and free iodine is formed, and the iodine is titrated with standard thiosulphate in presence of starch. The method is more particularly useful for the determination of copper in copper salts, in metallic copper, or alloys such as brass or german silver, or it can be used for estimating copper which has been previously separated as sulphide from other metals. The thiosulphate used in the estimation is best standardized against pure copper since the end point in the titration is not quite so easy to see as it is in a simple iodine titration where no copper is present.

The amount of material used for the analysis should contain 0·15–0·2 gram of copper. If the material consists of the metal or an alloy it should be dissolved in the minimum amount of a mixture of equal parts of strong nitric acid and water. Copper sulphide is similarly dissolved in cases where the copper has first to be separated as sulphide from other metals.

The solution is evaporated to dryness to drive off oxides of nitrogen and excess of nitric acid. If any oxides of nitrogen remain they are liable to liberate iodine from the potassium iodide added subsequently and cause an uncertain and inaccurate end-point. The residue is dissolved in about 20 c.c. of water with the addition of sufficient dilute nitric acid. Solution of any basic nitrate which may have separated can be hastened by warming. In order to remove free nitric

[1] de Haen, *Annalen*, 1854, **91**, 237. For other references and a detailed description of the method see Mellor's *Treatise on Quantitative Inorganic Analysis*, 1913, p. 351.

acid a solution of sodium carbonate is then added drop by drop until a small permanent precipitate is formed, which is dissolved by the addition of sufficient acetic acid.

Potassium iodide is now added to the cold copper solution. Where soluble neutral copper salts are being analysed, this can be done at once without any preliminary treatment. The potassium iodide is dissolved in a small amount of water before addition to the copper solution, and 3 grams should be used for every 0·2 gram of copper present. Theoretically, only 5·02 grams of KI are required for 1 gram of copper, but in practice excess has to be used to dissolve the iodine liberated. If the latter separates as a precipitate it dissolves only slowly during the titration with thiosulphate, and makes the end point difficult to detect.

To avoid loss of iodine the solution should be cold and kept cold. To avoid disturbance by atmospheric oxygen and consequent liberation of too much iodine the mixture should be titrated at once with the standard sodium thiosulphate; when the latter has been run in until the solution has only a faint yellow colour, a few drops of starch solution are added, and the titration is continued until the blue colour is discharged, and the tint suddenly changes to a cream colour. The blue colour slowly returns on exposure to the air owing to oxidation of the cuprous copper and subsequent reduction by iodide ions. The oxidation occurs according to the scheme

$$2Cu^{\cdot} + 2H^{\cdot} + O = 2Cu^{\cdot\cdot} + H_2O$$

and is dependent on the presence of hydrogen ions. The smaller the concentration of these, therefore, the less troublesome is the atmospheric oxidation. This is the chief reason for having as little free acid as possible present.

After the completion of the titration, the blue colour should not begin to reappear for at least two minutes. If it does it may indicate the presence of traces of nitrite, or that too little potassium iodide has been used. Too great dilution of the solution being titrated, as also the presence of considerable quantities of neutral salts, are liable to make

the end point slow of attainment. Instead of being reached suddenly the blue starch-iodide colour goes, then returns almost at once, and so on. This is because in dilute solution the reaction between cupric and iodide ions takes place slowly, while the effect of salts is probably mainly due to alterations caused in the concentration of $Cu^{\cdot\cdot}$ and $Cu^{\cdot}$ ions owing to formation of complex cupric or cuprous ions or to simple throwing back of the ordinary ionization.

It is worth while considering the theoretical aspect of the liberation of iodine by cupric salts in some detail.[1]

The reaction $2Cu^{\cdot\cdot} + 2I' \rightleftarrows 2Cu^{\cdot} + I_2$ is reversible, and Fedotieff [2] found that at 20° the equilibrium constant—

$$\frac{[Cu^{\cdot\cdot}]^2[I']_2}{[Cu^{\cdot}]^2[I_2]} = K = 4{\cdot}18 \times 10^{14}$$

In presence of cuprous iodide as solid phase the expression can be somewhat simplified. The solubility product of cuprous iodide at 18° is $[Cu^{\cdot}][I'] = 5{\cdot}06 \times 10^{-12}$.

Writing $L = [Cu^{\cdot}][I']$ in the above expression—

$$\frac{[Cu^{\cdot\cdot}]^2[I']^2}{[Cu^{\cdot}]^2[I_2]} = \frac{[Cu^{\cdot\cdot}]^2[I']^4}{L^2[I_2]} = 4{\cdot}18 \times 10^{14}$$

$$\text{whence } \frac{[Cu^{\cdot\cdot}]^2[I']^4}{[I_2]} = 1{\cdot}44 \times 10^{-8}$$

In other words, the reaction proceeds until there is practically no cupric ion left, a result determined mainly by the insolubility of cuprous iodide.

The tendency for the reaction $Cu^{\cdot\cdot} + \ominus \rightleftarrows Cu^{\cdot}$ to occur can be calculated as follows :—

The value of the electrode potential $(E.P.)_{Cu^{\cdot\cdot}}$ of copper dissolving as cupric ions is 0·606 volts. This is simply the value of $E_{Cu,Cu^{\cdot\cdot}}$ in a solution normal with respect to $Cu^{\cdot\cdot}$ ions. That is to say $E_{Cu,Cu^{\cdot\cdot}} = \frac{0{\cdot}058}{2} \log \frac{C}{K_{Cu^{\cdot\cdot}}} = \frac{0{\cdot}058}{2} \log \frac{1}{K_{Cu^{\cdot\cdot}}} = 0{\cdot}606$ volts when $C = [Cu^{\cdot\cdot}] = 1$.

[1] See Donnan in Abegg and Auerbach's *Handbuch der anorg. Chem.*, 1908, vol. **2**, pt. 1, 519–23.

[2] *Z. anorg. Chem.*, 1911, **69**, 22.

($K_{Cu^{\cdot\cdot}}$ is the equilibrium concentration of $Cu^{\cdot\cdot}$ ions corresponding to the electrolytic solution tension of copper and has the value $8 \cdot 3 \times 10^{-22}$ at 18°).

For copper in contact with a solution of cupric ions of concentration $[Cu^{\cdot\cdot}]$ we have $E_{Cu,Cu^{\cdot\cdot}} = \frac{0 \cdot 058}{2} \log \frac{[Cu^{\cdot\cdot}]}{K}$

$= 0 \cdot 606 + \frac{0 \cdot 058}{2} \log [Cu^{\cdot\cdot}]$.

It follows [1] from this that the *maximum* work which *could be done* per gram atom of cupric ion when reduced to copper from a concentration $[Cu^{\cdot\cdot}]$, that is to say by the reaction $Cu^{\cdot\cdot} + 2 \ominus \rightarrow Cu$ would be, in volt-coulombs :—

$$2F \left\{ 0 \cdot 606 + \frac{0 \cdot 058}{2} \log [Cu^{\cdot\cdot}] \right\}$$

Now for copper passing directly into cuprous ions at normal concentration [2] we have $(E.P.)_{Cu^{\cdot}} = 0 \cdot 731$ volts, so that to convert one gram atom of copper into one gram atom of cuprous ion of concentration $[Cu^{\cdot}]$ the *minimum* amount of work *required* would be, in volt-coulombs :—

$$F \left\{ 0 \cdot 731 + 0 \cdot 058 \log [Cu^{\cdot}] \right\}$$

It follows, therefore, that the maximum amount of work which could be done by the reaction $Cu^{\cdot\cdot} + \ominus \rightarrow Cu^{\cdot}$ would be, in volt-coulombs—

$$F \left\{ 2 (E.P.)_{Cu^{\cdot\cdot}} - (E.P.)_{Cu^{\cdot}} + 0 \cdot 058 \times \log \frac{[Cu^{\cdot\cdot}]}{[Cu^{\cdot}]} \right\}$$

$$= F \left\{ 1 \cdot 212 - 0 \cdot 731 + 0 \cdot 058 \log \frac{[Cu^{\cdot\cdot}]}{[Cu^{\cdot}]} \right\}$$

$$= F \left\{ 0 \cdot 481 + 0 \cdot 058 \log \frac{[Cu^{\cdot\cdot}]}{[Cu^{\cdot}]} \right\}$$

The tendency for cupric copper to be reduced to cuprous copper is thus defined by the expression—

$$\left\{ 0 \cdot 481 + 0 \cdot 058 \log \frac{[Cu^{\cdot\cdot}]}{[Cu^{\cdot}]} \right\}$$

[1] See page 246.

[2] See later, page 260.

which can be regarded either as a potential [1] measured in volts, or as a driving force measured in volt-coulombs per faraday. The expression measures the oxidizing power of the reaction cupric salt → cuprous salt, just as the expressions $\left\{0{\cdot}606 + \frac{{\cdot}058}{2} \log [Cu^{\cdot\cdot}]\right\}$ and $\left\{0{\cdot}731 + {\cdot}058 \log [Cu^{\cdot}]\right\}$ measure the oxidizing powers of the reactions $Cu^{\cdot\cdot} + 2\ominus \rightarrow Cu$, and $Cu^{\cdot} + \ominus \rightarrow Cu$.

In dealing with cuprous salts it is important to remember that cuprous ions tend to break up into cupric ions and metallic copper, according to the equation $2Cu^{\cdot} \rightleftarrows Cu^{\cdot\cdot} + Cu$. This is a reversible change governed by the mass-action expression—

$$\frac{[Cu^{\cdot}]^2}{[Cu^{\cdot\cdot}]\ [Cu]} = \text{constant, or } \frac{[Cu^{\cdot}]^2}{[Cu^{\cdot\cdot}]} = K,$$ since [Cu] may be regarded as constant.

The value of the constant K at 18° is $0{\cdot}5 \times 10^{-4}$. It follows, therefore, that if $[Cu^{\cdot\cdot}]$ is 2, the greatest value which $[Cu^{\cdot}]$ can have is 0·01 unless the solution becomes supersaturated with respect to metallic copper.

Clearly it would be impossible to get a solution normal with respect to $Cu^{\cdot}$ ions as it would have to be 2×10^4 normal with respect to $Cu^{\cdot\cdot}$ ions. At the same time, owing to the great tendency of $Cu^{\cdot}$ ions to form complex ions it is frequently possible to obtain solutions which contain a far higher concentration of *total cuprous copper* than corresponds to the $Cu^{\cdot\cdot}$ ion concentration. In such cases, however, practically none of the cuprous copper may be present as simple $Cu^{\cdot}$ ions.

According to measurements of the potentials of solutions of iodine in potassium iodide the value of the electrode potential $(E.P.)_{I'}$ of iodine in solutions saturated with respect to solid iodine is + 0·818 volt at 25°.[2] Hence the minimum

[1] At an unattackable electrode, at which the change from cupric to cuprous ions was taking place reversibly against the solution in contact with it, containing concentrations $[Cu^{\cdot\cdot}]$ and $[Cu^{\cdot}]$ of cupric and cuprous ions.

[2] See Abel and Halla in Abegg and Auerbach's *Handbuch der anorg. Chem.*, 1913, vol. **4**, pt. 2, 401.

amount of work required to oxidize one gram atom of iodine ion to iodine, in a solution saturated with respect to free iodine, according to the reaction $I' \rightarrow I + \ominus$ is $F\{0{\cdot}818 - 0{\cdot}058 \log [I']\}$ volt-coulombs.

The reaction $Cu'' + I' \rightarrow Cu' + I$ (solid) can therefore yield as a maximum the work

$$\left\{0{\cdot}481 + 0{\cdot}058 \log \frac{[Cu'']}{[Cu']} - 0{\cdot}818 + 0{\cdot}058 \log [I']\right\} \text{ or}$$

$$\left\{-0{\cdot}337 + 0{\cdot}058 \log \frac{[Cu'']}{[Cu']} + 0{\cdot}058 \log [I']\right\}$$

expressed as volt-coulombs per faraday.

This expression is a measure of the driving force of the reaction between cupric and iodine ions. In view of the negative component $-0{\cdot}337$ in the expression, it is clear that the driving force will have a positive value, even for the highest possible concentration of iodine ions, only when the ratio $\frac{[Cu'']}{[Cu']}$ is very great. Since $[Cu'']$ cannot be made very great, it follows that oxidation of I' ions will occur only when $[Cu']$ is exceedingly small. As has already been pointed out on page 258, the precipitation of the very insoluble cuprous iodide (solubility product $= [Cu'][I'] = 5{\cdot}06 \times 10^{-12}$) maintains the requisite very small concentration of Cu' ions and so enables the reaction to proceed. With a moderate excess of I' ions reduction of Cu'' ions is practically complete.

Iodimetric Estimation of Copper and Iron in Mixtures

The ferric ion is a stronger oxidizing agent than free iodine, and is therefore able to oxidize iodine ions to free iodine. This is somewhat similar to the action of the cupric ion with the difference, however, that the liberation of free iodine by cupric ion is only possible on account of the insolubility of cuprous iodide. Iodine is actually a stronger oxidizing agent than the cupric ion. Ferrous iodide is soluble but, in spite of that, the reaction

$$2Fe''' + 2I' \rightleftarrows 2Fe'' + I_2$$

proceeds until practically all $Fe^{\cdots}$ ions have been reduced to $Fe^{\cdot\cdot}$ ions.

The position of this equilibrium can be readily calculated[1] from a knowledge of the electrode potentials (E.P.) $_{Fe^{\cdots}, Fe^{\cdot\cdot}}$ and $(E.P.)_{I_2,I'}$, which are $+ 1{\cdot}02$ volt[2] and $+ 0{\cdot}818$ volt[3] respectively at 25°, the latter referring to solutions saturated with respect to solid iodine at 25°.

The tendency of a ferric ion to gain an electron and become a ferrous ion in a solution containing $[Fe^{\cdots}]$ and $[Fe^{\cdot\cdot}]$ gram atoms of ferric and ferrous ions per litre is $1{\cdot}02 + 0{\cdot}058 \log \frac{[Fe^{\cdots}]}{[Fe^{\cdot\cdot}]}$ volts. The tendency of neutral iodine to gain an electron and become an iodine ion is $0{\cdot}818 - 0{\cdot}058 \log [I']$ (in a solution saturated with respect to solid iodine). In a solution containing $Fe^{\cdot\cdot}$, $Fe^{\cdots}$, and I' ions equilibrium will be reached when the tendency of the ferric ions and neutral iodine atoms to gain electrons is equal, that is when

$$1{\cdot}02 + 0{\cdot}058 \log \frac{[Fe^{\cdots}]}{[Fe^{\cdot\cdot}]} = 0{\cdot}818 - 0{\cdot}058 \log [I']$$

that is when

$$\log \frac{[Fe^{\cdot\cdot}]}{[Fe^{\cdots}][I']} = \frac{0{\cdot}202}{0{\cdot}058} = 3{\cdot}483$$

$$\text{or} \quad \frac{[Fe^{\cdot\cdot}]}{[Fe^{\cdots}]\ [I']} = 3041$$

The equilibrium is obviously almost entirely in favour of ferrous ion and free iodine.

Ferric ions are, however, readily converted into comparatively stable complex ions. Thus addition of sufficient fluoride to a solution containing ferric ions will convert the $Fe^{\cdots}$ ions so completely into FeF_6''' ions that the solutions can no longer liberate free iodine from a solution of an iodide

This action of fluorides is the basis of a rapid method for estimating copper in presence of iron,[4] which is of use in the analysis of copper ores. The process is carried out as follows :

[1] Abegg, *Z. Elektrochem.*, 1903, **9**, 569.

[2] Maitland, *Z. Elektrochem.*, 1906, **12**, 263.

[3] Abel and Halla in Abegg and Auerbach's *Handbuch der anorg. Chem.*, 1913, vol. **4**, pt. 2, 401.

[4] Fraser, *J. Soc. Chem. Ind.*, 1915, **34**, 462.

1 gram of the sample, or, if very rich in copper, 0·5 gram is weighed into a porcelain basin of about 14 cm. diameter and treated with 5 c.c. of conc. hydrochloric acid, and 15–20 c.c. of a mixture of conc. nitric and sulphuric acids (12 to 1). Unless the results are wanted quickly, the sample is weighed out in the evening and left standing all night in the acids. In the morning the contents of the basin are evaporated to dryness on the water bath, and the heat is then increased till almost all the free sulphuric acid is driven off. The dish is cooled, 5–6 drops of dilute sulphuric acid (1 : 1) are added, followed by about 20–30 c.c. of water and the dish is warmed till all the copper sulphate has dissolved. After cooling, 10–20 c.c. of 20 per cent sodium acetate solution are added, followed by a solution of sodium fluoride. The latter is prepared by shaking thoroughly about 45 grams of the commercial salt with a litre of water, and decanting the clear solution after allowing to settle. The fluoride solution should be added until the red colour due to ferric acetate has disappeared. A further quantity of 10–15 c.c. should be introduced. Probably 20–50 c.c. in all of the fluoride solution will be required, but excess does not affect the accuracy of the determination. Potassium iodide crystals (3–5 grams) are then added, and the liberated iodine titrated in the usual way with $\frac{N}{10}$ thiosulphate and starch indicator. If the ore contains much dark-coloured gangue this is apt to impart a purple tinge to the precipitated cuprous iodide when it is vigorously stirred and may lead to the addition of a few drops excess of thiosulphate. In such cases it is well to titrate back with $\frac{N}{50}$ iodine solution until the liquid acquires a distinct blue tinge and deduct the amount needed for this from the reading of the thiosulphate titration.

The iron present in the ore or mixture can also be determined, by making use of the facts (1) that copper can be titrated almost equally well in the presence of small amounts of free sulphuric acid and in solutions the acidity of which is essentially

due to acetic acid and (2) that although the liberation of iodine by ferric ion occurs only slowly in sulphate solutions (owing to most of the iron not being in the form of $Fe^{\cdots}$ ions) the reaction is both rapid and complete in presence of copper.

When both the copper and iron are to be determined it is therefore best to proceed as follows. Two equal portions, *A* and *B*, of the sample are taken. The processes of solution in acid, evaporation, etc., are carried out as already described. No addition of sodium acetate, however, is made, for in acetate solutions the reduction of ferric salts by iodides is only partial, most of the iron being in a form other than $Fe^{\cdots}$ ions.[1]

To *B* a few drops of KCNS solution are added (to serve as an indicator) and then the sodium fluoride solution until the disappearance of the red coloration shows that all $Fe^{\cdots}$ ions have been converted into complex fluoride ions.

To *A* an equivalent volume of water is added. Both *A* and *B* are then titrated with thiosulphate after addition of potassium iodide. The amount of thiosulphate consumed by *A* gives the Cu and Fe, while that required by *B* gives the Cu only.

For slight disturbances caused by the presence of antimony or arsenic in the ores, the original paper should be consulted.

A very similar method for determining copper and iron in mixtures has been published by Wark.[2] The iron is prevented from liberating iodine during the titration of the copper by previously adding sodium phosphate. This precipitates ferric phosphate, and reduces the $Fe^{\cdots}$ ion concentration to such an extent that it cannot set iodine free. After titrating the iodine liberated by the copper, acid is added to dissolve the ferric phosphate. More iodine, equivalent to the ferric salt, is liberated and titrated.

It will be readily understood from the comparatively simple oxidation or reduction reactions that have been considered up to this point, that the oxidizing power of a substance depends on its tendency to take up one or more electrons. In the case of simple substances such as iodine

[1] See page 155.

[2] *J. Chem. Soc.*, 1922, **121**, 358.

or oxygen or simple ions such as $Cu^{\cdot\cdot}$ or $Fe^{\cdot\cdot\cdot}$ this tendency, and hence the oxidizing power, can be accurately and quantitatively expressed by means of the normal potentials [1] $E_{\cdot I_2,I'}$, $E_{\cdot Fe^{\cdot\cdot\cdot},\,Fe^{\cdot\cdot}}$, etc.

The greater the normal potential, the greater, as a rule, is the oxidizing power, although, as has been seen, for instance, in the case of cupric salts and iodine, the position may be greatly modified by various causes, and especially by the formation of insoluble compounds or complex ions. One is able to determine the normal potentials in these comparatively simple cases because it is possible to work under conditions where the concentrations of the reacting ions or substances are known with reasonable accuracy.

When one has to deal with more complex oxidizing or reducing agents, however, and especially the oxygenated ones, the matter becomes more complex and uncertain. There is no difficulty in determining the value of the oxidation or reduction potential in any given case, but it may be a matter of great difficulty and uncertainty to calculate from the observed potential the value of the normal potential. The observed potential will indicate the oxidizing or reducing power of the combinations in the special case under examination, but it becomes difficult or impossible to make calculations for other cases if the normal potential is not known. Qualitative deductions alone are possible, not quantitative ones. The kind of difficulty encountered may be illustrated by a consideration of the reactions between arsenious acid and iodine.

The reaction can be represented as occurring between H_3AsO_3 and I_3' ions according to the equation

$$H_3AsO_3 + I_3' + H_2O \rightleftarrows H_3AsO_4 + 3I' + 2H^{\cdot}$$

The reaction is reversible and it will be noticed that there is production of hydrogen ions during the conversion of H_3AsO_3 into H_3AsO_4. Such formation of hydrogen ions is characteristic of all oxidations of this character where oxygen derived either from gaseous oxygen or from water

[1] See *ante*, page 247.

is involved, and plays a very important part in determining the course which such a reversible reaction will follow. Thus it is evident that removal of hydrogen ions should favour the reaction from left to right and conversely—a deduction confirmed by experiment. In neutral or alkaline solutions H_3AsO_3 is readily oxidized by iodine, while in strong acid solutions the reduction of H_3AsO_4 by iodides may occur to a large extent.

The equilibrium conditions of the reaction have been studied by Roebuck.[1] The mass-action constant for the reaction, $K = \frac{[H_3AsO_4]\,[H^{\cdot}]^2\,[I']^3}{[H_3AsO_3]\,[I'_3]}$ has the value 0·06 to 0·08 at 25°, the concentrations being expressed in gram-formula weights (corresponding, that is to say, to H_3AsO_4, $H^{\cdot}$, I_3', etc.) per litre.

If certain assumptions are made, the most reasonable way of formulating the oxidizing power of arsenic acid (or reducing power of arsenious acid) can be deduced as follows.[2] Both arsenic and arsenious acids are amphoteric compounds, and their solutions must be supposed to contain very minute concentrations of $As^{\cdot\cdot\cdot\cdot\cdot}$ and $As^{\cdot\cdot\cdot}$ ions.[3] The oxidizing or reducing power of the solutions can be referred to these small concentrations, although the actual mechanism of the processes which occur is quite obscure.

The relationship between H_3AsO_4, AsO_4''', and $As^{\cdot\cdot\cdot\cdot\cdot}$ and between H_3AsO_3, AsO_3''' and $As^{\cdot\cdot\cdot}$ can be written in two ways :—

$$\begin{cases} 3H^{\cdot} + AsO_4''' \rightleftarrows H_3AsO_4 \overset{+\,H_2O}{\underset{-\,H_2O}{\rightleftarrows}} (HO)_5As \rightleftarrows As^{\cdot\cdot\cdot\cdot\cdot} + 5OH'; \\ H^{\cdot} + OH' \rightleftarrows H_2O \\ AsO_4''' \rightleftarrows As^{\cdot\cdot\cdot\cdot\cdot} + 4O''; \; 2H^{\cdot} + O'' \rightleftarrows H_2O \end{cases}$$

$$\begin{cases} 3H^{\cdot} + AsO_3''' \rightleftarrows H_3AsO_3 \rightleftarrows As^{\cdot\cdot\cdot} + 3OH' \\ AsO_3''' \rightleftarrows As^{\cdot\cdot\cdot} + 3O'' \end{cases}$$

[1] *J. Physical Chem.*, 1902, **6**, 365; and 1905, **9**, 727.

[2] See Abegg in Abegg and Auerbach's *Handbuch der anorg. Chem.*, 1907, vol. **3**, pt. 3, 551.

[3] See *ante*, pp. 117, 179.

whence
$$\begin{cases} [As^{\cdots\cdots}] = \text{const.} \dfrac{[H_3AsO_4]}{[OH']^5} = \text{const.} \quad [H_3AsO_4]\,[H^{\cdot}]^5 \\ [As^{\cdots\cdots}] = \text{const.} \dfrac{[AsO_4'''']}{[O'']^4} = \text{const.} \quad \begin{matrix}[AsO_4'''']\,[H^{\cdot}]^8 \\ [H_3AsO_4]\,[H^{\cdot}]^5\end{matrix} \end{cases}$$

and
$$\begin{cases} [As^{\cdots}] = \text{const.} \dfrac{[H_3AsO_3]}{[OH']^3} = \text{const.} \quad [H_3AsO_3]\,[H^{\cdot}]^3 \\ [As^{\cdots}] = \text{const.} \dfrac{[AsO_3''']}{[O'']^2} = \text{const.} \quad \begin{matrix}[AsO_3''']\,[H^{\cdot}]^6 \\ [H_3AsO_3]\,[H^{\cdot}]^3\end{matrix} \end{cases}$$

The ratio $\dfrac{[As^{\cdots\cdots}]}{[As^{\cdots}]}$ which determines the oxidizing power of the system is thus equal to $\dfrac{[H_3AsO_4]\,[H^{\cdot}]^2}{[H_3AsO_3]}$

The potential E of an arsenate-arsenite electrode will therefore be given by the equation—

$$E = E_O + \frac{0{\cdot}058}{2} \log \left[\frac{[H_3AsO_4]\ [H^{\cdot}]^2}{[H_3AsO_3]} \right]$$

where E_O is the value of the expression when all the concentrations in the logarithm have unit value. In other words, E_O is the normal potential. Measurements of the potentials of such electrodes which have been made lead to a value of about + 0·85 volt for E_O with reference to the absolute zero of potential. This is the potential taken up by a platinum electrode dipping into a solution which is molar with respect to H_3AsO_4, H_3AsO_3, and hydrogen ions.

The values of E calculated with the above equation agree very fairly with those experimentally observed in acid solutions when the total concentrations of -ic and -ous arsenic are used for $[H_3AsO_4]$ and $[H_3AsO_3]$ instead of the uncertain correct values which, of course, refer to the unionized acids. The total concentrations include any ions as well.

It will be noticed that the term $\dfrac{[H_3AsO_4]\,[H^{\cdot}]^2}{[H_3AsO_3]}$ is very similar to the terms $\dfrac{[Fe^{\cdots}]}{[Fe^{\cdot\cdot}]}$ and $\dfrac{[Cu^{\cdot\cdot}]}{[Cu^{\cdot}]}$, etc., in the expressions

for the potentials of electrodes at which the changes $Fe^{\cdot\cdot\cdot} \rightarrow Fe^{\cdot\cdot}$, and $Cu^{\cdot\cdot} \rightarrow Cu^{\cdot}$, etc., occur. It differs only by the inclusion of a term for the hydrogen ion. In all similar cases a term for the hydrogen ion has to be included, since the potential depends upon the $H^{\cdot}$ ion as well as upon the other constituents which bring about the oxidation.

The effect of the $H^{\cdot}$ ion concentration on the reaction between H_3AsO_3 and iodine is such that when it is not greater than that present in a sodium bicarbonate solution, oxidation to H_3AsO_4 is rapid and quantitative. More definitely alkaline solutions, even those containing Na_2CO_3, cannot be used, for they would react with iodine on their own account. The procedure followed in the titration of arsenious acid depends upon this.

The Titration of Arsenious Oxide with Iodine

As an illustration, the estimation of As_2O_3 in the commercial product may be quoted. One gram of the sample is dissolved in the minimum amount of warm strong caustic soda solution in a porcelain basin. The contents of the basin are rinsed into a 200 c.c. flask, a drop or two of phenolphthalein solution added, and the mixture is neutralized with hydrochloric acid. A solution of 5 grams of sodium bicarbonate in 100 c.c. of cold water is added and the contents of the flask are made up to the mark and mixed thoroughly. The arsenite solution is placed in the burette and 25 c.c. of standard $\frac{N}{10}$ iodine solution titrated with it, starch paste being used as indicator.

Titration of Antimonious Oxide with Iodine

The reaction $SbO_3''' + I_3' + H_2O \rightleftarrows SbO_4''' + 3I' + 2H^{\cdot}$ is precisely analogous to that involving the corresponding compounds of arsenic. Although the reaction does not seem to have been so well investigated, it is clear that the equilibrium conditions in the two cases are very similar. Antimonious antimony can be satisfactorily estimated by means of standard iodine solution in presence of bicarbonate in precisely the same way as arsenious arsenic.

Estimation of Pentavalent Arsenic or Antimony by means of Standard Sodium Thiosulphate

In presence of strong hydrochloric acid both arsenic and antimonic acids are completely reduced by iodide. Titration of the iodine liberated gives a measure of the arsenic or antimonic acid. The arsenic or antimonic compound in a small volume of liquid is treated with an equal volume of concentrated hydrochloric acid, followed by 3 grams of potassium iodide for each 0·15 gram As_2O_5 or Sb_2O_5 present. The mixture, after standing about 10 minutes to allow the reaction to proceed to completion, is diluted with one and a half times its volume of water, and the iodine is titrated with standard sodium thiosulphate.[1]

There are, however, two objections to this method of estimating arsenic or antimonic acids.

(1) There is some slight danger of incorrect results arising from the action of the strong acid present on the sodium thiosulphate during the titration. (2) In strongly acid solution I' ion tends to be oxidized comparatively readily by atmospheric oxygen :—

$$O_2 + 4H^{\cdot} + 4I' \rightleftarrows 2H_2O + 2I_2$$

Such action would lead to too much free iodine being found and also to an unstable end point, the blue starch-iodine colour tending to reappear owing to continued liberation of iodine by oxygen.

On account of the objection (1) a standard solution of stannous chloride is frequently used for titrating iodine in presence of much acid. The reaction which occurs can be written $SnCl_2 + I_2 + 2HCl = SnCl_4 + 2HI$. The stannous chloride solution is prepared by dissolving 10 grams stannous chloride ($SnCl_2.2H_2O$) in 60 grams of hydrochloric acid (sp. gr. 1·12), diluting to a litre and standardizing with iodine solution. It gives quite a sharp end point, although this is not very permanent owing to the above-mentioned action of atmospheric oxygen on the strongly

[1] Evidently, by a combination of this method with the preceding, arsenious and arsenic acids, or the corresponding antimony compounds, can be estimated in the presence of one another.

acid iodide solution. The chief objection to the use of standard solutions of stannous chloride is that they themselves are readily oxidized by the air and therefore do not keep at all well. Stannous chloride is a strong reducing agent, the value of the normal potential E.P.$_{Sn^{\cdots\cdot}, Sn^{\cdot\cdot}}$ on the absolute scale being only about + 0·27 volt.[1]

Another and perhaps a better method of procedure is to distil over the iodine liberated by the action of strong hydrochloric acid and potassium iodide on the arsenic or antimonic acid into a solution of potassium iodide. The iodine in the receiver is then titrated with standard sodium thiosulphate, and, since little acid is present, neither of the complications referred to above is likely to cause trouble. The distillation of the iodine must be carried out in an all-glass apparatus as in Bunsen's method for estimating substances like MnO_2, PbO_2, etc., which liberate chlorine on warming with hydrochloric acid.[2]

The Reaction between Iodate and Iodide [3]

Iodic acid is a strong oxidizing agent and oxidizes iodine ions to free iodine. The reaction is reversible and is best written ionically as follows :—

$$IO_3' + 5I' + 6H^{\cdot} \rightleftarrows 3I_2 + 3H_2O$$

The reaction from right to left represents the final result of the hydrolysis of iodine by water. This hydrolysis occurs to only a minute extent in pure water, but in alkaline solutions it occurs rapidly and completely, though hypoiodite (HIO) and possibly iodite (HIO_2) are formed as intermediate stages. In alkaline solution the equilibrium between iodate, iodide, and free iodine can be formulated thus :—

$$IO_3' + 5I' + 3H_2O \rightleftarrows 3I_2 + 6OH'$$

The equilibrium conditions for both acid and alkaline solutions have been studied, and it is found that, for the acid solutions at 25°, $K = \frac{[IO_3'][I']^5[H^{\cdot}]^6}{[I_2]^3} = 10^{-47}$

[1] Abegg and Auerbach, *Handbuch der anorg. Chem.*, 1909, vol. **3**, pt. 2, 569.

[2] Treadwell, *Analytical Chemistry*, 1919, vol. **2**, 663.

[3] Abel and Halla, Abegg and Auerbach's *Handbuch der anorg. Chem.*, 1913, vol. **4**, pt. 2, 519.

while in alkaline solutions at 25°, $K' = \frac{[IO'_3]\,[I']^5}{[I_2]^3\,[OH']^6} = 8 \times 10^{37}$.

These figures show that in acid solution the equilibrium is practically entirely in favour of free iodine, while in alkaline solution it is practically entirely in favour of iodate.

Estimation of Acidity Iodimetrically

It follows from this that if excess of a neutral mixture of iodate and iodide is added to a solution containing free acid, iodine will be liberated until the hydrogen ion concentration has been reduced practically to that present in pure water. The liberated iodine can be titrated with sodium thiosulphate and gives a measure of the acid originally present.[1] It is important that both the iodate and the iodide should be in excess, otherwise too little thiosulphate will be required. A deficiency of the former will be indicated by a liberation of iodine on adding iodate to the colourless liquid at the end of the titration. A deficiency of the latter is shown by the deposition of solid iodine. Boiled water must be used, since carbonic acid liberates iodine from the mixture of iodide and iodate.

Excessive dilution causes the liberation of iodine to be slow, and if great dilution is unavoidable there should be a delay of half an hour before the liberated iodine is titrated. The method works best when the acid is not less than about decinormal. It is not suitable for organic acids.

The potential of the iodate-iodine electrode, that is to say of the reaction :

$$2IO_3' + 12H^{\cdot} + 10\ominus \rightleftarrows I_2 + 6H_2O$$

has been measured directly by Luther and Sammet [2] by means of an unattackable electrode in iodic acid solutions saturated with iodine. The results agree with those calculated by the equation—

$$E = E_0 + \frac{0{\cdot}058}{10} \log \frac{[IO_3']^2\,[H^{\cdot}]^{12}}{[I_2]}$$

[1] See Fessel, *Z. anal. Chem.*, 1899, **38**, 449.

[2] *Z. Elektrochem.*, 1905, **11**, 293; *Z. physikal. Chem.*, 1905, **53**, 641.

the value $+1{\cdot}467$ being obtained for E_0 at 25°. This is the normal potential for the iodate-iodine electrode, and is the potential assumed by an unattackable electrode dipping into a solution which is saturated with iodine and normal with respect to IO_3' and $H^{\cdot}$ ions.

The expression $\frac{[IO_3']^2\ [H^{\cdot}]^{12}}{[I_2]}$ could be deduced in a similar way to that employed for the case of the reduction of arsenic to arsenious acids. The occurrence of $[H^{\cdot}]$ to the twelfth power in the expression shows how very dependent the oxidizing power of iodate is upon the acidity of the solution.

Titrations with Potassium Permanganate

Owing to the fact that it is a very powerful oxidizer, acts quickly, and has a very deep colour, potassium permanganate is one of the most important and useful oxidizing agents used in volumetric analysis. On reduction, salts of divalent manganese are formed which are practically colourless, so that potassium permanganate acts as its own indicator during a titration. It cannot, however, as a rule, be used with solutions containing more than very small amounts of chlorides, because it is reduced by them, even at the ordinary temperature and in comparatively weak solutions.

The reduction of permanganate to a salt of divalent manganese is doubtless a complex process. A number of intermediate stages are known, forming the series $KMnO_4$, K_2MnO_4, MnO_2, salts of trivalent manganese, and finally salts of divalent manganese. Written in terms of the active ions this becomes—

$$\underset{(=Mn^{\cdot\cdot\cdot\cdot\cdot\cdot})}{MnO_4'},\quad \underset{(=Mn^{\cdot\cdot\cdot\cdot\cdot})}{MnO_4''},\quad \underset{(=Mn^{\cdot\cdot\cdot\cdot})}{MnO_2},\quad Mn^{\cdot\cdot\cdot},\quad Mn^{\cdot\cdot}.$$

No derivative of pentavalent manganese is known.

Reduction of MnO_4' to each of the intermediate stages can be brought about under appropriate conditions, but whether all these stages are passed through in the course of an ordinary titration which ends with divalent manganese cannot be stated with certainty. The reductions may be pictured as occurring through the intermediary of the several polyvalent positive ions $Mn^{\cdot\cdot\cdot\cdot\cdot\cdot}$, $Mn^{\cdot\cdot\cdot\cdot\cdot}$, etc., formed in a

very minute amount by amphoteric ionization of $HMnO_4$, H_2MnO_4, etc. This method of representation can be used in all similar cases, though it is perhaps somewhat artificial. The procedure was indicated in the case of arsenic acid.

The electro-chemistry of the reduction of permanganate has been studied by Sackur and Taegener.[1]

The several reduction stages can be represented by the following ionic equations :—

(1) permanganate → manganate $MnO_4' + \ominus \rightleftarrows MnO_4''$

(2) permanganate → MnO_2
$$\begin{cases} MnO_4' + 2H_2O + 3\ominus \rightleftarrows MnO_2 + 4OH' \\ MnO_4' + 4H^{\cdot} + 3\ominus \rightleftarrows MnO_2 + 2H_2O \end{cases}$$

(3) permanganate → $Mn^{\cdot\cdot}$ $MnO_4' + 8H^{\cdot} + 5\ominus \rightleftarrows Mn^{\cdot\cdot} + 4H_2O$

(4) manganate → MnO_2
$$\begin{cases} MnO_4'' + 2H_2O + 2\ominus \rightleftarrows MnO_2 + 4OH' \\ MnO_4'' + 4H^{\cdot} + 2\ominus \rightleftarrows MnO_2 + 2H_2O \end{cases}$$

(5) $MnO_2 \rightarrow Mn^{\cdot\cdot}$ $MnO_2 + 4H^{\cdot} + 2\ominus \rightleftarrows Mn^{\cdot\cdot} + 2H_2O$

The potentials E, of unattackable electrodes, at which these several changes are taking place, are given by the following expressions, in which the underlined number represents the normal potential in volts of the respective electrode on the absolute scale, that is to say the value of E when the several concentrations in the logarithmic term are unity (or when the value of the whole concentration expression is unity; each concentration need not in all cases have unit value).

$$(1) \quad E = +\underline{0{\cdot}887} + 0{\cdot}058 \log \frac{[MnO_4']}{[MnO_4'']}$$

$$(2) \quad \begin{cases} E = +\underline{0{\cdot}797} + \dfrac{0{\cdot}058}{3} \log \dfrac{[MnO_4']}{[OH']^4} \\ E = +\underline{1{\cdot}907} + \dfrac{0{\cdot}058}{3} \log [MnO_4'][H^{\cdot}]^4 \end{cases}$$

$$(3) \quad E = +\underline{1{\cdot}797} + \frac{0{\cdot}058}{5} \log \frac{[MnO_4'][H^{\cdot}]^8}{[Mn^{\cdot\cdot}]}$$

[1] *Z. Elektrochem.*, 1912, **18**, 718; see also Abegg and Auerbach, *Handbuch der anorg. Chem.*, 1913, vol. **4**, pt. 2, 858.

$$(4)\quad \begin{cases} E = +\underline{0{\cdot}777} + \dfrac{0{\cdot}058}{2}\log\dfrac{[MnO_4'']}{[OH']^4} \\ E = +\underline{2{\cdot}397} + \dfrac{0{\cdot}058}{2}\log\,[MnO_4'']\,[H^{\cdot}]^8 \end{cases}$$

$$(5)\quad E = +\underline{1{\cdot}627} + \frac{0{\cdot}058}{2}\log\frac{[H^{\cdot}]^4}{[Mn^{\cdot\cdot}]}$$

In the case of the reactions which involve MnO_2 the solutions are of course saturated with respect to this very insoluble compound.

It is to be noted that since $H^{\cdot} + OH' \rightleftarrows HOH$, either $H^{\cdot}$ or OH' ions appearing in a chemical equation can be written in terms of the other ion as $H_2O - OH'$ or $H_2O - H^{\cdot}$ respectively. The bracketed equations above are related in this way, and really express the same thing, though the equation containing $H^{\cdot}$ ions is more convenient when considering the conditions in acid solutions, and vice versa.

The normal potentials of the several electrodes can all be calculated either on the basis of $[H^{\cdot}] = 1$ or $[OH'] = 1$, and, of course, different values are obtained in the two cases. Those for $[H^{\cdot}] = 1$ show the relative strengths of the several oxidizing reactions in acid solution while those for $[OH'] = 1$ give the relative strengths in alkaline solutions. These two sets of values are tabulated below.

Reaction	Normal potential in volts for $[H^{\cdot}] = 1$	Reaction	Normal potential in volts for $[OH'] = 1$
$(MnO_4' \rightarrow MnO_4''$	$+0{\cdot}887)$		
$O_2 \rightarrow H_2O$ [1]	$+1{\cdot}507$	$O_2 \rightarrow OH'$	$+0{\cdot}687$
$MnO_2 \rightarrow Mn^{\cdot\cdot}$	$+1{\cdot}627$	$MnO_4'' \rightarrow MnO_2$	$+0{\cdot}777$
$MnO_4' \rightarrow Mn^{\cdot\cdot}$	$+1{\cdot}797$	$MnO_4' \rightarrow MnO_2$	$+0{\cdot}797$
$MnO_4' \rightarrow MnO_2$	$+1{\cdot}907$	$MnO_4' \rightarrow MnO_4''$	$+0{\cdot}887$
$(MnO_4'' \rightarrow MnO_2$	$+2{\cdot}397)$		

[1] This is the customary and convenient way of writing the change which occurs at the oxygen electrode in acid solution. It actually consists of the two changes, $O_2 + 4\ominus = 2\,O''$, followed by $2O'' + 4H^{\cdot} = 2H_2O$, since, in acid solution, neither O'' nor OH' ions can exist in any appreciable concentration.

It will be seen that either in acid or alkaline solution, permanganate, manganate, and manganese dioxide are stronger oxidizing agents than oxygen of atmospheric pressure.

The figures show that only the reaction $MnO_4' \rightarrow MnO_4''$ is independent of the acidity. Practically, however, neither it nor the reaction $MnO_4'' \rightarrow MnO_2$ are realizable in acid solution. The tendencies for these two reactions to occur in normal acid solutions can be calculated, however, and are given above in brackets.

The driving force of the reaction $MnO_4'' + 4H^{\cdot} + 2 \ominus \rightarrow MnO_2 + 2H_2O$ is so great in acid solution that it overcomes the feebler change $MnO_4' + \ominus \rightarrow MnO_4''$. The consequence is that MnO_4'' is unstable in acid solution, and gives rise both to MnO_2 and MnO_4' according to the equation $3MnO_4'' + 4H^{\cdot} \rightarrow 2MnO_4' + MnO_2 + 2H_2O$. This is accompanied by a change of colour from green to reddish violet and is a well-known qualitative reaction of manganese.

In most volumetric processes involving permanganate it is the reaction $MnO_4' \rightarrow Mn^{\cdot\cdot}$ which is used. A glance at the equations relating to this change will show that it depends markedly on the hydrogen ion concentration. Sufficient acid should always be present, therefore, since otherwise the MnO_4' ions may be reduced either partially, or completely only to the stage MnO_2, for the change $MnO_4' \rightarrow MnO_2$ is less dependent on the acidity.

Titration of Ferrous Iron with Potassium Permanganate

This is one of the best known processes in volumetric analysis, and one of the easiest to carry out. For most purposes a potassium permanganate solution of about decinormal strength is the most convenient. It is made up by weighing to approximately the correct strength, but has to be standardized subsequently. The solution should be kept for about a week before standardization, in order to give time for any traces of oxidizable matter (dust, etc.) to be oxidized. Once this has occurred the solution will retain

its strength unaltered for long periods if kept in the dark in well stoppered, ungreased, bottles.[1] The standardization can be effected against pure electrolytic iron, which is dissolved in dilute sulphuric acid just before the titration in an atmosphere of carbon dioxide, or by means of an oxalic acid solution of known strength, or lastly by means of standard sodium thiosulphate and potassium iodide. This last method is a very convenient one: 3 grams of potassium iodide are dissolved in 10 c.c. of water, 5 c.c. of hydrochloric acid (1 : 5) are added, and then 25 c.c. of the potassium permanganate solution. The liberated iodine is titrated with the standard sodium thiosulphate, using starch paste as indicator.

Ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4.6H_2O$, is also a convenient standardizing agent for permanganate solutions, especially when such standardization has to be done frequently. Since, however, the commercial double sulphate does not always have quite the correct composition it is generally as well to check the standardization by one of the other methods.

The actual titration of ferrous solutions with the standard permanganate is very simple. The ferrous solution is strongly acidified with sulphuric acid, adding about 10 c.c. of 2N acid for every 50 c.c. of solution. It should not be unnecessarily dilute and should be free from chlorides. It is then titrated at the ordinary temperature with the standard potassium permanganate. Towards the end of the titration the permanganate should be added cautiously until half a drop imparts a permanent pale pink colour to the solution. Owing to the deep colour of $\frac{N}{10}$ permanganate it is best to read from the top of the meniscus and not from the bottom.

The oxidation of ferrous iron by potassium permanganate in sulphuric acid solution is generally represented by the equation :—

[1] The permanganate solution will keep better if filtered through ignited arbestos before standardization. This is to remove MnO_2 which catalyses the decomposition of potassium permanganate, MnO_2 and oxygen being formed.

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

which can be simplified to the ionic equation :—

$$2MnO_4' + 10Fe^{\cdot\cdot} + 16H^{\cdot} = 2Mn^{\cdot\cdot} + 10Fe^{\cdot\cdot\cdot} + 8H_2O$$

The oxidation occurs so readily and rapidly because the normal potential of the reaction $MnO_4' \rightarrow Mn^{\cdot\cdot}$ (+ 1·797 volts) is so much greater than the normal potential of the reaction $Fe^{\cdot\cdot\cdot} \rightarrow Fe^{\cdot\cdot}$, which is only + 1·02 volts. The above equation represents only the final result of the oxidation. What intermediate stages are passed through is doubtful. Some indication of these is, however, obtained from a study of the behaviour of ferrous salts with permanganate in presence of hydrochloric acid.

Titration of Ferrous Iron with Potassium Permanganate in Presence of Hydrochloric Acid

Titration of ferrous iron in hydrochloric acid solution by means of potassium permanganate in the ordinary way gives too high results. The ferrous salt is oxidized, but so is some of the hydrochloric acid, with liberation of chlorine.

If permanganate solution is added to cold dilute hydrochloric acid in the absence of ferrous salt, reduction of the permanganate does not occur, nor does it in the presence of ferric chloride. Some product formed by the interaction of the permanganate and ferrous salt is therefore involved in the oxidation of the hydrochloric acid. If permanganate is added to a hydrochloric acid solution of a ferrous salt which also contains much manganous salt no chlorine is liberated while the ferrous iron is oxidized completely to the ferric condition with consumption of the theoretical amount of permanganate.

The normal potential for the change $Cl_2 \rightarrow Cl'$ (chlorine at atmospheric pressure) is + 1·694 volts, while that for the change $MnO_4' \rightarrow Mn^{\cdot\cdot}$ is + 1·797 volts.

It is clear, therefore, that permanganate should be able to liberate chlorine from hydrochloric acid solution. There is

not a large difference between the normal potentials, so that the tendency for chlorine to be liberated will not be very great and the reaction may not always occur, for the potentials of the two reactions depend, in any given case, upon the prevailing concentrations of Cl_2, Cl', MnO_4', $Mn^{\cdot\cdot}$, and $H^{\cdot}$. Even if it should occur it may do so with extreme slowness.

Since the presence of ferrous salts leads to the oxidation of weak hydrochloric acid by permanganate, although acid of the same strength without the ferrous salt is either not oxidized at all or only very slowly, it is reasonable to suppose that some more potent oxidizing agent than permanganate is produced by the interaction of the latter with the ferrous salt. The mechanism, however, of this " induced " oxidation of the hydrochloric acid is still very obscure

Manchot [1] supposes that in all cases of oxidation the primary product is of a peroxidic nature. When ferrous salts are oxidized, Fe_2O_5 is formed in the first instance, but at once breaks up into Fe_2O_3, and " active oxygen " which carries on the oxidation. The " active oxgyen " so formed can often effect oxidations which the original oxidizing agent cannot. Thus, in the present case it oxidizes Cl' to Cl_2 as well as $Fe^{\cdot\cdot}$ to $Fe^{\cdot\cdot\cdot}$. In presence of manganous salts, however, it oxidizes them instead, forming MnO_2, which oxidizes more ferrous salt.

Whether there is any need to suppose that such a hypothetical compound as Fe_2O_5 is formed may be doubted. The observed phenomena would seem to be capable of satisfactory explanation in the manner indicated below.

That the reduction of MnO_4' to $Mn^{\cdot\cdot}$ occurs in steps is extremely likely, and $Mn^{\cdot\cdot\cdot}$ is probably the stage immediately preceding $Mn^{\cdot\cdot}$. Now by electrolysis of strong sulphuric acid solutions of manganous salts considerable amounts of tetravalent and trivalent manganese compounds are produced, though the concentration of $Mn^{\cdot\cdot\cdot\cdot}$ and $Mn^{\cdot\cdot\cdot}$ ions is uncertain. Potential measurements on such solutions enable approximate values for the normal potentials $Mn^{\cdot\cdot\cdot\cdot} \rightarrow Mn^{\cdot\cdot\cdot}$ and $Mn^{\cdot\cdot\cdot} \rightarrow Mn^{\cdot\cdot}$ to be calculated. These are found to be $+ 1{\cdot}927$ and

[1] *Annalen*, 1902, **325**, 93, 105.

1·827 volts respectively.[1] There is not a great difference between these values and the normal potential (+ 1·797 volts) of the reaction $MnO_4' \rightarrow Mn''$, and so far as the oxidation of Cl' to Cl_2 is concerned one would hardly have expected Mn''' to be much more effective than MnO'_4. Since, however, the reduction process $Mn''' \rightarrow Mn''$ is much simpler than the reduction process $MnO_4' \rightarrow Mn''$, oxidation by Mn''' might well be considerably more rapid than oxidation by MnO_4' if the conditions of concentration, etc., were at all comparable.

The oxidation of dilute hydrochloric acid which occurs when ferrous iron is oxidized by permanganate may really be brought about by manganic ions (Mn''') produced by interaction of the permanganate and ferrous iron. It is quite possible that Mn'''' ions might similarly play some part in such a process, but it is more likely that it is the Mn''' ions which are chiefly concerned. What is said below would be equally applicable to the case of Mn'''' ions. The disturbance caused by this oxidation of hydrochloric acid by Mn''' ions could be eliminated or made negligible if the oxidation potential of the Mn''' could be reduced to such an extent that it was still sufficient to oxidize Fe'' to Fe''', but not to oxidize Cl' to Cl_2. This should clearly be possible since there is a big difference in the normal potentials of the reactions $Fe''' \rightarrow Fe''$ and $\frac{1}{2}Cl_2 \rightarrow Cl'$, which are + 1·02 and + 1·694 volts respectively.

It must be remembered, when discussing these matters in terms of the normal potentials, that the conclusions reached are, as a rule, only of qualitative value since the concentrations of the several constituents concerned in the reaction or reactions under consideration are not generally known, and it has already been shown,[2] when dealing with the oxidation of I' to I_2 by cupric and ferric ions, that the course of an oxidation can be profoundly modified in several ways.

Now, addition of manganous salts, that is to say of Mn'' ions, to the reacting system where Mn''' ions are being formed

[1] See Miolati in Abegg and Auerbach's *Handbuch der anorg. Chem.*, 1913, vol. **4**, pt. 2, 804.

[2] p. 261.

as an intermediate stage in the reduction of MnO_4' to $Mn^{\cdot\cdot}$ will probably have two effects. First it would lead to some increase in the $Mn^{\cdot\cdot\cdot}$ ion concentration owing to such reactions as $MnO_4' + 4Mn^{\cdot\cdot} + 8H^{\cdot} \rightleftarrows 5Mn^{\cdot\cdot\cdot} + 4H_2O$. In view of the respective normal potentials of the reactions $MnO_4' \rightarrow Mn^{\cdot\cdot}$ ($+1{\cdot}797$ volts) and $Mn^{\cdot\cdot\cdot} \rightarrow Mn^{\cdot\cdot}$ ($+1{\cdot}827$ volts) any formation of $Mn^{\cdot\cdot\cdot}$ from MnO_4' and $Mn^{\cdot\cdot}$ would generally be small.

A second, and more important, effect of increase in the $Mn^{\cdot\cdot}$ ion concentration would be to increase the stability of the $Mn^{\cdot\cdot\cdot}$ ion and so diminish its capacity for oxidation. This effect of the $Mn^{\cdot\cdot}$ ion is allowed for in the expression for the oxidation potential of an electrode at which the reaction $Mn^{\cdot\cdot\cdot} \rightarrow Mn^{\cdot\cdot}$ is proceeding. This potential has the value $1{\cdot}827 + 0{\cdot}058 \log \frac{[Mn^{\cdot\cdot\cdot}]}{[Mn^{\cdot\cdot}]}$ volts at 17° if the normal potential is assumed to be $+1{\cdot}827$ volts.

Now the manganic ($Mn^{\cdot\cdot\cdot}$) ion, like the ferric ion, gives rise to comparatively stable complex sulphate ions, while the complex chloride ions are less stable. The more any $Mn^{\cdot\cdot\cdot}$ ions formed, either by direct reduction of MnO_4', or by interaction of MnO_4' and $Mn^{\cdot\cdot}$ were locked up in complex ions the more the oxidation potential of the $Mn^{\cdot\cdot\cdot}$ would be reduced owing to the decrease in the $Mn^{\cdot\cdot\cdot}$ ion concentration.

The manganese salt added to prevent disturbance due to hydrochloric acid in the ferrous-permanganate titration is always added as sulphate, together with a considerable amount of sulphuric acid as well. It seems not improbable, therefore, that the sulphate addition may be almost as important as the $Mn^{\cdot\cdot}$ addition, both helping to lower the oxidation potential of the change $Mn^{\cdot\cdot\cdot} \rightarrow Mn^{\cdot\cdot}$. Statements that addition of considerable amounts of sulphuric acid alone[1] or of magnesium sulphate[2] or mercuric sulphate[3] is effective in preventing the disturbance due to hydrochloric acid would seem to support this possibility.[4]

[1] Krutwig and Cocheteux, *Ber.*, 1883, **16**, 1534; see, however, Beringer, *Text Book of Assaying* (1906), p. 241.

[2] Hood, *Chem. News*, 1884, **50**, 278.

[3] Cady and Ruediger, *J. Amer. Chem. Soc.*, 1897, **19**, 575.

[4] See also Skrabal, *Z. anal. Chem.*, 1903, **42**, 359.

The actual titration in presence of hydrochloric acid, if the best conditions for accuracy are to be observed, is carried out as follows[1]:—The permanganate solution $\left(\frac{N}{10}\right)$ must be added slowly and with constant shaking. The concentration of hydrochloric acid should not exceed $\frac{N}{4}$; the volume titrated should not be greater than 200 c.c. and the weight of manganous sulphate, $MnSO_4.4H_2O$,[2] added should be not less than 2 grams. These figures refer to a titration requiring about 25 c.c. of $\frac{N}{10}$ permanganate. Under these conditions the end point is well defined.

In titrating ferrous iron with permanganate in presence of hydrochloric acid, phosphoric acid[3] is frequently added as well as manganous sulphate. Ferric iron in presence of hydrochloric acid gives rise to complex anions such as $FeCl_4'$ of rather a dark brownish yellow colour, which tends to mask the end point. Phosphoric acid removes this colour owing to formation of colourless ferri-phosphate anions. If the oxidation of hydrochloric acid during the permanganate titration is due to Mn''' ions phosphoric acid would also be effective in diminishing this action owing to formation of complex mangani-phosphate anions which would be less active than the simple Mn''' ions. As an example of the application of manganous sulphate plus phosphoric acid, the estimation of total iron in an oxide ore may be given.[4]

An amount of the ore which contains about 0·14 gram of iron is dissolved by digesting with 25 c.c. of hydrochloric acid (sp. gr. 1·1) and the solution is reduced with as little stannous chloride solution as possible. So long as any ferric salt remains the strongly acid solution has a brownish yellow colour due to $FeCl_4'$ ions, and a little more stannous

[1] Friend, *J. Chem. Soc.*, 1909, **95**, 1228.

[2] The ordinary commercial salt usually has a composition corresponding to the tetrahydrate, although that hydrate is really metastable (Cottrell, *J. Physical Chem.*, 1900, **4**, 651).

[3] Reinhardt, *Chem. Zeit.*, 1889, **13**, 323.

[4] Jones and Jeffery, *Analyst*, 1909, **34**, 306.

chloride is added than is needed to bleach the solution. 10 c.c. of saturated mercuric chloride solution are then added to oxidize any small excess of stannous chloride, followed by 10 c.c. of Reinhardt's solution. The mixture, after dilution with water to 400 c.c., is titrated very slowly with the standard permanganate solution.

The Reinhardt solution is prepared as follows:— 20 grams of manganous sulphate ($MnSO_4.4H_2O$) are dissolved in 100 c.c. of water and a cooled mixture of 40 c.c. conc. sulphuric acid and 60 c.c. of water is then added, followed by 100 c.c. of phosphoric acid (sp. gr. 1·13).

Titration of Manganese with Potassium Permanganate (Volhard's Process) [1]

Permanganate is able to oxidize manganous salts to MnO_2 owing to the fact that the normal potential $MnO_4' \rightarrow MnO_2$ is $+ 1{\cdot}907$ volts, while the normal potential $MnO_2 \rightarrow Mn^{\cdot\cdot}$ is only $+ 1{\cdot}627$ volts. These are the values of the potentials when $[H^{\cdot}] = 1$. From the equations given on page 273 it can be readily calculated that in neutral solution, where $[H^{\cdot}] = 10^{-7}$, the values for the potentials would be $+ 1{\cdot}375$ for $MnO_4' \rightarrow MnO_2$ and $+ 0{\cdot}815$ volt for $MnO_2 \rightarrow Mn^{\cdot\cdot}$. The difference between the two potentials in the neutral solution has a value twice as great as in a solution normal with respect to hydrogen ion. Evidently the oxidation of $Mn^{\cdot\cdot}$ to MnO_2 by permanganate should proceed more rapidly and readily in a neutral or only faintly acid solution.

If solutions of pure manganous sulphate are titrated with potassium permanganate it is found that the precipitated oxide does not have quite the correct composition for (hydrated) MnO_2. It contains a certain amount of MnO which varies from experiment to experiment so that it is impossible to obtain consistent results in the titrations. The precipitate must be regarded as consisting essentially either of hydrated MnO_2 mixed with a variable amount of hydrated manganese manganite (e.g. $MnO.MnO_2$), or else

[1] *Annalen*, 1879, **198**, 218.

of hydrated MnO_2 which has adsorbed a certain amount of manganous compound. The hydrated MnO_2 is a negative colloid: its coagulation is doubtless caused by the positive ions present in the solution and these will be effective in proportion to their concentrations and electro-affinity.[1] Whether carrying down of $Mn^{\cdot\cdot}$ in this way is regarded as adsorption or as due to manganese manganite formation does not matter very much; there is no sharp line of division between definite chemical compounds and adsorption complexes (see Chapter VII). To overcome the analytical difficulty due to the carrying down of $Mn^{\cdot\cdot}$ by the precipitate some other ion should be present in such concentration that the coagulation of the hydrated MnO_2 will be caused by it, and practically not at all by the manganous ion. Volhard and others have found empirically that the presence of magnesium, calcium, barium, mercuric, or, best of all, zinc salts ensures complete oxidation of manganous salts to MnO_2 by $KMnO_4$ in weak acid solutions.

The reaction between $KMnO_4$ and $MnSO_4$ is represented by the molecular equation:—

$$2KMnO_4 + 3MnSO_4 + 2H_2O = K_2SO_4 + 2H_2SO_4 + 5MnO_2$$

and the ratio $2KMnO_4 : 3MnSO_4$ must be borne in mind when making calculations. Permanganate solution which is to be used for this estimation is best standardized as follows against manganese sulphate (not against iron or oxalic acid). To 20 c.c. of $\frac{N}{10}$ manganese sulphate solution[2] in a conical flask 40 c.c. of zinc sulphate solution (containing 200 grams per litre) are added; the liquid is then diluted to 200 c.c. and heated nearly to boiling; the potassium permanganate solution is run in slowly, with continuous shaking, until

[1] It always contains some potassium as well as manganous compound.

[2] Using $\frac{N}{10}$ $KMnO_4$ solution as ordinarily defined, that is one containing $\frac{1}{50}$ grm. mol. $KMnO_4$ per litre, an $\frac{N}{10}$ solution of $MnSO_4$ will contain $\frac{3}{100}$ grm. mol. $MnSO_4$ (= 4·53 grms. anhydrous $MnSO_4$). Volume for volume these two solutions will be equivalent from the point of view of the present reaction.

the liquid above the precipitate remains of a faint pink colour. The solution should not be boiled, for precipitated MnO_2 slowly catalyses the decomposition of permanganate with liberation of oxygen, and this occurs more readily the higher the temperature. Owing to the presence of the precipitated MnO_2, which does not settle very well and obscures the colour, the titration must be carried out cautiously. Towards the end of the titration the precipitate should be allowed to settle sufficiently after each addition to show whether or not the liquid is coloured pink; this is best determined by observing the upper edges of the liquid against a white background. If the pink colour fades, more permanganate is added.

If a manganous chloride solution is to be estimated, this must first be evaporated with sulphuric acid until all the hydrochloric acid is expelled. After the evaporation the residue is diluted with water, nearly neutralized with sodium carbonate, and finally with a small excess of an emulsion of zinc oxide.[1] Zinc sulphate solution is then added, and the titration is carried out as described above.

In presence of iron, even in the ferric condition, the reaction between manganous salts and permanganate does not proceed quantitatively according to the equation given above. Iron must, therefore, be removed—after conversion into the ferric form if necessary. The solution is nearly neutralized with sodium carbonate, then treated with a small excess of the zinc oxide emulsion. This precipitates all the iron as ferric hydroxide, which is filtered off along with the excess of zinc oxide. The manganese in the filtrate is then titrated as above.

[1] This is best prepared by treating zinc oxide with insufficient hydrochloric acid to dissolve it completely, warming the mixture with a little bromine (to oxidize and precipitate any dissolved iron or manganese), filtering, and precipitating with ammonia (not excess, of course). The precipitated hydroxide is washed several times by decantation with hot water, and then rinsed into a bottle and kept for use as above.

Estimation of Oxalic Acid by means of Potassium Permanganate

Potassium permanganate oxidizes oxalic acid to carbon dioxide according to the equations—

$$\begin{cases} 2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O \\ 2MnO_4' + 5H_2C_2O_4 + 6H^{\cdot} = 2Mn^{\cdot\cdot} + 10CO_2 + 8H_2O. \end{cases}$$

The second equation could also be written—

$$2MnO_4' + 5C_2O_4'' + 16H^{\cdot} = 2Mn^{\cdot\cdot} + 10CO_2 + 8H_2O$$

and the oxidation of the oxalic acid may be regarded as dependent on the tendency of the C_2O_4'' ion to be oxidized to CO_2. This would be measured by the normal potential of the oxalic acid-carbon dioxide electrode, which is very uncertain, though, according to Schaper,[1] $E_{CO_2 \rightarrow C_2O_4''}$ has a value of about $+ 0{\cdot}18$ volt on the absolute scale (CO_2 pressure = 1 atmosphere, oxalate concentration = 1 gram mol. per litre).

It is evident that potassium permanganate should oxidize oxalic acid far more readily than it does ferrous iron. This is not the case, however, and for this reason oxalic acid is always titrated in hot (about 70°) solution in order to hasten the reaction. The difference in the rate of oxidation may be connected with the fact that while in the case of $Fe^{\cdot\cdot}$ ion merely the loss of one electron is involved, a considerable electronic readjustment is probably required when the C_2O_4'' ion is converted into $2CO_2$.

The rate of oxidation of oxalic acid by the permanganate is greatly accelerated by the presence of manganous ions. It is generally found during a titration that the first drops of permanganate solution are not decolorized until after an appreciable time, which is greater the lower the temperature. Once the reaction has started, however, it proceeds promptly enough to its conclusion. If some manganous salt is added to start with, then the first drop of permanganate is at once decolorized. After addition of manganous sulphate the whole titration can in fact be carried out at the ordinary temperature.

[1] *Z. physikal. Chem.*, 1910, **72**, 308.

There is no particular advantage in this, however, and the time required for the titration is longer than when titrating the warm solution, as is customary. The kinetics of the reaction have been studied by Harcourt and Esson [1] and others,[2] and it seems certain that the accelerating effect of the $Mn^{\cdot\cdot}$ ion is due to its being converted rapidly by the $KMnO_4$ into some higher stage of oxidation such as $Mn^{\cdot\cdot\cdot}$, which is able to oxidize the oxalic acid more rapidly than can the MnO_4'. Manganic oxalate complexes appear to play some part in the process.

The actual titration of oxalic acid by potassium permanganate is simple enough. An amount of oxalic acid or oxalate equivalent to about 25 c.c. $\frac{N}{10}$ permanganate is dissolved in water or dilute sulphuric acid, 10 c.c. of dilute sulphuric acid (1 : 4) are added, and the mixture is diluted to about 100 c.c. The solution is heated to about 70° and titrated with the standard permanganate. To start with, the solution remains red for several seconds, but it shortly becomes colourless, and the further permanganate added is at once decolorized until all the oxalic acid has been oxidized. According to Bruhns [3] finely crystalline oxalic acid is the best substance to use for standardizing permanganate solutions.

Estimation of Nitrite by means of Potassium Permanganate

When properly carried out this is an excellent method for determining nitrite. The oxidation of nitrous acid to nitric acid is another reaction which proceeds only slowly at the ordinary temperature, and for this reason the titration has to be carried out in warm solutions. Since, however, nitrous acid is volatile it is necessary to add the nitrite solution from the burette to the acid solution of potassium permanganate,

[1] *Phil. Trans.*, 1866, **156**, 193.

[2] Ehrenfeld, *Z. anorg. Chem.*, 1903, **33**, 117; Luther and Schilow, *Z. physikal. Chem.*, 1903, **46**, 790; Schilow, *Ber.*, 1903, **36**, 2735; Skrabal, *Z. anorg. Chem.*, 1904, **42**, 1.

[3] *Chem. Zeit.*, 1923, **47**, 613.

$\frac{N}{10}$ or $\frac{N}{2}$, according to circumstances, heated to a temperature of about 40°. Even at this temperature the oxidation proceeds comparatively slowly, especially towards the end of the titration, which, therefore, must not be hurried unduly. A higher temperature and the use of too strong solutions are not advisable, as hydrated manganese dioxide is apt to separate under such conditions. The separation gives trouble, though it does not prevent the titration being carried to completion, the dioxide going into solution again before the end of the titration. The nitrite solution run in from the burette may be an aqueous solution of a soluble nitrite (e.g. sodium nitrite), the " nitrous vitriol " from the Gay-Lussac tower of a sulphuric acid works, or " mixed acid " ($H_2SO_4 + HNO_3$) used for preparing nitro-organic compounds, which generally contains small amounts of nitrous acid. Even a strongly ammoniacal solution can be run in from the burette, as may be necessary in certain cases to retain copper, zinc, etc., in solution.

When the nitrous acid content of " nitrous vitriol " or " mixed acid " is being determined, the strong acid must be run from the burette into the permanganate solution with some care, and it may be necessary even to cool the permanganate in order to keep the temperature at about 40°. No additional acid is required in this case. If an ammoniacal solution or one of sodium nitrite is being analysed, sulphuric acid must be added to the permanganate solution in such amount as to ensure a considerable excess at the end of the titration.

The Reaction between Hydrogen Peroxide and Potassium Permanganate [1]

Potassium permanganate and hydrogen peroxide react readily in presence of sulphuric acid. Oxygen is liberated and the permanganate is reduced to manganous salt in accordance with the molecular equation—

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O$$

[1] See Abegg and Auerbach's *Handbuch der anorg. Chem.*, 1908, vol. **2**, pt. **1**, 90–100.

which simplifies to the ionic equation—

$$2MnO_4' + 6H^{\cdot} + 5H_2O_2 = 2Mn^{\cdot\cdot} + 5O_2 + 8H_2O$$

It is usually considered that hydrogen peroxide is a strong oxidizing agent, and that in the above reaction half the oxygen comes from the hydrogen peroxide and half from the potassium permanganate. As a matter of fact both of these views are probably erroneous.

In dilute solution hydrogen peroxide behaves rather as a reducing agent than as an oxidizing agent; it is frequently a strong oxidizing agent in concentrated solutions, but only exceptionally so in weak ones.

A cell constructed on the plan :—$Pt/H_2/2N\ H_2SO_4$[1]$/O_2/Pt$, the hydrogen and oxygen being at a pressure of 760 mm., shows a difference of potential of 1·23 volts between the two electrodes. This value is the normal potential of the oxygen electrode, that is to say, of the change $O_2 \rightarrow H_2O$ in acid solution where $[H^{\cdot}] = 1$, if the hydrogen electrode is taken as zero. On the absolute scale this becomes + 1·507 volts. If now sufficient hydrogen peroxide is added to the electrolyte surrounding the oxygen electrode to make it normal (molar) with respect to H_2O_2 then the difference of potential between the two electrodes sinks to about 0·8 volts.[2] Consequently, + 0·8 volt on the hydrogen scale, or + 1·077 volt on the absolute scale is the normal potential of the H_2O_2 electrode at which the change $H_2O_2 \rightarrow O_2 + H_2$ occurs. This potential is below the normal potential of many common oxidizing agents, including oxygen at atmospheric pressure, which are consequently able to oxidize hydrogen peroxide to water and oxygen. The value + 1·077 volts is therefore called the reduction potential of hydrogen peroxide, since it is the potential with which it acts when behaving as a reducing agent.

It is possible to calculate the normal potential of an electrode at which the change $2H_2O_2 = 2H_2O + O_2$ occurs, although it cannot be measured directly. Its value is found to be + 1·937 volts, and this is the oxidation potential of hydrogen

[1] $2NH_2SO_4$ is approximately normal with respect to hydrogen ion.

[2] Haber, *Z. Elektrochem.*, 1901, **7**, 444.

peroxide. The high value indicates that when hydrogen peroxide does act as an oxidizing agent it is a very strong one—stronger than oxygen at atmospheric pressure.

It is clear that whether H_2O_2 is supposed to act with its reducing potential or its oxidizing potential it will be unstable with reference to oxygen and tend to break up into water and oxygen. In the one case this would be due to the H_2O_2 reducing oxygen to oxygen ions (or water)—

$$\underset{(O'' + 2H^{\cdot})}{O + H_2O_2} \longrightarrow OH_2 + O_2$$

while in the second case it would be due to the H_2O_2 oxidizing oxygen ions, or water, to oxygen—

$$H_2O + \underset{(2H^{\cdot} + O'')}{O + H_2O} \longrightarrow H_2O + OH_2 + O.$$

It is well known that H_2O_2 does break up slowly into water and oxygen.

The reaction between potassium permanganate and hydrogen peroxide depends on the fact that the oxidation potential of the process $MnO_4' \rightarrow Mn^{\cdot\cdot}$ is greater than the reduction potential of the process $H_2O_2 \rightarrow H_2 + O_2$.

If the reaction is imagined to occur in a cell of the form

$$\text{Pt} \left| \begin{matrix} KMnO_4 \\ H_2SO_4 \end{matrix} \right| \begin{matrix} H_2O_2 \\ H_2SO_4 \end{matrix} \left| \text{Pt} \right.$$

formed by connecting a permanganate electrode with a hydrogen peroxide electrode, then on connecting the two terminals electrons will flow along the connecting wire from the hydrogen peroxide electrode (the cathode) to the permanganate electrode (the anode) and the reactions occurring at the two electrodes will be—

$$MnO_4' + 8H^{\cdot} + 5\ominus = Mn^{\cdot\cdot} + 4H_2O.$$

$$H_2O_2 - 2\ominus = O_2 + 2H^{\cdot}.$$

According to this view of the matter the oxygen evolved is all derived from the hydrogen peroxide.

The reaction between $KMnO_4$ and H_2O_2 frequently does not start for quite a long time although on addition of some

manganous sulphate it begins at once and proceeds rapidly. This catalytic action of manganous salt, already noted in connexion with the reaction between $KMnO_4$ and oxalic acid, is even more marked with the H_2O_2 reaction, but the explanation would appear to be much the same in the two cases. Some higher stage of oxidation such as $Mn^{\cdot\cdot\cdot}$ is produced by the action of MnO_4' on $Mn^{\cdot\cdot}$, and the reaction between $Mn^{\cdot\cdot\cdot}$ and H_2O_2 proceeds more rapidly than that between MnO_4' and H_2O_2.

Estimation of Hydrogen Peroxide by means of Potassium Permanganate

An amount of the peroxide solution equivalent to about 25 c.c. $\frac{N}{10}$ permanganate is placed in a flask or beaker. It is diluted with water to about 100 c.c., about 25 c.c. of sulphuric acid (1 : 4) are added and $\frac{N}{10}$ permanganate is run in from the burette. It often happens that the first drop of permanganate produces a pink coloration which does not disappear, owing to the fact that the reaction with permanganate will not start until some $Mn^{\cdot\cdot}$ ion is present. In this event addition of a drop of manganous sulphate solution will at once start the reaction, which will then proceed smoothly to the end of the titration.

Catalysis

In dealing with potassium permanganate titrations several instances of catalytic effects have been mentioned.

As is well known, catalysis is the term employed to describe the acceleration of a chemical change (or more rarely a retardation) brought about by some substance which appears to take no part itself in the change which it accelerates (or retards). Substances producing such effects are called catalysts and they may act either in a homogeneous system or a heterogeneous one. The most varied substances can function as catalysts, but those which can act as catalysts for any given reaction in a homogeneous system are generally few in number; the action is highly specific.

When a catalyst acts in a heterogeneous system—for example, a solid catalyst accelerating a reaction between gases or between substances in solution—there is a specific effect, as a rule, but the substances capable of functioning as catalysts for any given reaction, are generally numerous. The subject of catalysts is one of great interest and difficulty, but also of great practical importance. A useful historical account of the large amount of experimental work which had been carried out in connexion with it up to 1918 will be found in Rideal and Taylor's *Catalysis in Theory and Practice.* Since that date numerous papers on the subject have been published by E. F. Armstrong, E. K. Rideal, H. S. Taylor, and others.

It is not often, perhaps, that catalytic effects play any very important part either in gravimetric or ordinary volumetric analysis. Such effects, however, are encountered, and in the case of the permanganate titrations they are so striking that they can hardly be missed.

The accelerating action of manganous salt (or $Mn^{\cdot\cdot}$ ion) on the reactions between potassium permanganate and oxalic acid or hydrogen peroxide is a good instance of catalysis in homogeneous systems. The action of manganous sulphate in preventing or delaying the oxidation of hydrochloric acid by permanganate can be regarded as an instance of negative catalysis.

Since the oxidation potential $MnO_4' \rightarrow MnO_2$ is so much greater than that of oxygen it is clear that potassium permanganate is really unstable and should give off oxygen. In the absence of a catalyst the decomposition either does not occur or does so only with excessive slowness. Hydrated MnO_2, however, is quite an effective catalyst for the decomposition, and for that reason should be excluded as far as possible from standard solutions of potassium permanganate. This is a good instance of catalysis in a heterogeneous system.

Titrations with Potassium Dichromate

Potassium dichromate in acid solution is a strong oxidizing agent, but it is considerably weaker than potassium permanganate under similar conditions. Owing to some

doubt about the precise nature of chromic acid solutions (proportion of CrO_4'', Cr_2O_7'', H_2CrO_4, etc., present) and to the difficulty of getting reversible electrodes, it is not certain what is the precise value of its normal oxidation potential.

According to Luther [1] the following are the approximate values of the normal potentials of the oxidation changes of chromium indicated :—

$$CrO_4'' \rightarrow Cr''' \quad + 1{\cdot}8 \text{ volts.}$$
$$Cr''' \rightarrow Cr'' \quad - 0{\cdot}1 \text{ volts.}$$

Two points are to be noted here. In the first place, the change $Cr''' \rightarrow Cr''$ requires a very strong reducing agent to bring it about so that under all ordinary circumstances when acid dichromate solutions are reduced the reduction does not proceed further than the Cr''' stage. In the second place the normal potential of the change $CrO_4'' \rightarrow Cr'''$ is not much greater than that of the change $\frac{1}{2}Cl_2 \rightarrow Cl'$. It is even possible that the normal potential of the change $CrO_4'' \rightarrow Cr'''$ is as low as $+ 1{\cdot}6$ volts and actually less than that of the change $\frac{1}{2}Cl_2 \rightarrow Cl'$. As a result of this, chromic acid does not oxidize chlorine ions to chlorine except in strong solutions or at high temperatures.

On the other hand, chromic acid readily oxidizes ferrous iron to ferric. Potassium dichromate is important in analytical chemistry, mainly because of its sluggishness towards hydrochloric acid, for this enables ferrous iron to be readily titrated in presence of considerable amounts of hydrochloric acid. This is of some consequence since hydrochloric acid is the only satisfactory solvent for ferric oxide and many technically important substances containing iron. Such solutions can be readily reduced and the total iron estimated by titration with standard potassium dichromate solution. From the figures given, the normal potentials of the changes $MnO'_4 \rightarrow Mn''$ and $CrO_4'' \rightarrow Cr'''$ appear to be very similar. In the case of the reduction of dichromate, however, there is no possibility of intermediate stages with very high oxidation potentials causing complications. When permanganate is reduced to Mn'' it is probable

[1] *Z. physikal. Chem.*, 1901, **36**, 385.

that $Mn^{\cdots}$ is always formed first. The difference in the behaviour of dichromate and permanganate towards hydrochloric acid is in all probability due chiefly to this.

The titration of ferrous solutions with potassium dichromate suffers from the one drawback, that owing to the green colour of the chromic salt formed by reduction the end point of the titration is not directly visible. The procedure adopted, therefore, is to remove occasionally a drop of the solution being titrated and to test it for the presence of ferrous iron with a drop of potassium ferricyanide solution. So long as any unoxidized ferrous iron remains, a blue coloration is obtained on mixing the drops, owing to formation of Turnbull's blue. When there is much ferrous iron this is easily seen, but towards the end of the titration the blue with the yellow of the ferricyanide solution causes the mixed drops to appear merely green and this is most clearly visible against a white background at the points where the two drops slowly mix. As soon as no trace of green is visible on mixing, the reaction is to be taken as finished. In order not to have too deep a yellow colour, due to the ferricyanide, which would make it difficult to see the end point with accuracy, the solution of ferricyanide used for the tests should not be stronger than 2 per cent. It must also be absolutely free from ferrocyanide, which would of course give a blue colour with the ferric salt, and must therefore be freshly prepared, since on exposure to light it undergoes decomposition with formation of ferrocyanide.

Ferricyanide (the normal potential of the change $Fe(CN)_6^{\cdots} \rightarrow Fe(CN)_6^{\cdots\cdot}$ is $+ 0{\cdot}677$ volt) is slowly reduced to ferrocyanide by dust which may be present in small amount on the surface of the potassium ferricyanide crystals. To avoid this possible source of disturbance it is best to wash the crystals two or three times with a little cold water just before dissolving them to make the test solution.

Titration of Ferrous Iron with Potassium Dichromate

The reaction proceeds according to the molecular equation

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O.$$

A decinormal solution of potassium dichromate, prepared by direct weighing, is the most suitable one to employ as a rule. The salt used for the purpose is purified by recrystallizing the best commercial salt from water, the solution being stirred during crystallization, so that only small crystals form. The fine crystals are well drained on the water pump, dried in a dish on the water bath, and finally to constant weight in an air oven at about 130°.

The acid solution of the ferrous salt, containing from 0·1 to 0·15 gram of iron in 100 c.c., is placed in a beaker, and the standard dichromate solution run in from the burette until no trace of green colour is given with the ferricyanide indicator used in the manner already described. A second titration is carried out in a similar way, but the ferricyanide tests are not started until as much dichromate solution has been added as was used in the first titration. Only two or three tests with ferricyanide will then be required before the end point is reached, and the error caused by removal of the solution will be negligible. The first titration is inaccurate owing to the large number of drops which have to be removed for testing.

The method requires a little more practice than the titration with potassium permanganate, but when carried out properly gives excellent results. The presence of suspended matter in the liquid being titrated does not interfere with the end point of the dichromate titration, though it is apt to affect that of the permanganate titration.

Standardization of Sodium Thiosulphate Solutions with Potassium Dichromate

Potassium dichromate is an excellent substance to use for standardizing sodium thiosulphate solutions. Either 25 c.c. of $\frac{N}{10}$ potassium dichromate solution, or an equivalent amount of the pure solid, is placed in a beaker and treated with 3 grams of potassium iodide dissolved in a little water, and then 5 c.c. of hydrochloric acid (1 : 5). The mixture is diluted to about 400 c.c. with water and the liberated

iodine is titrated with the sodium thiosulphate solution, some starch paste being added as usual towards the end. The end point is shown by a sudden change from blue to light green, which is quite sharp when the mixture is diluted sufficiently before titrating.

Titration of Antimony with Standard Sodium Bromate Solution

Sodium bromate in acid solution oxidizes antimonious salts to antimonic in accordance with the molecular equation—

$$NaBrO_3 + 3SbCl_3 + 6HCl = NaBr + 3SbCl_5 + 3H_2O$$

The normal potential for the change $BrO_3' \rightarrow Br'$ is $+ 1{\cdot}697$ volt,[1] which shows that an acid bromate solution is a strong oxidizing agent. It acts comparatively slowly, however, because of the complex series of stages followed by the reduction, but in hot acid solution the above reaction proceeds smoothly and quantitatively, and forms the basis of one of the best and quickest methods for estimating antimony.[2] It is particularly valuable because it is available in presence of tin. The applicability of the reaction as a volumetric process depends upon the ingenious method used for determining the end point. A small amount of methyl orange is added towards the end of the titration. The pink colour due to this persists until all the antimony has been oxidized. The methyl orange is then itself oxidized to colourless products so that the end point is given by the disappearance of the pink colour.

Either sodium or potassium bromate can be used for the titration, but the former is preferable as the commercial product is practically pure. A decinormal solution is made by weighing, but should be standardized against the purest commercial antimony (the so-called "star" metal), which should contain not less than 99·6 per cent antimony, with arsenic and lead as the chief impurities, and traces of iron, copper, and sulphur.

[1] See Abegg and Auerbach, *Handbuch der anorg. Chem.*, 1913, vol. **4**, pt. 2, 300–4.

[2] Originally due to Györy, *Z. anal. Chem.*, 1893, **32**, 415: modified by others, especially Rowell, *J. Soc. Chem. Ind.*, 1906, **25**, 1181.

In addition to the bromate solution there are required a 0·1 per cent solution of methyl orange (sodium salt) and a saturated solution of bromine in concentrated hydrochloric acid.

The standardization of the bromate solution is carried out as follows. The same procedure as regards the titration is followed in the actual determination of antimony, though the method of solution of the material may differ somewhat according to its nature.

Finely powdered (agate mortar) metal—0·3 gram—is weighed out into a tall glass beaker of 250 c.c. capacity, about 10 c.c. of the bromine + HCl solution are added, and then a few small pieces of pumice or similar material. The beaker is covered with a watch glass and the contents are boiled till the excess of bromine is removed, by which time all metal will be in solution. After cooling and, if necessary, adding a little more conc. HCl, about 2 grams of pure crystalline sodium sulphite are added, and the solution again heated to boiling and evaporated until NaCl shows signs of crystallizing. Heating is then stopped and the cover and sides of beaker are washed with conc. HCl, which is added until the volume of liquid is about 20 c.c. After diluting the mixture to about 75 c.c. with boiling distilled water, it is boiled and about 40 c.c. bromate solution are run in, in a slow stream, with constant stirring. About 5 c.c. more of the bromate solution are added to the boiling mixture, and then 4 drops of methyl orange solution. Bromate solution is then run in drop by drop till the pink colour vanishes, which happens at the end point.

The method gives excellent results, and burette readings can be made to agree within one drop (= less than 0·1 per cent error). The quantities of reagents used should be of the order indicated, and the final volume (after titration) should not exceed 150 c.c. The critical point is in the evaporation after adding sulphite, at which stage SO_2 must be removed entirely. Any arsenic present is also volatilized, being in the arsenious condition. The presence of either compound gives erroneous results, but both sources of error are entirely avoided by evaporation to incipient crystalliza-

tion. Crystalline NaCl is precipitated when excess of HCl is added, but immediately dissolves on adding water.

The methyl orange solution should be treated as a volumetric solution, i.e. should be of exact strength and free from undissolved sediment. It should be delivered from a small pipette of such size that the drops are as nearly equal to the drops from the burette as possible, i.e. tips should be of equal cross section.

Under these conditions 4 drops of 0·1 per cent methyl orange solution in acid solution are exactly decolorized by 1 drop bromate solution ; in fact, with care, a very fine back titration can be made.

The end point is quite sharp and gives a marked colour change. If the methyl orange is added too soon the colour rapidly fades, as the bromate is added, from deep pink to quite pale pink, but even then the sudden disappearance of the pink colour is quite noticeable. This fading is observed particularly when appreciable quantities of iron are present, in which case it is best to carry out a second titration on a fresh amount of metal and run in the bromate to within 0·5 c.c. of the end point before adding the methyl orange. In all cases the titration must be made with the solution at, or nearly at, its boiling point.

The process works well in the presence of lead, zinc, tin, silver, and sulphuric acid, none of which affect the sulphurous acid. Stannic salts are not reduced by sulphurous acid, that is why tin does not interfere ; a stannous solution would, of course, be oxidized by the bromate. Copper and iron, if not present in the substance being analysed to a greater extent than one and five per cent respectively, do not appreciably affect the results, for neither cupric nor ferric salts are appreciably reduced by sulphurous acid under the conditions of the experiment. Very few $Cu^{..}$ or $Fe^{...}$ ions are present, since nearly all the copper and iron are in the form of complex chloride anions, and these are relatively stable in presence of the large amount of hydrochloric acid. Slight reduction does occur, however, and a small amount of bromate solution is consumed by the cuprous and ferrous compounds formed. This has the effect of raising the apparent

antimony content of the substance under examination. According to Rowell,[1] for every 0·1 per cent of copper in the sample up to 1 per cent, 0·012 per cent of antimony should be subtracted from the result given by the titration. He also states that 1 per cent of iron raises the apparent antimony content by 0·02 per cent, while 5 per cent of iron has very little more effect.

Most of the oxidation potentials to which reference has been made in the present chapter have been collected into the following table for the purpose of ready comparison. The values given are the "normal potentials" in volts on the absolute scale at temperatures in the neighbourhood of 20°.

NORMAL POTENTIALS OF OXIDIZING AGENTS

Reaction	Normal potential volts.	Remarks
$\frac{1}{2}Cl_2 \rightarrow Cl'$	+ 1·694	Chlorine at 760 mm. pressure.
$\frac{1}{2}I_2 \rightarrow I'$	+ 0·903	Normal iodine sol. 25°.
$\frac{1}{2}I_2 \rightarrow I'$	+ 0·813	Solution saturated with iodine at 25°.
$IO_3' \rightarrow \frac{1}{2}I_2$	+ 1·467	Solution sat. with iodine.
$BrO_3' \rightarrow Br'O$	+ 1·697	
$2H_2O_2 \rightarrow 2H_2O + O_2$	+ 1·937	So-called "oxidation potential" of H_2O_2.
$H_2O_2 \rightarrow H_2 + O_2$	+ 1·077	So-called "reduction potential" of H_2O_2.
$\frac{1}{2}O_2 \rightarrow H_2O$	+ 1·507	$[H^{\cdot}] = 1$.
$\frac{1}{2}O_2 \rightarrow OH'$	+ 0·687	$[OH'] = 1$.
$AsO_4''' \quad AsO_3'''$	+ 0·85	$[H^{\cdot}] = 1$.
$Fe(CN)_6'''' \rightarrow Fe(CN)_6''''$	+ 0·677	
$Sn'''' \rightarrow Sn''$	+ 0·27	
$Cu'' \rightarrow Cu'$	+ 0·481	
$Fe''' \rightarrow Fe''$	+ 1·02	
$MnO_4' \rightarrow MnO_2$	+ 1·907	$[H^{\cdot}] = 1$. Sol. sat. with MnO_2.
$MnO_4' \rightarrow Mn''$	+ 1·797	$[H^{\cdot}] = 1$.
$MnO_2 \rightarrow Mn''$	+ 1·627	$[H^{\cdot}] = 1$. Sol. sat. with MnO_2.
$MnO_4' \rightarrow MnO_4''$	+ 0·887	$[OH'] = 1$.
$MnO_4' \rightarrow MnO_2$	+ 0·797	$[OH'] = 1$. Sol. sat. with MnO_2.
$MnO_4'' \rightarrow MnO_2$	+ 0·777	$[OH'] = 1$. Sol. sat. with MnO_2.
$Mn'''' \rightarrow Mn'''$	+ 1·927	
$Mn''' \rightarrow Mn''$	+ 1·827	
$CrO_4'' \rightarrow Cr'''$	about + 1·8	
$Cr''' \rightarrow Cr''$	about − 0·1	
$CO_2 \rightarrow C_2O_4''$	about + 0·18	

[1] *Loc. cit.*

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