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# CHAPTER 11

## GRAVIMETRY

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### 11.1 INTRODUCTION TO GRAVIMETRIC ANALYSIS

Gravimetric analysis or quantitative analysis by weight is the process of isolating and weighing an element or a definite compound of the element in as pure a form as possible. The element or compound is separated from a weighed portion of the substance being examined. A large proportion of the determinations in gravimetric analysis is concerned with the transformation of the element or radical to be determined into a pure stable compound which can be readily converted into a form suitable for weighing. The weight of the element or radical may then be readily calculated from a knowledge of the formula of the compound and the relative atomic masses of the constituent elements.

The separation of the element or of the compound containing it may be effected in a number of ways, the most important of which are: (a) precipitation methods; (b) volatilisation or evolution methods; (c) electroanalytical methods; and (d) extraction and chromatographic methods. Only (a) and (b) will be discussed in this chapter: (c) is considered in Part E, and (d) in Part C.

It is appropriate to mention at this stage the reasons for the continuing use of gravimetric analysis despite the disadvantage that it is generally somewhat time-consuming. The advantages offered by gravimetric analysis are:

- (a) it is accurate and precise when using modern analytical balances;
- (b) possible sources of error are readily checked, since filtrates can be tested for completeness of precipitation and precipitates may be examined for the presence of impurities;
- (c) it has the important advantage of being an absolute method, i.e. one involving direct measurement without any form of calibration being required;
- (d) determinations can be carried out with relatively inexpensive apparatus, the most expensive requirements being a muffle furnace and, in some cases, platinum crucibles.

Two general applications of gravimetric analysis are:

- (a) the analysis of standards which are to be used for the testing and/or calibration of instrumental techniques;
- (b) analyses requiring high accuracy, although the time-consuming nature of gravimetry limits this application to small numbers of determinations.

## 11.2 PRECIPITATION METHODS

These are perhaps the most important with which we are concerned in gravimetric analysis. The constituent being determined is precipitated from solution in a form which is so slightly soluble that no appreciable loss occurs when the precipitate is separated by filtration and weighed. Thus, in the determination of silver, a solution of the substance is treated with an excess of sodium chloride or potassium chloride solution, the precipitate is filtered off, well washed to remove soluble salts, dried at 130–150 °C, and weighed as silver chloride. Frequently the constituent being determined is weighed in a form other than that in which it was precipitated. Thus magnesium is precipitated, as ammonium magnesium phosphate  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , but is weighed, after ignition, as the pyrophosphate  $\text{Mg}_2\text{P}_2\text{O}_7$ . The following factors determine a successful analysis by precipitation.

1. The precipitate must be so insoluble that no appreciable loss occurs when it is collected by filtration. In practice this usually means that the quantity remaining in solution does not exceed the minimum detectable by the ordinary analytical balance, viz. 0.1 mg.
2. The physical nature of the precipitate must be such that it can be readily separated from the solution by filtration, and can be washed free of soluble impurities. These conditions require that the particles are of such size that they do not pass through the filtering medium, and that the particle size is unaffected (or, at least, not diminished) by the washing process.
3. The precipitate must be convertible into a pure substance of definite chemical composition; this may be effected either by ignition or by a simple chemical operation, such as evaporation, with a suitable liquid.

Factor 1, which is concerned with the completeness of precipitation, has already been dealt with in connection with the solubility-product principle, and the influence upon the solubility of the precipitate of (i) a salt with a common ion, (ii) salts with no common ion, (iii) acids and bases, and (iv) temperature (Sections 2.6–2.11).

It was assumed throughout that the compound which separated out from the solution was chemically pure, but this is not always the case. The purity of the precipitate depends *inter alia* upon the substances present in solution both before and after the addition of the reagent, and also upon the exact experimental conditions of precipitation. In order to understand the influence of these and other factors, it will be necessary to give a short account of the properties of colloids.

Problems which arise with certain precipitates include the coagulation or flocculation of a colloidal dispersion of a finely divided solid to permit its filtration and to prevent its re-peptisation upon washing the precipitate. It is therefore desirable to understand the basic principles of the colloid chemistry of precipitates, for which an appropriate textbook should be consulted (see the Bibliography, Section 11.80). However, some aspects of the colloidal state relevant to quantitative analysis are indicated below.

## 11.3 THE COLLOIDAL STATE

The colloidal state of matter is distinguished by a certain range of particle size, as a consequence of which certain characteristic properties become apparent.

Before discussing these, mention must be made of the various units which are employed in expressing small dimensions. The most important of these are:

$$1 \mu\text{m} = 10^{-3} \text{ mm}; \quad 1 \text{ nm} = 10^{-6} \text{ mm};$$

$$1 \text{ \AA} = 10^{-10} \text{ metre} = 10^{-7} \text{ mm} = 0.1 \text{ nm}.$$

Colloidal properties are, in general, exhibited by substances of particle size ranging between  $0.1 \mu\text{m}$  and  $1 \text{ nm}$ . Ordinary quantitative filter paper will retain particles down to a diameter of about  $10^{-2} \text{ mm}$  or  $10 \mu\text{m}$ , so that colloidal solutions in this respect behave like true solutions and are not filterable (size of molecules is of the order of  $0.1 \text{ nm}$  or  $10^{-8} \text{ cm}$ ). The limit of vision under the microscope is about  $0.2 \mu\text{m}$ . If a powerful beam of light is passed through a colloidal solution and the solution viewed at right angles to the incident light, a scattering of light is observed. This is the so-called **Tyndall effect**, which is not exhibited by true solutions.

An important consequence of the smallness of the size of colloidal particles is that the ratio of surface area to weight is extremely large. Phenomena, such as adsorption, which depend upon the size of the surface will therefore play an important part with substances in the colloidal state.

For convenience, colloids are divided into two main groups, designated as **lyophobic** and **lyophilic colloids**. The chief properties of each class are summarised in Table 11.1, although it must be emphasised that the distinction is not an absolute one, since some gelatinous precipitates (e.g. aluminium hydroxide and other metallic hydroxides) have properties intermediate between those of lyophobic and lyophilic colloids.

**Table 11.1**

Lyophobic colloids	Lyophilic colloids
(1) The dispersion (or sols) are only slightly viscous. Examples: sols of metals, silver halides, metallic sulphides, etc.	(1) The dispersions are very viscous; they set to jelly-like masses known as gels. Examples: sols of silicic acid, tin(IV) oxide, gelatin.
(2) A comparatively minute concentration of an electrolyte results in flocculation. The change is, in general, irreversible; water has no effect upon the flocculated solid.	(2) Comparatively large concentrations of electrolytes are required to cause precipitation ('salting out'). The change is, in general, reversible, and reversal is effected by the addition of a solvent (water).
(3) Lyophobic colloids, ordinarily, have an electric charge of definite sign, which can be changed only by special methods.	(3) Most lyophilic colloids change their charge readily, e.g. they are positively charged in an acid medium and negatively charged in an alkaline medium.
(4) The ultra-microscope reveals bright particles in vigorous motion (Brownian movement).	(4) Only a diffuse light cone is exhibited under the ultra-microscope.

The process of dispersing a gel or a flocculated solid to form a sol is called **peptisation**, and is briefly dealt with on page 421 and in Section 11.8.

The stability of lyophobic colloids is intimately associated with the electrical charge on the particles.\* Thus in the formation of an arsenic(III) sulphide sol

\* Lyophilic colloids are mainly stabilised by solvation.

by precipitation with hydrogen sulphide in acid solution, sulphide ions are primarily adsorbed (since every precipitate has a tendency to adsorb its own ions), and some hydrogen ions are secondarily adsorbed. The hydrogen ions or other ions which are secondarily adsorbed have been termed 'counter-ions'. Thus the so-called electrical double layer is set up between the particles and the solution. An arsenic(III) sulphide particle is represented diagrammatically in Fig. 11.1. The colloidal particle of arsenic(III) sulphide has a negatively charged surface, with positively charged counter-ions which impart a positive charge to the liquid immediately surrounding it. If an electric current is passed through the solution, the negative particles will move towards the anode; the speed is comparable with that of electrolytic ions. The electrical conductivity of a sol is, however, quite low because the number of current-carrying particles is small compared with that in a solution of an electrolyte at an appreciable concentration; the large charge carried by the colloidal particles is not sufficient to compensate for their smaller number.

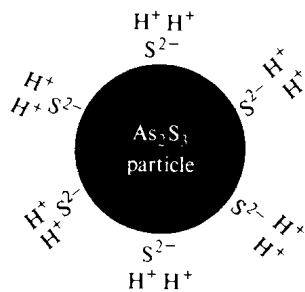


Fig. 11.1

If the electrical double layer is destroyed, the sol is no longer stable, and the particles will flocculate, thereby reducing the large surface area. Thus if barium chloride solution is added, barium ions are preferentially adsorbed by the particles; the charge distribution on the surface is disturbed and the particles flocculate. After flocculation, it is found that the dispersion medium is acid owing to the liberation of the hydrogen counter-ions. It appears that ions of opposite charge to those primarily adsorbed on the surface are necessary for coagulation. The minimum amount of electrolyte necessary to cause flocculation of the colloid is called the **flocculation** or **coagulation value**. It has been found that the latter depends primarily upon the charge numbers of the ions of the opposite charge to that on the colloidal particles: the nature of the ions has some influence also.

If two sols of opposite sign are mixed, mutual coagulation usually occurs owing to the neutralisation of charges. The above remarks apply largely to lyophobic colloids. Lyophilic colloids are generally much more difficult to coagulate than lyophobic colloids. If a lyophilic colloid, e.g. of gelatin, is added to a lyophobic colloid, e.g. of gold, then the lyophobic colloid appears to be strongly protected against the flocculating action of electrolytes. It is probable that the particles of the lyophilic colloid are adsorbed by the lyophobic colloid and impart their own properties to the latter. The lyophilic colloid is known as a **protective colloid**. This explains the relative stability produced by the addition of a little gelatin to the otherwise unstable gold sols. For this reason

also, organic matter, which might form a protective colloid, is generally destroyed before proceeding with an inorganic analysis.

During the flocculation of a colloid by an electrolyte, the ions of opposite sign to that of the colloid are adsorbed to a varying degree on the surface; the higher the charge of the ion, the more strongly is it adsorbed. In all cases, the precipitate will be contaminated by surface adsorption. Upon washing the precipitate with water, part of the adsorbed electrolyte is removed, and a new difficulty may arise. The electrolyte concentration in the supernatant liquid may fall below the coagulation value, and the precipitate may pass into colloidal solution again. This phenomenon, which is known as **peptisation**, is of great importance in quantitative analysis. By way of illustration, consider the precipitation of silver by excess of chloride ions in acid solution and the subsequent washing of the coagulated silver chloride with water; the adsorbed hydrogen ions will be removed by the washing process and a portion of the precipitate may pass through the filter. If, however, washing is carried out with dilute nitric acid, no peptisation occurs. For this reason, precipitates are always washed with a suitable solution of an electrolyte which does not interfere with the subsequent steps in the determination.

#### 11.4 SUPERSATURATION AND PRECIPITATE FORMATION

The solubility of a substance at any given temperature in a given solvent is the amount of the substance dissolved by a known weight of that solvent when the substance is in equilibrium with the solvent. The solubility depends upon the particle size, when these are smaller than about 0.01 mm in diameter; the solubility increases greatly the smaller the particles, owing to the increasing role played by surface effects. (The definition of solubility given above refers to particles larger than 0.01 mm.) A supersaturated solution is one that contains a greater concentration of solute than corresponds to the equilibrium solubility at the temperature under consideration. Supersaturation is therefore an unstable state which may be brought to a state of stable equilibrium by the addition of a crystal of the solute ('seeding' the solution) or of some other substance, or by mechanical means such as shaking or stirring. The difficulty of precipitation of ammonium magnesium phosphate will at once come to mind as an example of supersaturation.

According to von Weimarn, supersaturation plays an important part in determining the particle size of a precipitate. He deduced that the initial velocity of precipitation is proportional to  $(Q - S)/S$ , where  $Q$  is the total concentration of the substance that is to precipitate, and  $S$  is the equilibrium solubility;  $(Q - S)$  will denote the supersaturation at the moment precipitation commences. The expression applies approximately only when  $Q$  is large compared with  $S$ . The influence of the degree of supersaturation is well illustrated by von Weimarn's results for the precipitation of barium sulphate from solutions of barium thiocyanate and manganese sulphate respectively. When the concentrations of these solutions were greater than molar, a gelatinous precipitate was instantly obtained, whereas with very dilute solutions ( $< 10^{-3}M$ ) the precipitate appeared after about one month and contained relatively large crystal particles (e.g.  $0.03 \text{ mm} \times 0.015 \text{ mm}$ ).

These results indicated that the particle size of a precipitate decreases with increasing concentration of the reactants. For the production of a crystalline

precipitate, for which the adsorption errors will be least and filtration will be easiest,  $(Q - S)/S$  should be as small as possible. There is obviously a practical limit to reducing  $(Q - S)/S$  by making  $Q$  very small, since for a precipitation to be of value in analysis, it must be complete in a comparatively short time and the volumes of solutions involved must not be too large. There is, however, another method which may be used, viz. that of increasing  $S$ . For example, barium sulphate is about 50 times more soluble in 2M hydrochloric acid than in water: if 0.05M solutions of barium chloride and sulphuric acid are prepared in boiling 2M hydrochloric acid and the solutions mixed, a typical crystalline precipitate of barium sulphate is slowly formed.<sup>26,27</sup>

Applications of the above conceptions are to be found in the following recognised procedures in gravimetric analysis.

1. Precipitation is usually carried out in hot solutions, since the solubility generally increases with rise in temperature.
2. Precipitation is effected in dilute solution and the reagent is added slowly and with thorough stirring. The slow addition results in the first particles precipitated acting as nuclei which grow as further material precipitates.
3. A suitable reagent is often added to increase the solubility of the precipitate and thus lead to larger primary particles.
4. A procedure which is commonly employed to prevent supersaturation from occurring is that of precipitation from homogeneous solution. This is achieved by generating the precipitating agent within the solution by means of a homogeneous reaction at a similar rate to that required for precipitation of the species.

### 11.5 THE PURITY OF THE PRECIPITATE: CO-PRECIPITATION

When a precipitate separates from a solution, it is not always perfectly pure: it may contain varying amounts of impurities dependent upon the nature of the precipitate and the conditions of precipitation. The contamination of the precipitate by substances which are normally soluble in the mother liquor is termed **co-precipitation**. We must distinguish between two important types of co-precipitation. The first is concerned with adsorption at the *surface* of the particles exposed to the solution, and the second relates to the occlusion of foreign substances during the process of crystal growth from the primary particles.

With regard to surface adsorption, this will, in general, be greatest for gelatinous precipitates and least for those of pronounced macrocrystalline character. Precipitates with ionic lattices appear to conform to the Paneth-Fajans-Hahn adsorption rule, which states that the ion that is most strongly adsorbed by an ionic substance (crystal lattice) is that ion which forms the least soluble salt. Thus on sparingly soluble sulphates, it is found that calcium ions are adsorbed preferentially over magnesium ions because calcium sulphate is less soluble than magnesium sulphate. Also silver iodide adsorbs silver acetate much more strongly than it does silver nitrate under comparable conditions, since the former is the less soluble. The deformability of the adsorbed ions and the electrolytic dissociation of the adsorbed compound also have a considerable influence; the smaller the dissociation of the compound, the greater is the

adsorption. Thus hydrogen sulphide, a weak electrolyte, is strongly adsorbed by metallic sulphides.

The second type of co-precipitation may be visualised as occurring during the building up of the precipitate from the primary particles. The latter will be subject to a certain amount of surface adsorption, and during their coalescence the impurities will either be partially eliminated if large single crystals are formed and the process takes place slowly, or, if coalescence is rapid, large crystals composed of loosely bound small crystals may be produced and some of the impurities may be entrained within the walls of the large crystals. If the impurity is isomorphous or forms a solid solution with the precipitate, the amount of co-precipitation may be very large, since there will be no tendency for elimination during the 'ageing' process. The latter actually occurs during the precipitation of barium sulphate in the presence of alkali nitrates; in this particular case X-ray studies have shown that the abnormally large co-precipitation (which may be as high as 3.5 per cent if precipitation occurs in the presence of high concentrations of nitrate) is due to the formation of solid solutions. Fortunately, however, such cases are comparatively rare in analysis.

Appreciable errors may also be introduced by **post-precipitation**. This is the precipitation which occurs on the surface of the first precipitate *after* its formation. It occurs with sparingly soluble substances which form supersaturated solutions; they usually have an ion in common with the primary precipitate. Thus in the precipitation of calcium as oxalate in the presence of magnesium, magnesium oxalate separates out gradually upon the calcium oxalate; the longer the precipitate is allowed to stand in contact with the solution, the greater is the error due to this cause. A similar effect is observed in the precipitation of copper or mercury(II) sulphide in 0.3M hydrochloric acid in the presence of zinc ions; zinc sulphide is slowly post-precipitated.

Post-precipitation differs from co-precipitation in several respects:

- (a) The contamination increases with the time that the precipitate is left in contact with the mother liquor in post-precipitation, but usually decreases in co-precipitation.
- (b) With post-precipitation, contamination increases the faster the solution is agitated by either mechanical or thermal means. The reverse is usually true with co-precipitation.
- (c) The magnitude of contamination by post-precipitation may be much greater than in co-precipitation.

It is convenient to consider now the influence of **digestion**. This is usually carried out by allowing the precipitate to stand for 12–24 hours at room temperature, or sometimes by warming the precipitate for some time in contact with the liquid from which it was formed: the object is, of course, to obtain complete precipitation in a form which can be readily filtered. During the process of digestion or of the ageing of precipitates, at least two changes occur. The very small particles, which have a greater solubility than the larger ones, will, after precipitation has occurred, tend to pass into solution, and will ultimately re-deposit upon the larger particles; co-precipitation on the minute particles is thus eliminated and the total co-precipitation on the ultimate precipitate reduced. The rapidly formed crystals are probably of irregular shape and possess a comparatively large surface; upon digestion these tend to become more regular in character and also more dense, thus resulting in a decrease in the area of the

surface and a consequent reduction of adsorption. The net result of digestion is usually to reduce the extent of co-precipitation and to increase the size of the particles, rendering filtration easier.

### 11.6 CONDITIONS OF PRECIPITATION

No universal rules can be given which are applicable to all cases of precipitation, but, by the intelligent application of the principles enumerated in the foregoing paragraphs, a number of fairly general rules may be stated:

1. Precipitation should be carried out in dilute solution, due regard being paid to the solubility of the precipitate, the time required for filtration, and the subsequent operations to be carried out with the filtrate. This will minimise the errors due to co-precipitation.
2. The reagents should be mixed slowly and with constant stirring. This will keep the degree of supersaturation small and will assist the growth of large crystals. A slight excess of the reagent is all that is generally required; in exceptional cases a large excess may be necessary. In some instances the order of mixing the reagents may be important. Precipitation may be effected under conditions which increase the solubility of the precipitate, thus further reducing the degree of supersaturation (compare Section 11.5).
3. Precipitation is effected in hot solutions, provided the solubility and the stability of the precipitate permit. Either one or both of the solutions should be heated to just below the boiling point or other more favourable temperature. At the higher temperature: (*a*) the solubility is increased with a consequent reduction in the degree of supersaturation, (*b*) coagulation is assisted and sol formation decreased, and (*c*) the velocity of crystallisation is increased, thus leading to better-formed crystals.
4. Crystalline precipitates should be digested for as long as practical, preferably overnight, except in those cases where post-precipitation may occur. As a rule, digestion on the steam bath is desirable. This process decreases the effect of co-precipitation and gives more readily filterable precipitates. Digestion has little effect upon amorphous or gelatinous precipitates.
5. The precipitate should be washed with the appropriate dilute solution of an electrolyte. Pure water may tend to cause peptisation. (For theory of washing, see Section 11.8 below.)
6. If the precipitate is still appreciably contaminated as a result of co-precipitation or other causes, the error may often be reduced by dissolving it in a suitable solvent and then re-precipitating it. The amount of foreign substance present in the second precipitation will be small, and consequently the amount of the entrainment by the precipitate will also be small.

### 11.7 PRECIPITATION FROM HOMOGENEOUS SOLUTION

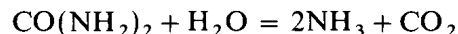
The major objective of a precipitation reaction is the separation of a pure solid phase in a compact and dense form which can be filtered easily. The importance of a small degree of supersaturation has long been appreciated, and it is for this reason that a dilute solution of a precipitating agent is added slowly and with stirring. In the technique known as precipitation from homogeneous solution, the precipitant is not added as such but is slowly generated by a homogeneous



chemical reaction within the solution. The precipitate is thus formed under conditions which eliminate the undesirable concentration effects which are inevitably associated with the conventional precipitation process. The precipitate is dense and readily filterable; co-precipitation is reduced to a minimum. Moreover, by varying the rate of the chemical reaction producing the precipitant in homogeneous solution, it is possible to alter further the physical appearance of the precipitate — the slower the reaction, the larger (in general) are the crystals formed.

Many different anions can be generated at a slow rate; the nature of the anion is important in the formation of compact precipitates. It is convenient to deal with the subject under separate headings.

**Hydroxides and basic salts.** The necessity for careful control of the pH has long been recognised. This is accomplished by making use of the hydrolysis of urea, which decomposes into ammonia and carbon dioxide as follows:



Urea possesses negligible basic properties ( $K_b = 1.5 \times 10^{-14}$ ), is soluble in water and its hydrolysis rate can be easily controlled. It hydrolyses rapidly at 90–100 °C, and hydrolysis can be quickly terminated at a desired pH by cooling the reaction mixture to room temperature. The use of a hydrolytic reagent *alone* does not result in the formation of a compact precipitate; the physical character of the precipitate will be very much affected by the presence of certain anions. Thus in the precipitation of aluminium by the urea process, a dense precipitate is obtained in the presence of succinate, sulphate, formate, oxalate, and benzoate ions, but not in the presence of chloride, chlorate, perchlorate, nitrate, sulphate, chromate, and acetate ions. The preferred anion for the precipitation of aluminium is succinate. It would appear that the main function of the 'suitable anion' is the formation of a basic salt which seems responsible for the production of a compact precipitate. The pH of the initial solution must be appropriately adjusted.

The following are suitable anions for urea precipitations of some metals: sulphate for gallium, tin, and titanium; formate for iron, thorium, and bismuth; succinate for aluminium and zirconium.

The urea method generally results in the deposition on the surface of the beaker of a thin, tenacious, and somewhat transparent film of the basic salt. This film cannot be removed by scraping with a 'policeman'. It is dissolved by adding a few millilitres of hydrochloric acid, covering the beaker with a clockglass, and refluxing for 5–10 minutes; the small amount of metallic ion is precipitated by ammonia solution and filters readily through the same filter containing the previously precipitated basic salt.

The urea hydrolysis method may be applied also to:

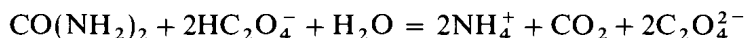
1. the precipitation of barium as barium chromate in the presence of ammonium acetate;
2. the precipitation of large amounts of nickel as the dimethylglyoximate; and
3. the precipitation of aluminium as the oxinate.

**Phosphates.** Insoluble orthophosphates may be precipitated with phosphate ion derived from trimethyl or triethyl phosphate by stepwise hydrolysis. Thus 1.8M sulphuric acid containing zirconyl ions and trimethyl phosphate on

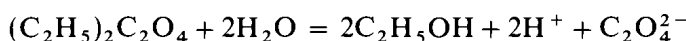
heating gives a dense precipitate of variable composition, which is ignited to and weighed as the dipolyphosphate (pyrophosphate)  $\text{ZrP}_2\text{O}_7$ .

Metaphosphoric acid may also be used; it hydrolyses in warm acid solution forming phosphoric(V) acid. Thus bismuth may be precipitated as bismuth phosphate in a dense, crystalline form.

**Oxalates.** Urea may be employed to raise the pH of an acid solution containing hydrogenoxalate ion  $\text{HC}_2\text{O}_4^-$ , thus affording a method for the slow generation of oxalate ion. Calcium oxalate may thus be precipitated in a dense form:



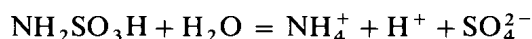
Dimethyl oxalate and diethyl oxalate can also be hydrolysed to yield oxalate ion:



Diethyl oxalate is usually preferred because of its slower rate of hydrolysis. Satisfactory results are obtained in the precipitation of calcium, magnesium, and zinc: thorium is precipitated using dimethyl oxalate.

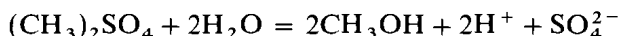
Calcium can be determined as the oxalate by precipitation from homogeneous solution by cation release from the EDTA complex in the presence of oxalate ion.<sup>28</sup>

**Sulphates.** Sulphate ion may be generated by the hydrolysis of aminosulphonic (sulphamic) acid:



The reaction has been used to produce barium sulphate in a coarsely crystalline form.

The hydrolysis of dimethyl sulphate also provides a source of sulphate ion, and the reaction has been used for the precipitation of barium, strontium, and calcium as well as lead:



### 11.8 WASHING THE PRECIPITATE

The experimental aspect of this important subject is dealt with in Section 3.36. Only some general theoretical considerations will be given here. Most precipitates are produced in the presence of one or more soluble compounds, and it is the object of the washing process to remove these as completely as possible. It is evident that only surface impurities will be removed in this way. The composition of the wash solution will depend upon the solubility and chemical properties of the precipitate and upon its tendency to undergo peptisation, the impurities to be removed, and the influence of traces of the wash liquid upon the subsequent treatment of the precipitate before weighing. Pure water cannot, in general, be employed owing to the possibility of producing partial peptisation of the precipitate and, in many cases, the occurrence of small losses as a consequence of the slight solubility of the precipitate: a solution of some electrolyte is employed. This should possess a common ion with the precipitate in order to reduce solubility errors, and should easily be volatilised in the preparation of the precipitate for weighing. For these reasons, ammonium salts, ammonia solution, and dilute acids are commonly employed. If the filtrate is required in

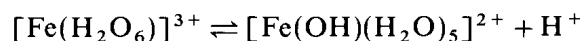
a subsequent determination, the selection is limited to substances which will not interfere in the sequel. Also, hydrolysable substances will necessitate the use of solutions containing an electrolyte which will depress the hydrolysis (compare Section 2.19). Whether the wash liquid is employed hot or at some other temperature will depend primarily upon the solubility of the precipitate; if permissible, hot solutions are to be preferred because of the greater solubility of the foreign substances and the increased speed of filtration.

It is convenient to divide wash solutions into three classes:

1. *Solutions which prevent the precipitate from becoming colloidal and passing through the filter.* This tendency is frequently observed with gelatinous or flocculated precipitates but rarely with well-defined crystalline precipitates. The wash solution should contain an electrolyte. The nature of the electrolyte is immaterial, provided it is without action upon the precipitate either during washing or ignition. Ammonium salts are therefore widely used. Thus dilute ammonium nitrate solution is employed for washing iron(III) hydroxide [hydrated iron(III) oxide], and 1 per cent nitric acid for washing silver chloride.

2. *Solutions which reduce the solubility of the precipitate.* The wash solution may contain a moderate concentration of a compound with one ion in common with the precipitate, use being made of the fact that substances tend to be less soluble in the presence of a slight excess of a common ion. Most salts are insoluble in ethanol and similar solvents, so that organic solvents can sometimes be used for washing precipitates. Sometimes a mixture of an organic solvent (e.g. ethanol) and water or a dilute electrolyte is effective in reducing the solubility to negligible proportions. Thus 100 mL of water at 25 °C will dissolve 0.7 mg of calcium oxalate, but the same volume of dilute ammonium oxalate solution dissolves only a negligible weight of the salt. Also 100 mL of water at room temperature will dissolve 4.2 mg of lead sulphate, but dilute sulphuric acid or 50 per cent aqueous ethanol has practically no solvent action on the compound.

3. *Solutions which prevent the hydrolysis of salts of weak acids and bases.* If the precipitate is a salt of weak acid and is slightly soluble it may exhibit a tendency to hydrolyse, and the soluble product of hydrolysis will be a base; the wash liquid must therefore be basic. Thus  $\text{Mg}(\text{NH}_4)\text{PO}_4$  may hydrolyse appreciably to give the hydrogenphosphate ion  $\text{HPO}_4^{2-}$  and hydroxide ion, and should accordingly be washed with dilute aqueous ammonia. If salts of weak bases, such as hydrated iron(III), chromium(III), or aluminium ion, are to be separated from a precipitate, e.g. silica, by washing with water, the salts may be hydrolysed and their insoluble basic salts or hydroxides may be produced together with an acid:



The addition of an acid to the wash solution will prevent the hydrolysis of iron(III) or similar salts: thus dilute hydrochloric acid will serve to remove iron(III) and aluminium salts from precipitates that are insoluble in this acid.

Solubility losses are reduced by employing the minimum quantity of wash solution consistent with the removal of impurities. It can be readily shown that washing is more efficiently carried out by the use of many small portions of liquid than with a few large portions, the total volume being the same in both instances. Under ideal conditions, where the foreign substance is simply

mechanically associated with the particles of the precipitate, the following expression may be shown to hold:

$$x_n = x_0 \left( \frac{u}{u+v} \right)^n$$

where  $x_0$  is the concentration of impurity before washing,  $x_n$  is the concentration of impurity after  $n$  washings,  $u$  is the volume in millilitres of the liquid remaining with the precipitate after draining, and  $v$  is the volume in millilitres of the solution used in each washing. It follows from this expression that it is best: (a) to allow the liquid to drain as far as possible in order to maintain  $u$  at a minimum; and (b) to use a relatively small volume of liquid and to increase the number of washings. Thus if  $u = 1$  mL and  $v = 9$  mL, five washings would reduce the surface impurity to  $10^{-6}$  of its original value; one washing with the same volume of liquid, viz. 45 mL, would only reduce the concentration to  $1/46$  or  $2.2 \times 10^{-2}$  of its initial concentration.

In practice, the washing process is not quite so efficient as the above simple theory would indicate, since the impurities are not merely mechanically associated with the surface. Furthermore, solubility losses are not so great as one would expect from the solubility data because the wash solution passing through the filter is not saturated with respect to the precipitate. Frequent qualitative tests must be made upon portions of the filtrate for some foreign ion which is known to be present in the original solution; as soon as these tests are negative, the washing is discontinued.

### 11.9 IGNITION OF THE PRECIPITATE: THERMOGRAVIMETRIC METHOD OF ANALYSIS

In addition to superficially adherent water, precipitates may contain:

- (a) adsorbed water, present on all solid surfaces in amount dependent on the humidity of the atmosphere;
- (b) occluded water, present in solid solution or in cavities within crystals;
- (c) sorbed water, associated with substances having a large internal surface development, e.g. hydrous oxides; and
- (d) essential water, present as water of hydration or crystallisation [e.g.  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  or  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ] or as water of constitution [the water is not present as such but is formed on heating, e.g.  $\text{Ca}(\text{OH})_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$ ].

In addition to the evolution of water, the ignition of precipitates often results in thermal decomposition reactions involving the dissociation of salts into acidic and basic components, e.g. the decomposition of carbonates and sulphates; the decomposition temperatures will obviously be related to the thermal stabilities.

The temperatures at which precipitates may be dried, or ignited to the required chemical form, can be determined from a study of the **thermogravimetric curves** for the individual substances. It should be emphasised, however, that thermogravimetric curves must be interpreted with care, paying due regard to the different experimental conditions which apply in thermogravimetry (temperature is usually changing at a regular rate) and in routine gravimetric analysis (the precipitate is brought to a specified temperature and maintained at that temperature for a definite time). A concise account of the principles and

applications of thermogravimetry follows and a small number of illustrative experiments are described in Section 11.78.

**Thermogravimetry** is a technique in which a change in the weight of a substance is recorded as a function of temperature or time. The basic instrumental requirement for thermogravimetry is a precision balance with a furnace programmed for a linear rise of temperature with time. The results may be presented (1) as a thermogravimetric (TG) curve, in which the weight change is recorded as a function of temperature or time, or (2) as a derivative thermogravimetric (DTG) curve where the first derivative of the TG curve is plotted with respect to either temperature or time.

A typical thermogravimetric curve, for copper sulphate pentahydrate  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , is given in Fig. 11.2.

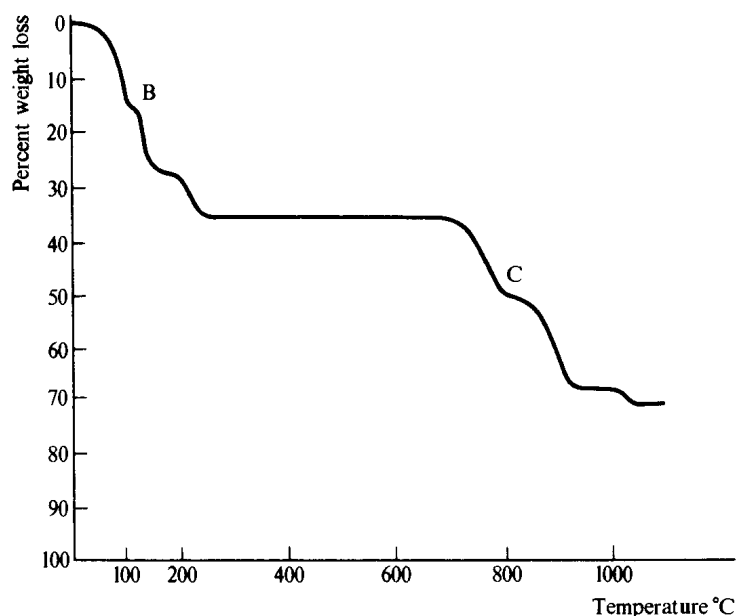


Fig. 11.2

The following features of the TG curve should be noted:

- (a) the horizontal portions (plateaus) indicate the regions where there is no weight change;
- (b) the curved portions are indicative of weight losses;
- (c) since the TG curve is quantitative, calculations on compound stoichiometry can be made at any given temperature.

As Fig. 11.2 shows, copper sulphate pentahydrate has four distinct regions of decomposition:

	Approximate temperature region
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot \text{H}_2\text{O}$	90–150 °C
$\text{CuSO}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CuSO}_4$	200–275 °C
$\text{CuSO}_4 \rightarrow \text{CuO} + \text{SO}_2 + \frac{1}{2}\text{O}_2$	700–900 °C
$2\text{CuO} \rightarrow \text{Cu}_2\text{O} + \frac{1}{2}\text{O}_2$	1000–1100 °C

The precise temperature regions for each of the reactions are dependent upon the experimental conditions (see Section 11.78). Although in Fig. 11.2 the ordinate is shown as the percentage weight loss, the scale on this axis may take other forms:

1. as a true weight scale;
2. as a percentage of the total weight;
3. in terms of relative molecular mass units.

An additional feature of the TG curve (Fig. 11.2) should now be examined, namely the two regions B and C where there are changes in the slope of the weight loss curve. If the rate of change of weight with time  $dW/dt$  is plotted against temperature, a derivative thermogravimetric (DTG) curve is obtained (Fig. 11.3). In the DTG curve when there is no weight loss then  $dW/dt = 0$ . The peak on the derivative curve corresponds to a maximum slope on the TG curve. When  $dW/dt$  is a minimum but not zero there is an inflexion, i.e. a change of slope on the TG curve. Inflexions B and C on Fig. 11.2 may imply the formation of intermediate compounds. In fact the inflexion at B arises from the formation of the trihydrate  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ , and that at point C is reported by Duval<sup>29</sup> to be due to formation of a golden-yellow basic sulphate of composition  $2\text{CuO} \cdot \text{SO}_3$ . Derivative thermogravimetry is useful for many complicated determinations and any change in the rate of weight loss may be readily identified as a trough indicating consecutive reactions; hence weight changes occurring at close temperatures may be ascertained.

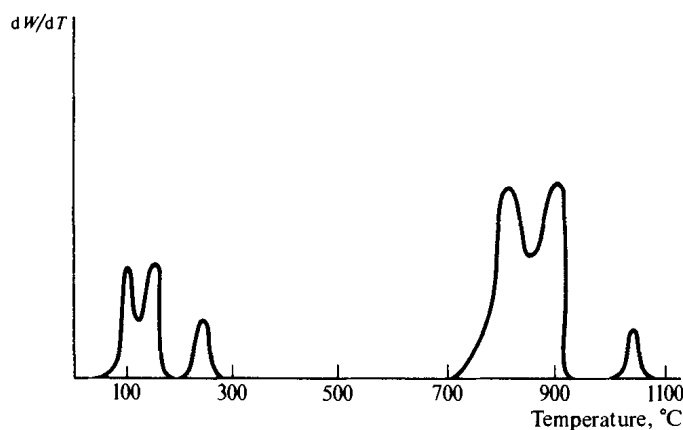


Fig. 11.3

**Experimental factors.** In the previous section it was stated that the precise temperature regions for each reaction of the thermal decomposition of copper sulphate pentahydrate is dependent upon experimental conditions. When a variety of commercial thermobalances became available in the early 1960s it was soon realised that a wide range of factors could influence the results obtained. Reviews of these factors have been made by Simons and Newkirk<sup>30</sup> and by Coats and Redfern<sup>31</sup> as a basis for establishing criteria necessary to obtain meaningful and reproducible results.

The factors which may affect the results can be classified into the two main groups of instrumental effects and the characteristics of the sample.

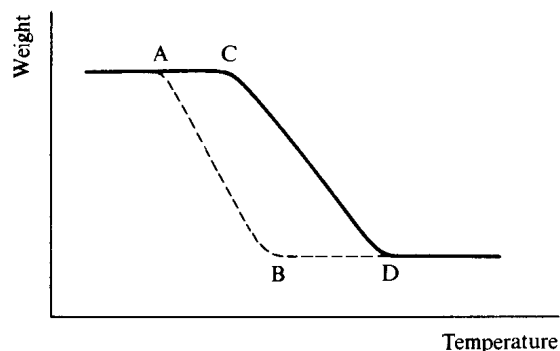


Fig. 11.4

**Instrumental factors. Heating rate.** When a substance is heated at a fast rate, the temperature of decomposition will be higher than that obtained at a slower rate of heating. The effect is shown for a single-step reaction in Fig. 11.4. The curve AB represents the decomposition curve at a slow heating rate, whereas the curve CD is that due to the faster heating rate. If  $T_A$  and  $T_C$  are the decomposition temperatures at the start of the reaction and the final temperatures on completion of the decomposition are  $T_B$  and  $T_D$ , the following features can be noted:

$$T_A < T_C$$

$$T_B < T_D$$

$$T_B - T_A < T_D - T_C$$

The heating rate has only a small effect when a fast reversible reaction is considered. The points of inflexion B and C obtained on the thermogravimetric curve for copper sulphate pentahydrate (Fig. 11.2) may be resolved into a plateau if a slower heating rate is used. Hence the detection of intermediate compounds by thermogravimetry is very dependent upon the heating rate employed.

**Furnace atmosphere.** The nature of the surrounding atmosphere can have a profound effect upon the temperature of a decomposition stage. For example, the decomposition of calcium carbonate occurs at a much higher temperature if carbon dioxide rather than nitrogen is employed as the surrounding atmosphere. Normally the function of the atmosphere is to remove the gaseous products evolved during thermogravimetry, in order to ensure that the nature of the surrounding gas remains as constant as possible throughout the experiment. This condition is achieved in many modern thermobalances by heating the test sample *in vacuo*.

The most common atmospheres employed in thermogravimetry are:

1. 'static air' (air from the surroundings flows through the furnace);
2. 'dynamic air', where compressed air from a cylinder is passed through the furnace at a measured flow rate;
3. nitrogen gas (oxygen-free) which provides an inert environment.

Atmospheres that take part in the reaction — for example, humidified air —

have been used in the study of the decomposition of such compounds as hydrated metal salts.

Since thermogravimetry is a dynamic technique, convection currents arising in a furnace will cause a continuous change in the gas atmosphere. The exact nature of this change further depends upon the furnace characteristics so that widely differing thermogravimetric data may be obtained from different designs of thermobalance.

**Crucible geometry.** The geometry of the crucible can alter the slope of the thermogravimetric curve. Generally, a flat, plate-shaped crucible is preferred to a 'high-form' cone shape because the diffusion of any evolved gases is easier with the former type.

**Sample characteristics.** The weight, particle size, and the mode of preparation (the pre-history) of a sample all govern the thermogravimetric results. A large sample can often create a deviation from linearity in the temperature rise. This is particularly true when a fast exothermic reaction is studied, for example the evolution of carbon monoxide during the decomposition of calcium oxalate to calcium carbonate. A large volume of sample in a crucible can impede the diffusion of evolved gases through the bulk of the solid large crystals, especially those of certain metallic nitrates which may undergo decrepitation ('spitting' or 'spattering') when heated. Other samples may swell, or foam and even bubble. In practice a small sample weight with as small a particle size as practicable is desirable for thermogravimetry.

Diverse thermogravimetric results can be obtained from samples with different pre-histories; for example, TG and DTG curves showed that magnesium hydroxide prepared by precipitation methods has a different temperature of decomposition from that for the naturally occurring material.<sup>32</sup> It follows that the source and/or the method of formation of the sample should be ascertained.

**Applications.** Some of the applications of thermogravimetry are of particular importance to the analyst. These are:

1. the determination of the purity and thermal stability of both primary and secondary standards;
2. the investigation of correct drying temperatures and the suitability of various weighing forms for gravimetric analysis;
3. direct application to analytical problems (automatic thermogravimetric analysis);
4. the determination of the composition of complex mixtures.

Thermogravimetry is a valuable technique for the assessment of the purity of materials. Analytical reagents, especially those used in titrimetric analysis as primary standards, e.g. sodium carbonate, sodium tetraborate, and potassium hydrogenphthalate, have been examined. Many primary standards absorb appreciable amounts of water when exposed to moist atmospheres. TG data can show the extent of this absorption and hence the most suitable drying temperature for a given reagent may be determined.

The thermal stability of EDTA as the free acid and also as the more widely used disodium salt,  $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ , has been reported by Wendlandt.<sup>33</sup> He showed that the dehydration of the disodium salt commences at between 110



and 125 °C, which served to confirm the view of Blaedel and Knight<sup>34</sup> that Na<sub>2</sub>EDTA,2H<sub>2</sub>O could be safely heated to constant weight at 80 °C.

Undoubtedly the most widespread application of thermogravimetry in analytical chemistry has been in the study of the recommended drying temperatures of gravimetric precipitates. Duval studied over a thousand gravimetric precipitates by this method and gave the recommended drying temperatures. He further concluded that only a fraction of these precipitates are suitable weighing forms for the elements. The results recorded by Duval were obtained with materials prepared under specified conditions of precipitation and this must be borne in mind when assessing the value of a given precipitate as a weighing form, since conditions of precipitation can have a profound effect on the pyrolysis curve. It must be stressed that the rejection of a precipitate because it does not give a stable plateau on the pyrolysis curve at one given rate is unjustified. Further, the limits of the plateau should not be taken as indicative of thermal stability within the complete temperature range. The weighing form is not necessarily isothermally stable at all temperatures that lie on the horizontal portion of a thermogravimetric curve. A slow rate of heating is to be preferred, especially with a large sample weight, over the temperature ranges in which chemical changes take place. Thermogravimetric curves must be interpreted with due regard to the fact that while they are being obtained the temperature is changing at a uniform rate, whereas in routine gravimetric analysis the precipitate is often brought rapidly to a specified temperature and maintained at that temperature for a definite time.

Thermogravimetry may be used to determine the composition of binary mixtures. If each component possesses a characteristic unique pyrolysis curve, then a resultant curve for the mixture will afford a basis for the determination of its composition. In such an automatic gravimetric determination the initial weight of the sample need not be known. A simple example is given by the automatic determination of a mixture of calcium and strontium as their carbonates.

Both carbonates decompose to their oxides with the evolution of carbon dioxide. The decomposition temperature for calcium carbonate is in the temperature range 650–850 °C, whilst strontium carbonate decomposes between 950 and 1150 °C. Hence the amount of calcium and strontium present in a mixture may be calculated from the weight losses due to the evolution of carbon dioxide at the lower and higher temperature ranges respectively. This method could be extended to the analysis of a three-component mixture, as barium carbonate is reported to decompose at an even higher temperature (~1300 °C) than strontium carbonate.

Thermogravimetric analysis has also been used in conjunction with other techniques, such as differential thermal analysis (DTA), gas chromatography, and mass spectrometry, for the study and characterisation of complex materials such as clays, soils and polymers.<sup>35</sup>

## QUANTITATIVE SEPARATIONS BASED UPON PRECIPITATION METHODS

### 11.10 FRACTIONAL PRECIPITATION

The simple theory of fractional precipitation has been given in Section 2.8. It