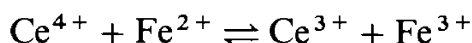


OXIDATION–REDUCTION TITRATIONS

10.89 CHANGE OF THE ELECTRODE POTENTIAL DURING THE TITRATION OF A REDUCTANT WITH AN OXIDANT

In Sections 10.11–10.16 it is shown how the change in pH during acid–base titrations may be calculated, and how the titration curves thus obtained can be used (a) to ascertain the most suitable indicator to be used in a given titration, and (b) to determine the titration error. Similar procedures may be carried out for oxidation–reduction titrations. Consider first a simple case which involves only change in ionic charge, and is theoretically independent of the hydrogen-ion concentration. A suitable example, for purposes of illustration, is the titration of 100 mL of 0.1 M iron(II) with 0.1 M cerium(IV) in the presence of dilute sulphuric acid:



The quantity corresponding to $[\text{H}^+]$ in acid–base titrations is the ratio $[\text{Ox}]/[\text{Red}]$. We are concerned here with two systems, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ion electrode (1), and the $\text{Ce}^{4+}/\text{Ce}^{3+}$ ion electrode (2).

For (1) at 25 °C:

$$E_1 = E_1^\ominus + \frac{0.0591}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = +0.75 + 0.0591 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

For (2), at 25 °C:

$$E_2 = E_2^\ominus + \frac{0.0591}{1} \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} = +1.45 + 0.0591 \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]}$$

The equilibrium constant of the reaction is given by (Section 2.33):

$$\log K = \log \frac{[\text{Ce}^{3+}] \times [\text{Fe}^{3+}]}{[\text{Ce}^{4+}] \times [\text{Fe}^{2+}]} = \frac{1}{0.0591} (1.45 - 0.75) = 11.84$$

or

$$K = 7 \times 10^{11}$$

The reaction is therefore virtually complete.

During the addition of the cerium(IV) solution up to the equivalence point, its only effect will be to oxidise the iron(II) (since K is large) and consequently change the ratio $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$. When 10 mL of the oxidising agent have been added, $[\text{Fe}^{3+}]/[\text{Fe}^{2+}] = 10/90$ (approx.) and

$$E_1 = 0.75 + 0.0591 \log 10/90 = 0.75 - 0.056 = 0.69 \text{ volt}$$

With 50 mL of the oxidising agent, $E_1 = E_1^\ominus = 0.75 \text{ volt}$

With 90 mL, $E_1 = 0.75 + 0.0591 \log 90/10 = 0.81 \text{ volt}$

With 99 mL, $E_1 = 0.75 + 0.0591 \log 99/1 = 0.87 \text{ volt}$

With 99.9 mL, $E_1 = 0.75 + 0.0591 \log 99.9/0.1 = 0.93 \text{ volt}$

At the equivalence point (100.0 mL) $[\text{Fe}^{3+}] = [\text{Ce}^{3+}]$ and $[\text{Ce}^{4+}] = [\text{Fe}^{2+}]$,

and the electrode potential is given by:*

$$\frac{E_1^\ominus + E_2^\ominus}{2} = \frac{0.75 + 1.45}{2} = 1.10 \text{ volts}$$

The subsequent addition of cerium(IV) solution will merely increase the ratio $[\text{Ce}^{4+}]/[\text{Ce}^{3+}]$. Thus:

With 100.1 mL, $E_2 = 1.45 + 0.0591 \log 0.1/100 = 1.27$ volts

With 101 mL, $E_2 = 1.45 + 0.0591 \log 1/100 = 1.33$ volts

With 110 mL, $E_2 = 1.45 + 0.0591 \log 10/100 = 1.39$ volts

With 190 mL, $E_2 = 1.45 + 0.0591 \log 90/100 = 1.45$ volts

These results are shown in Fig. 10.14.

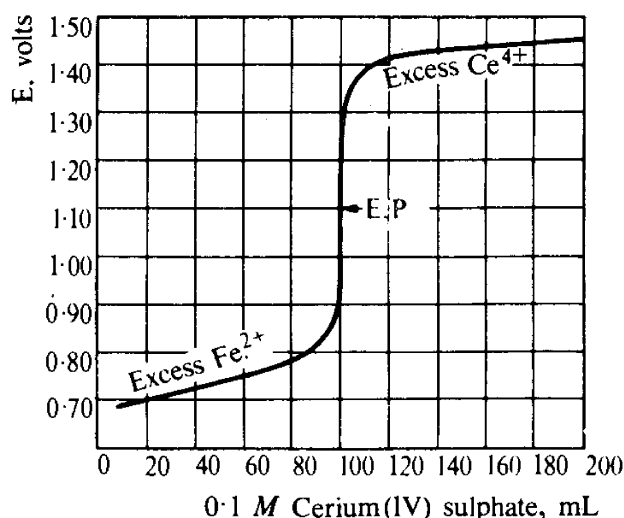


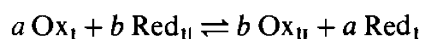
Fig. 10.14 Titration of 100 mL of 0.1M iron(II) with 0.1M cerium(IV) sulphate (calculated).

It is of interest to calculate the iron(II) concentration in the neighbourhood of the equivalence point. When 99.9 mL of the cerium(IV) solution have been added, $[\text{Fe}^{2+}] = 0.1 \times 0.1/199.9 = 5 \times 10^{-5}$, or $\text{pFe}^{2+} = 4.3$. The concentration at the equivalence point is given by (Section 2.33):

$$[\text{Fe}^{3+}]/[\text{Fe}^{2+}] = \sqrt{K} = \sqrt{7 \times 10^{11}} = 8.4 \times 10^5$$

Now $[\text{Fe}^{3+}] = 0.05M$, hence $[\text{Fe}^{2+}] = 5 \times 10^{-2}/8.4 \times 10^5 = 6 \times 10^{-8}M$, or $\text{pFe}^{2+} = 7.2$. Upon the addition of 100.1 mL of cerium(IV) solution, the reduction potential (see above) is 1.27 volts. The $[\text{Fe}^{3+}]$ is practically unchanged at $5 \times 10^{-2}M$, and we may calculate $[\text{Fe}^{2+}]$ with sufficient accuracy for our

* For a deduction of this expression and a discussion of the approximations involved, see a textbook of electrochemistry. It can similarly be shown that for the reaction:



the potential at the equivalence point is given by:

$$E_0 = \frac{b E_1^\ominus + a E_2^\ominus}{a + b}$$

where E_1^\ominus refers to $\text{Ox}_I, \text{Red}_I$, and E_2^\ominus to $\text{Ox}_{II}, \text{Red}_{II}$.

purpose from the equations:

$$E = E_1^\ominus + 0.0591 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$1.27 = 0.75 + 0.0591 \log \frac{5 \times 10^{-2}}{[\text{Fe}^{2+}]}$$

$$[\text{Fe}^{2+}] = 1 \times 10^{-10}$$

or

$$\text{pFe}^{2+} = 10$$

Thus pFe^{2+} changes from 4.3 to 10 between 0.1 per cent before and 0.1 per cent after the stoichiometric end point. These quantities are of importance in connection with the use of indicators for the detection of the equivalence point.

It is evident that the abrupt change of the potential in the neighbourhood of the equivalence point is dependent upon the standard potentials of the two oxidation–reduction systems that are involved, and therefore upon the equilibrium constant of the reaction; it is independent of the concentrations unless these are extremely small. The change in redox potential for a number of typical oxidation–reduction systems is exhibited graphically in Fig. 10.15. For the MnO_4^- , Mn^{2+} system and others which are dependent upon the pH of the

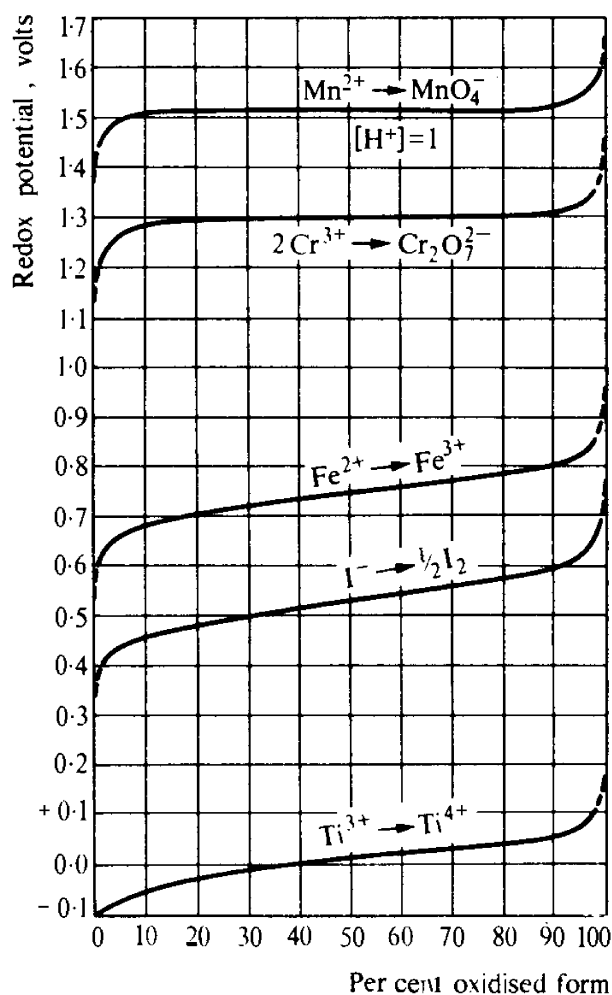


Fig. 10.15 Variation of redox potentials with oxidant/reductant ratio.

solution, the hydrogen-ion concentration is assumed to be molar: lower acidities give lower potentials. The value at 50 per cent oxidised form will, of course, correspond to the standard redox potential. As an indication of the application of the curves, consider the titration of iron(II) with potassium dichromate. The titration curve would follow that of the Fe(II)/Fe(III) system until the end-point was reached, then it would rise steeply and continue along the curve for the $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ system: the potential at the equivalence point can be determined as already described.

It is possible to titrate two substances by the same titrant provided that the standard potentials of the substances being titrated, and their oxidation or reduction products, differ by about 0.2 V. Stepwise titration curves are obtained in the titration of mixtures or of substances having several oxidation states. Thus the titration of a solution containing Cr(VI), Fe(III) and V(V) by an acid titanium(III) chloride solution is an example of such a mixture: in the first step Cr(VI) is reduced to Cr(III) and V(V) to V(IV); in the second step Fe(III) is reduced to Fe(II); in the third step V(IV) is reduced to V(III); chromium is evaluated by difference of the volumes of titrant used in the first and third steps. Another example is the titration of a mixture of Fe(II) and V(IV) sulphates with Ce(IV) sulphate in dilute sulphuric acid: in the first step Fe(II) is oxidised to Fe(III) and in the second 'jump' V(IV) is oxidised to V(V) the latter change is accelerated by heating the solution after oxidation of the Fe(II) ion is complete. The titration of a substance having several oxidation states is exemplified by the stepwise reduction by acid chromium(II) chloride of Cu(II) ion to the Cu(I) state and then to the metal.

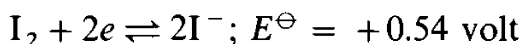
10.90 FORMAL POTENTIALS

Standard potentials E^\ominus are evaluated with full regard to activity effects and with all ions present in simple form: they are really limiting or ideal values and are rarely observed in a potentiometric measurement. In practice, the solutions may be quite concentrated and frequently contain other electrolytes; under these conditions the activities of the pertinent species are much smaller than the concentrations, and consequently the use of the latter may lead to unreliable conclusions. Also, the actual active species present (see example below) may differ from those to which the ideal standard potentials apply. For these reasons 'formal potentials' have been proposed to supplement standard potentials. The formal potential is the potential observed experimentally in a solution containing one mole each of the oxidised and reduced substances together with other specified substances at specified concentrations. It is found that formal potentials vary appreciably, for example, with the nature and concentration of the acid that is present. The formal potential incorporates in one value the effects resulting from variation of activity coefficients with ionic strength, acid-base dissociation, complexation, liquid-junction potentials, etc., and thus has a real practical value. Formal potentials do not have the theoretical significance of standard potentials, but they are observed values in actual potentiometric measurements. In dilute solutions they usually obey the Nernst equation fairly closely in the form:

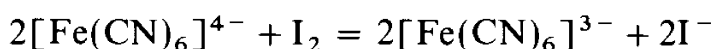
$$E = E^{\ominus'} + \frac{0.0591}{n} \log \frac{[\text{Ox}]}{[\text{Red}]} \text{ at } 25^\circ\text{C}$$

where $E^{\ominus'}$ is the formal potential and corresponds to the value of E at *unit* concentrations of oxidant and reductant, and the quantities in square brackets refer to molar concentrations. It is useful to determine and to tabulate $E^{\ominus'}$ with equivalent amounts of various oxidants and their conjugate reductants at various concentrations of different acids. If one is dealing with solutions whose composition is identical with or similar to that to which the formal potential pertains, more trustworthy conclusions can be derived from formal potentials than from standard potentials.

To illustrate how the use of standard potentials may occasionally lead to erroneous conclusions, consider the hexacyanoferrate(II)–hexacyano-ferrate(III) and the iodide–iodine systems. The standard potentials are:



It would be expected that iodine would quantitatively oxidise hexacyanoferrate(II) ions:



In fact $[\text{Fe}(\text{CN})_6]^{4-}$ ion oxidises iodide ion quantitatively in media containing 1M hydrochloric, sulphuric, or perchloric acid. This is because in solutions of low pH, protonation occurs and the species derived from $\text{H}_4\text{Fe}(\text{CN})_6$ are weaker than those derived from $\text{H}_3\text{Fe}(\text{CN})_6$; the activity of the $[\text{Fe}(\text{CN})_6]^{4-}$ ion is decreased to a greater extent than that of the $[\text{Fe}(\text{CN})_6]^{3-}$ ion, and therefore the reduction potential is increased. The actual redox potential of a solution containing equal concentrations of both cyanoferrates in 1M HCl, H_2SO_4 or HClO_4 is +0.71 volt, a value that is greater than the potential of the iodine–iodide couple.

Some results of formal potential measurements may now be mentioned. If there is no great difference in complexation of either the oxidant or its conjugate reductant in various acids, the formal potentials lie close together in these acids. Thus for the Fe(II)–Fe(III) system $E^{\ominus} = +0.77$ volt, $E^{\ominus'} = +0.73$ volt in 1M HClO_4 , +0.70 volt in 1M HCl, +0.68 volt in 1M H_2SO_4 , and +0.61 volt in 0.5M H_3PO_4 + 1M H_2SO_4 . It would seem that complexation is least in perchloric acid and greatest in phosphoric(V) acid.

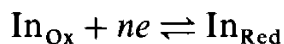
For the Ce(III)–Ce(IV) system $E^{\ominus'} = +1.44$ volts in 1M H_2SO_4 , +1.61 volts in 1M HNO_3 , and +1.70 volts in 1M HClO_4 . Perchloric acid solutions of cerium(IV) perchlorate, although unstable on standing, react rapidly and quantitatively with many inorganic compounds and have greater oxidising power than cerium(IV) sulphate–sulphuric acid or cerium(IV) nitrate–nitric acid solutions.

10.91 DETECTION OF THE END POINT IN OXIDATION–REDUCTION TITRATIONS

A. Internal oxidation–reduction indicators. As discussed in Sections 10.10–10.16, acid–base indicators are employed to mark the sudden change in pH during acid–base titrations. Similarly an oxidation–reduction indicator should mark the sudden change in the oxidation potential in the neighbourhood of the equivalence point in an oxidation–reduction titration. The ideal oxidation–reduction indicator will be one with an oxidation potential intermediate between

that of the solution titrated and that of the titrant, and which exhibits a sharp, readily detectable colour change.

An oxidation-reduction indicator (redox indicator) is a compound which exhibits different colours in the oxidised and reduced forms:



The oxidation and reduction should be reversible. At a potential E the ratio of the concentrations of the two forms is given by the Nernst equation:

$$E = E_{\text{In}}^{\ominus} + \frac{RT}{nF} \ln a_{\text{In.Ox}}/a_{\text{In.Red}}$$

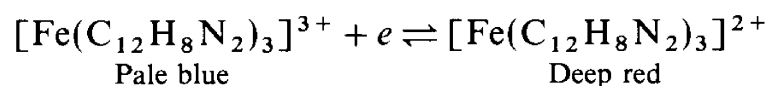
$$E \approx E_{\text{In}}^{\ominus} + \frac{RT}{nF} \ln \frac{[\text{In}_{\text{Ox}}]}{[\text{In}_{\text{Red}}]}$$

where E_{In}^{\ominus} is the standard (strictly the formal) potential of the indicator. If the colour intensities of the two forms are comparable a practical estimate of the colour-change interval corresponds to the change in the ratio $[\text{In}_{\text{Ox}}]/[\text{In}_{\text{Red}}]$ from 10 to $\frac{1}{10}$, this leads to an interval of potential of:

$$E = E_{\text{In}}^{\ominus} \pm \frac{0.0591}{1} \text{ volts at } 25^{\circ}\text{C}$$

If the colour intensities of the two forms differ considerably the intermediate colour is attained at potential somewhat removed from E_{In}^{\ominus} , but the error is unlikely to exceed 0.06 volt. For a sharp colour change at the end point, E_{In}^{\ominus} should differ by about at least 0.15 volt from the standard (formal) potentials of the other systems involved in the reaction.

One of the best oxidation-reduction indicators is the 1,10-phenanthroline-iron(II) complex. The base 1,10-phenanthroline combines readily in solution with iron(II) salts in the molecular ratio 3 base:1 iron(II) ion forming the intensely red 1,10-phenanthroline-iron(II) complex ion; with strong oxidising agents the iron(III) complex ion is formed, which has a pale blue colour. The colour change is a very striking one:



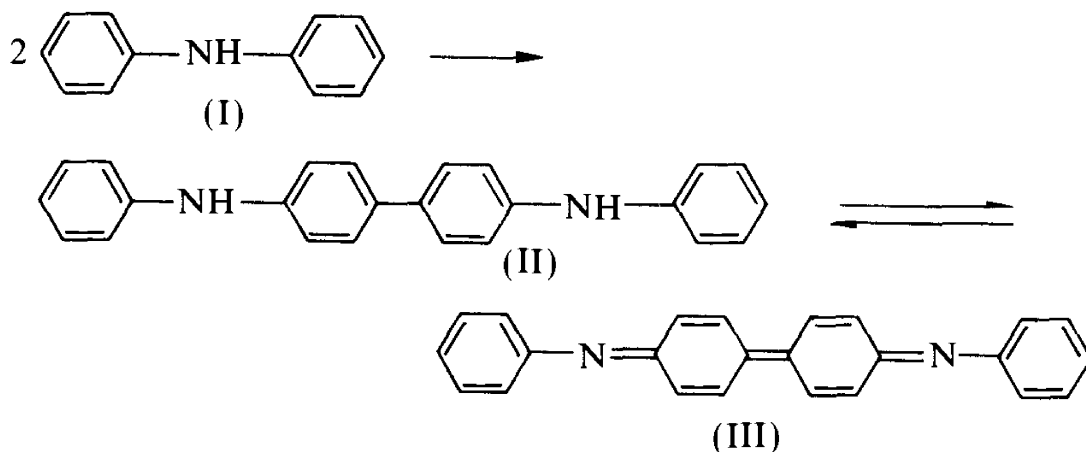
The standard redox potential is 1.14 volts; the formal potential is 1.06 volts in 1 *M* hydrochloric acid solution. The colour change, however, occurs at about 1.12 volts, because the colour of the reduced form (deep red) is so much more intense than that of the oxidised form (pale blue). The indicator is of great value in the titration of iron(II) salts and other substances with cerium(IV) sulphate solutions. It is prepared by dissolving 1,10-phenanthroline hydrate (relative molecular mass = 198.1) in the calculated quantity of 0.02 *M* acid-free iron(II) sulphate, and is therefore 1,10-phenanthroline-iron(II) complex sulphate (known as **ferroin**). One drop is usually sufficient in a titration: this is equivalent to less than 0.01 mL of 0.05 *M* oxidising agent, and hence the indicator blank is negligible at this or higher concentrations.

It has been shown (Section 10.89) that the potential at the equivalence point is the mean of the two standard redox potentials. In Fig. 10.14, the curve shows the variation of the potential during the titration of 0.1 *M* iron(II) ion with

0.1 *M* cerium(IV) solution, and the equivalence point is at 1.10 volts. Ferroin changes from deep red to pale blue at a redox potential of 1.12 volts: the indicator will therefore be present in the red form. After the addition of, say, a 0.1 per cent excess of cerium(IV) sulphate solution the potential rises to 1.27 volts, and the indicator is oxidised to the pale blue form. It is evident that the titration error is negligibly small.

The standard or formal potential of ferroin can be modified considerably by the introduction of various substituents in the 1,10-phenanthroline nucleus. The most important substituted ferroin is 5-nitro-1,10-phenanthroline iron(II) sulphate (nitroferroin) and 4,7-dimethyl-1,10-phenanthroline iron(II) sulphate (dimethylferroin). The former ($E^\ominus = 1.25$ volts) is especially suitable for titrations using Ce(IV) in nitric or perchloric acid solution where the formal potential of the oxidant is high. The 4,7-dimethylferroin has a sufficiently low formal potential ($E^\ominus = 0.88$ volt) to render it useful for the titration of Fe(II) with dichromate in 0.5 *M* sulphuric acid.

Mention should be made of one of the earliest internal indicators. This is a 1 per cent solution of diphenylamine in concentrated sulphuric acid, and was introduced for the titration of iron(II) with potassium dichromate solution. An intense blue-violet coloration is produced at the end point. The addition of phosphoric(V) acid is desirable, for it lowers the formal potential of the Fe(III)–Fe(II) system so that the equivalence point potential coincides more nearly with that of the indicator. The action of diphenylamine (I) as an indicator depends upon its oxidation first into colourless diphenylbenzidine (II), which is the real indicator and is reversibly further oxidised to diphenylbenzidine violet (III). Diphenylbenzidine violet undergoes further oxidation if it is allowed to stand with excess of dichromate solution; this further oxidation is irreversible, and red or yellow products of unknown composition are produced.



A solution of diphenylbenzidine in concentrated sulphuric acid acts similarly to diphenylamine. The reduction potential of the system II, III is 0.76 volt in 0.5–1 *M* sulphuric acid. It is therefore evident that a lowering of the potential of the Fe(III)–Fe(II) system is desirable, as already mentioned, in order to obtain a sharp colour change. The disadvantage of diphenylamine and of diphenylbenzidine is their slight solubility in water. This has been overcome by the use of the soluble barium or sodium diphenylaminesulphonate, which is employed in 0.2 per cent aqueous solution. The redox potential (E_{in}^\ominus) is slightly higher (0.85 volt in 0.5 *M* sulphuric acid), and the oxidised form has a reddish-violet colour resembling that of potassium permanganate, but the colour

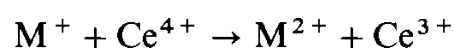
slowly disappears on standing; the presence of phosphoric(V) acid is desirable in order to lower the redox potential of the system.

A list of selected redox indicators, together with their colour changes and reduction potentials in an acidic medium, is given in Table 10.9.

Table 10.9 Some oxidation–reduction indicators

Indicator	Colour change		Formal potential at pH = 0 (volts)
	Oxidised form	Reduced form	
5-Nitro-1,10-phenanthroline iron(II) sulphate (nitroferroin)	Pale blue	Red	1.25
1,10-Phenanthroline iron(II) sulphate (ferroin)	Pale blue	Red	1.06
2,2'-Bipyridyl iron(II) sulphate	Faint blue	Red	1.02
5,6-Dimethylferroin	Pale blue	Red	0.97
N-Phenylanthranilic acid, 4,7-Dimethyl-1,10-phenanthroline iron(II) sulphate (4,7-dimethylferroin)	Purple red	Colourless	0.89
Diphenylaminesulphonic acid	Pale blue	Red	0.88
Diphenylbenzidine	Red–violet	Colourless	0.85
Diphenylamine	Violet	Colourless	0.76
3,3'-Dimethylnaphthidine	Violet	Colourless	0.76
Starch–I ₃ [–] , KI	Purplish-red	Colourless	0.71
Methylene blue	Blue	Colourless	0.53
	Blue	Colourless	0.52

At this stage reference may be made to **potential mediators**, i.e. substances which undergo reversible oxidation–reduction and reach equilibrium *rapidly*. If we have a mixture of two ions, say M^{2+} and M^+ , which reaches equilibrium slowly with an inert electrode, and a very small quantity of cerium(IV) salt is added, then the reaction:



takes place until the tendency of M^+ to be oxidised to M^{2+} is exactly balanced by the tendency of Ce^{3+} to be oxidised to Ce^{4+} , that is, until the M^{2+} , M^+ and Ce^{4+} , Ce^{3+} potentials are equal. A platinum or other inert electrode rapidly attains equilibrium with the Ce(III) and Ce(IV) ions, and will soon register a stable potential which is also that due to the $M^{2+} + e \rightleftharpoons M^+$ system. If the potential mediator is employed in small amount, then a negligible quantity of M^+ is converted into M^{2+} when equilibrium is reached, and the measured potential may be regarded as that of the original system. Potential mediators are, of course, useful in the measurement of the oxidation–reduction potentials of redox systems; in this connection mention may be made of the use of potassium iodide (≡ iodide–iodine system) in the arsenate–arsenite system in acid solution. It is evident that redox indicators (e.g. 1,10-phenanthroline–iron(II) ion) may act as potential mediators.

B. Self-indicating reagents. This is well illustrated by potassium permanganate, one drop of which will impart a visible pink coloration to several hundred millilitres of solution, even in the presence of slightly coloured ions, such as iron(III). The colours of cerium(IV) sulphate and of iodine solutions have also been employed in the detection of end points, but the colour change is not so marked as for potassium permanganate; here, however, sensitive internal

indicators (1,10-phenanthroline-iron(II) ion or *N*-phenylanthranilic acid and starch respectively) are available.

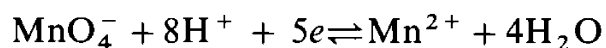
This method has the drawback that an excess of oxidising agent is always present at the end point. For work of the highest accuracy, the indicator blank may be determined and allowed for, or the error may be considerably reduced by performing the standardisation and determination under similar experimental conditions.

C. Potentiometric methods. This is a procedure which depends upon measurement of the e.m.f. between a reference electrode and an indicator (redox) electrode at suitable intervals during the titration, i.e. a potentiometric titration is carried out. The procedure is discussed fully in Chapter 15; let it suffice at this stage to point out that the procedure is applicable not only to those cases where suitable indicators are available, but also to those cases, e.g. coloured or very dilute solutions, where the indicator method is inapplicable, or of limited accuracy.

OXIDATIONS WITH POTASSIUM PERMANGANATE

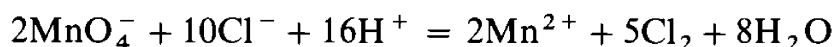
10.92 DISCUSSION

This valuable and powerful oxidising agent was first introduced into titrimetric analysis by F. Margueritte for the titration of iron(II). In acid solutions, the reduction can be represented by the following equation:



The standard potential in acid solution, E^\ominus , has been calculated to be 1.51 volts; hence the permanganate ion in acid solution is a strong oxidising agent.

Sulphuric acid is the most suitable acid, as it has no action upon permanganate in dilute solution. With hydrochloric acid, there is a likelihood of the reaction:



taking place, and some permanganate may be consumed in the formation of chlorine. This reaction is particularly liable to occur with iron salts unless special precautions are adopted (see below). With a small excess of free acid, a very dilute solution, low temperature and slow titration with constant shaking, the danger from this cause is minimised. There are, however, some titrations, such as those with arsenic(III) oxide, antimony(III), and hydrogen peroxide, which can be carried out in the presence of hydrochloric acid.

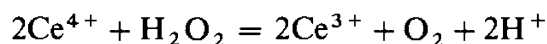
In the analysis of iron ores, solution is frequently effected in concentrated hydrochloric acid; the iron(III) is reduced and the iron(II) is then determined in the resultant solution. To do this, it is best to add about 25 mL of **Zimmermann and Reinhardt's solution** (this is sometimes termed **preventive solution**), which is prepared by dissolving 50 g of crystallised manganese(II) sulphate ($\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$) in 250 mL water, adding a cooled mixture of 100 mL concentrated sulphuric acid and 300 mL water, followed by 100 mL syrupy orthophosphoric acid. The manganese(II) sulphate lowers the reduction potential of the $\text{MnO}_4^- - \text{Mn(II)}$ couple (compare Section 2.31) and thereby makes it a weaker oxidising agent; the tendency of the permanganate ion to oxidise chloride ion is thus reduced. It has been stated that a further function of the manganese(II)

ferroin or *N*-phenylanthranilic acid as indicator. Repeat the titration with two further portions of the nitrite solution. Standardise the iron solution by titrating 25 mL of it with the cerium(IV) solution in the presence of dilute sulphuric acid.

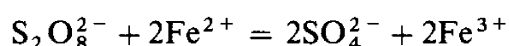
Determine the volume of the standard cerium(IV) sulphate solution which has reacted with the nitrite solution, and therefrom calculate the purity of the sodium nitrite employed.

Note. Cerium(IV) sulphate may also be used for the following analyses.

Hydrogen peroxide. The diluted solution, which may contain nitric or hydrochloric acid in any concentration between 0.5 and 3 *M* or sulphuric acid in the concentration range 0.25 to 1.5 *M*, is titrated directly with standard cerium(IV) sulphate solution, using ferroin or *N*-phenylanthranilic acid as indicator. The reaction is:



Persulphate (peroxydisulphate). Persulphate cannot be determined directly by reduction with iron(II) because the reaction is too slow:



An excess of a standard solution of iron(II) must therefore be added and the excess back-titrated with standard cerium(IV) sulphate solution. Erratic results are obtained, depending upon the exact experimental conditions, because of induced reactions leading to oxidation by air of iron(II) ion or to decomposition of the persulphate; these induced reactions are inhibited by bromide ion in concentrations not exceeding 1 *M* and, under these conditions, the determination may be carried out in the presence of organic matter.

To 25.0 mL of 0.01–0.015 *M* persulphate solution in a 150 mL conical flask, add 7 mL of 5 *M* sodium bromide solution and 2 mL of 3 *M* sulphuric acid. Stopper the flask. Swirl the contents, then add excess of 0.05 *M* ammonium iron(II) sulphate (15.0 mL), and allow to stand for 20 minutes. Add 1 mL of 0.001 *M* ferroin indicator, and titrate the excess of Fe^{2+} ion with 0.02 *M* cerium(IV) sulphate in 0.5 *M* sulphuric acid to the first colour change from orange to yellow.

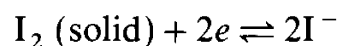
Oxalates. Oxalates can be determined by means of the indirect method described in Section 10.106.

Hexacyanoferrate(II). This can be determined by titration in 1 *M* H_2SO_4 using *N*-phenylanthranilic acid.

OXIDATION AND REDUCTION PROCESSES INVOLVING IODINE: IODOMETRIC TITRATIONS

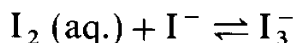
10.110 GENERAL DISCUSSION

The direct iodometric titration method (sometimes termed **iodimetry**) refers to titrations with a standard solution of iodine. The indirect iodometric titration method (sometimes termed **iodometry**) deals with the titration of iodine liberated in chemical reactions. The normal reduction potential of the reversible system:

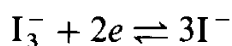


is 0.5345 volt. The above equation refers to a saturated aqueous solution in the presence of solid iodine; this half-cell reaction will occur, for example, towards the end of a titration of iodide with an oxidising agent such as potassium permanganate, when the iodide ion concentration becomes relatively low. Near the beginning, or in most iodometric titrations, when an excess of iodide ion is

present, the tri-iodide ion is formed

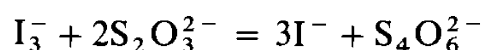


since iodine is readily soluble in a solution of iodide. The half-cell reaction is better written:

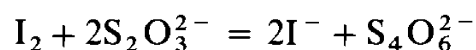


and the standard reduction potential is 0.5355 volt. Iodine or the tri-iodide ion is therefore a much weaker oxidising agent than potassium permanganate, potassium dichromate, and cerium(IV) sulphate.

In most direct titrations with iodine (iodimetry) a solution of iodine in potassium iodide is employed, and the reactive species is therefore the tri-iodide ion I_3^- . Strictly speaking, all equations involving reactions of iodine should be written with I_3^- rather than with I_2 , e.g.



is more accurate than

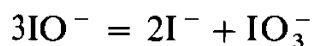
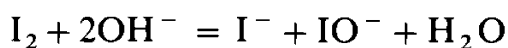


For the sake of simplicity, however, the equations in this book will usually be written in terms of molecular iodine rather than the tri-iodide ion.

Strong reducing agents (substances with a much lower reduction potential), such as tin(II) chloride, sulphurous acid, hydrogen sulphide, and sodium thiosulphate, react completely and rapidly with iodine even in acid solution. With somewhat weaker reducing agents, e.g. arsenic(III), or antimony(III), complete reaction occurs only when the solution is kept neutral or very faintly acid; under these conditions the reduction potential of the reducing agent is a minimum, or its reducing power is a maximum.

If a strong oxidising agent is treated in neutral or (more usually) acid solution with a large excess of iodide ion, the latter reacts as a reducing agent and the oxidant will be quantitatively reduced. In such cases, an equivalent amount of iodine is liberated, and is then titrated with a standard solution of a reducing agent, which is usually sodium thiosulphate.

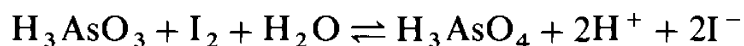
The normal reduction potential of the iodine–iodide system is independent of the pH of the solution so long as the latter is less than about 8; at higher values iodine reacts with hydroxide ions to form iodide and the extremely unstable hypoiodite, the latter being transformed rapidly into iodate and iodide by self-oxidation and reduction:



The reduction potentials of certain substances increase considerably with increasing hydrogen ion concentration of the solution. This is the case with systems containing permanganate, dichromate, arsenate, antimonate, bromate, etc., i.e. with anions which contain oxygen and therefore require hydrogen for complete reduction. Many weak oxidising anions are completely reduced by iodide ions if their reduction potentials are raised considerably by the presence in solution of a large amount of acid.

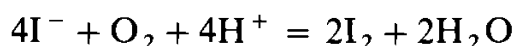
By suitable control of the pH of the solution, it is sometimes possible to

titrate the reduced form of a substance with iodine, and the oxidised form, after the addition of iodide, with sodium thiosulphate. Thus with the arsenite–arsenate system:



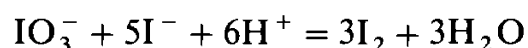
the reaction is completely reversible. At pH values between 4 and 9, arsenite can be titrated with iodine solution. In strongly acid solutions, however, arsenate is reduced to arsenite and iodine is liberated. Upon titration with sodium thiosulphate solution, the iodine is removed and the reaction proceeds from right to left.

Two important **sources of error in titrations involving iodine** are: (a) loss of iodine owing to its appreciable volatility; and (b) acid solutions of iodide are oxidised by oxygen from the air:



In the presence of excess of iodide, the volatility is decreased markedly through the formation of the tri-iodide ion; at room temperature the loss of iodine by volatilisation from a solution containing at least 4 per cent of potassium iodide is negligible provided the titration is not prolonged unduly. Titrations should be performed in cold solutions in conical flasks and not in open beakers. If a solution is to stand it should be kept in a glass-stoppered vessel. The atmospheric oxidation of iodide is negligible in neutral solution in the absence of catalysts, but the rate of oxidation increases rapidly with decreasing pH. The reaction is catalysed by certain metal ions of variable charge value (particularly copper), by nitrite ion, and also by strong light. For this reason titrations should not be performed in direct sunlight, and solutions containing iodide should be stored in amber glass bottles. Furthermore, the air oxidation of iodide ion may be induced by the reaction between iodide and the oxidising agent, especially when the main reaction is slow. Solutions containing an excess of iodide and acid must therefore not be allowed to stand longer than necessary before titration of the iodine. If prolonged standing is necessary (as in the titration of vanadate or Fe^{3+} ions) the solution should be free from air before the addition of iodide and the air displaced from the titration vessel by carbon dioxide [e.g. by adding small portions (0.2–0.5 g) of pure sodium hydrogencarbonate to the acid solution, or a little solid carbon dioxide, dry ice]; potassium iodide is then introduced and the glass stopper replaced immediately.

It seems appropriate to refer at this point to the uses of a standard solution containing **potassium iodide and potassium iodate**. This solution is quite stable and yields iodine when treated with acid:



The standard solution is prepared by dissolving a weighed amount of pure potassium iodate in a solution containing a slight excess of pure potassium iodide, and diluting to a definite volume. This solution has two important uses. The first is as a source of a known quantity of iodine in titrations [compare Section 10.115(A)]; it must be added to a solution containing strong acid; it cannot be employed in a medium which is neutral or possesses a low acidity.

The second use is in the determination of the acid content of solutions iodometrically or in the **standardisation of solutions of strong acids**. It is evident from the above equation that the amount of iodine liberated is equivalent to

the acid content of the solution. Thus if, say, 25 mL of an approximately 0.1 *M* solution of a strong acid is treated with a slight excess of potassium iodate (say, 25 mL of 0.02 *M* potassium iodate solution, Section 10.126) and a slight excess of potassium iodide solution (say, 10 mL of a 10 per cent solution), and the liberated iodine titrated with standard 0.1 *M* sodium thiosulphate with the aid of starch as an indicator, the concentration of the acid may be readily evaluated.

10.111 DETECTION OF THE END POINT

A solution of iodine in aqueous iodide has an intense yellow to brown colour. One drop of 0.05 *M* iodine solution imparts a perceptible pale yellow colour to 100 mL of water, so that in otherwise colourless solutions iodine can serve as its own indicator. The test is made much more sensitive by the use of a solution of starch as indicator. Starch reacts with iodine in the presence of iodide to form an intensely blue-coloured complex, which is visible at very low concentrations of iodine. The sensitivity of the colour reaction is such that a blue colour is visible when the iodine concentration is 2×10^{-5} *M* and the iodide concentration is greater than 4×10^{-4} *M* at 20 °C. The colour sensitivity decreases with increasing temperature of the solution; thus at 50 °C it is about ten times less sensitive than at 25 °C. The sensitivity decreases upon the addition of solvents, such as ethanol: no colour is obtained in solutions containing 50 per cent ethanol or more. It cannot be used in a strongly acid medium because hydrolysis of the starch occurs.

Starches can be separated into two major components, amylose and amylopectin, which exist in different proportions in various plants. Amylose, which is a straight-chain compound and is abundant in potato starch, gives a blue colour with iodine and the chain assumes a spiral form. Amylopectin, which has a branched-chain structure, forms a red-purple product, probably by adsorption.

The great merit of starch is that it is inexpensive. It possesses the following disadvantages: (1) insolubility in cold water; (2) instability of suspensions in water; (3) it gives a water-insoluble complex with iodine, the formation of which precludes the addition of the indicator early in the titration (for this reason, in titrations of iodine, the starch solution should not be added until just prior to the end point when the colour begins to fade); and (4) there is sometimes a 'drift' end point, which is marked when the solutions are dilute.

Most of the shortcomings of starch as an indicator are absent in **sodium starch glycollate**. This is a white, non-hygroscopic powder, readily soluble in hot water to give a faintly opalescent solution, which is stable for many months; it does not form a water-insoluble complex with iodine, and hence the indicator may be added at any stage of the reaction. With excess of iodine (e.g. at the beginning of a titration with sodium thiosulphate) the colour of the solution containing 1 mL of the indicator (0.1 per cent aqueous solution) is green; as the iodine concentration diminishes the colour changes to blue, which becomes intense just before the end point is reached. The end point is very sharp and reproducible and there is no 'drift' in dilute solution.

Carbon tetrachloride has been used in certain reactions instead of starch solution. One litre of water at 25 °C will dissolve 0.335 g of iodine, but the same volume of carbon tetrachloride will dissolve about 28.5 g. Iodine is therefore about 85 times as soluble in carbon tetrachloride as it is in water, and the carbon

tetrachloride solution is highly coloured. When a little carbon tetrachloride is added to an aqueous solution containing iodine and the solution well shaken, the great part of the iodine will dissolve in the carbon tetrachloride; the latter will fall to the bottom since it is immiscible with water, and the colour of the organic layer will be much deeper than that of the original aqueous solution. The reddish-violet colour of iodine in carbon tetrachloride is visible in very low concentrations of iodine; thus on shaking 10 mL of carbon tetrachloride with 50 mL of $10^{-5} M$ iodine, a distinct violet coloration is produced in the organic layer. This enables many iodometric determinations to be carried out with comparative ease. The titrations are performed in 250 mL glass-stoppered bottles or flasks with accurately ground stoppers. After adding the excess of potassium iodide solution and 5–10 mL of carbon tetrachloride to the reaction mixture, the titration with sodium thiosulphate is commenced. At first the presence of iodine in the aqueous solution will be apparent, and gentle rotation of the liquid causes sufficient mixing. Towards the end of the titration the bottle or flask is stoppered and shaken after each addition of sodium thiosulphate solution; the end point is reached when the carbon tetrachloride just becomes colourless. Equally satisfactory results can be obtained with chloroform.

Preparation and use of starch solution. Make a paste of 0.1 g of soluble starch with a little water, and pour the paste, with constant stirring, into 100 mL of boiling water, and boil for 1 minute. Allow the solution to cool and add 2–3 g of potassium iodide. Keep the solution in a stoppered bottle.

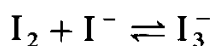
Only freshly prepared starch solution should be used. Two millilitres of a 1 per cent solution per 100 mL of the solution to be titrated is a satisfactory amount; the same volume of starch solution should always be added in a titration. In the titration of iodine, starch must not be added until just before the end point is reached. Apart from the fact that the fading of the iodine colour is a good indication of the approach at the end point, if the starch solution is added when the iodine concentration is high, some iodine may remain adsorbed even at the end point. The indicator blank is negligibly small in iodimetric and iodometric titrations of $0.05 M$ solutions; with more dilute solutions, it must be determined in a liquid having the same composition as the solution titrated has at the end point.

A solid solution of starch in urea may also be employed. Reflux 1 g of soluble starch and 19 g of urea with xylene. At the boiling point of the organic solvent the urea melts with little decomposition, and the starch dissolves in the molten urea. Allow to cool, then remove the solid mass and powder it; store the product in a stoppered bottle. A few milligrams of this solid added to an aqueous solution containing iodine then behaves like the usual starch indicator.

Preparation and use of sodium starch glycollate indicator. Sodium starch glycollate, prepared as described below, dissolves slowly in cold but rapidly in hot water. It is best dissolved by mixing, say, 5.0 g of the finely powdered solid with 1–2 mL ethanol, adding 100 mL cold water, and boiling for a few minutes with vigorous stirring: a faintly opalescent solution results. This 5 per cent stock solution is diluted to 1 per cent concentration as required. The most convenient concentration for use as an indicator is 0.1 mg mL^{-1} , i.e. 1 mL of the 1 per cent aqueous solution is added to 100 mL of the solution being titrated.

10.112 PREPARATION OF 0.05*M* IODINE SOLUTION

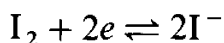
Discussion. In addition to a small solubility (0.335 g of iodine dissolves in 1 L of water at 25 °C), aqueous solutions of iodine have an appreciable vapour pressure of iodine, and therefore decrease slightly in concentration on account of volatilisation when handled. Both difficulties are overcome by dissolving the iodine in an aqueous solution of potassium iodide. Iodine dissolves readily in aqueous potassium iodide: the more concentrated the solution, the greater is the solubility of the iodine. The increased solubility is due to the formation of a tri-iodide ion:



The resulting solution has a much lower vapour pressure than a solution of iodine in pure water, and consequently the loss by volatilisation is considerably diminished. Nevertheless, the vapour pressure is still appreciable so that **precautions should always be taken to keep vessels containing iodine closed except during the actual titrations.** When an iodide solution of iodine is titrated with a reductant, the free iodine reacts with the reducing agent, this displaces the equilibrium to the left, and eventually all the tri-iodide is decomposed; the solution therefore behaves as though it were a solution of free iodine.

For the preparation of standard iodine solutions, resublimed iodine and iodate-free potassium iodide should be employed. The solution may be standardised against pure arsenic(III) oxide or with a sodium thiosulphate solution which has been recently standardised against potassium iodate.

The equation for the ionic reaction is:

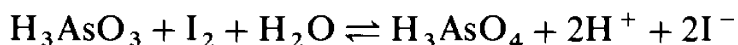


Procedure: Preparation of 0.05*M* iodine. Dissolve 20 g of iodate-free potassium iodide in 30–40 mL of water in a glass-stoppered 1 L graduated flask. Weigh out about 12.7 g of resublimed iodine on a watchglass on a rough balance (never on an analytical balance on account of the iodine vapour), and transfer it by means of a small dry funnel into the concentrated potassium iodide solution. Insert the glass stopper into the flask, and shake in the cold until all the iodine has dissolved. Allow the solution to acquire room temperature, and make up to the mark with distilled water.

The iodine solution is best preserved in small glass-stoppered bottles. These should be filled completely and kept in a cool, dark place.

10.113 STANDARDISATION OF IODINE SOLUTIONS

(A) **With arsenic(III) oxide: Discussion.** As already indicated (Section 10.94), arsenic(III) oxide which has been dried at 105–110 °C for two hours is an excellent primary standard. The reaction between this substance and iodine is a reversible one:



and only proceeds quantitatively from left to right if the hydrogen iodide is removed from the solution as fast as it is formed. This may be done by the addition of sodium hydrogencarbonate: sodium carbonate and sodium hydroxide cannot be used, since they react with the iodine, forming iodide,

hypoiodite, and iodate. Actually it has been shown that complete oxidation of the arsenite occurs when the pH of the solution lies between 4 and 9, the best value being 6.5, which is very close to the neutral point. Buffer solutions are employed to maintain the correct pH. A 0.12 M solution of sodium hydrogencarbonate saturated with carbon dioxide has a pH of 7; a solution saturated with both sodium tetraborate and boric acid has a pH of about 6.2, whilst a $\text{Na}_2\text{HPO}_4\text{--NaH}_2\text{PO}_4$ solution is almost neutral. Any of these three buffer solutions is suitable, but as already stated the first-named is generally employed.

Procedure. Weigh out accurately about 2.5 g of finely powdered arsenic(III) oxide, transfer to a 500 mL beaker, and dissolve it in a concentrated solution of sodium hydroxide, prepared from 2 g of iron-free sodium hydroxide and 20 mL of water. Dilute to about 200 mL, and neutralise the solution with 1M hydrochloric acid, using a pH meter. When the solution is faintly acid transfer the contents of the beaker quantitatively to a 500 mL graduated flask, add 2 g of pure sodium hydrogencarbonate, and, when all the salt has dissolved, dilute to the mark and shake well.

Using a burette or a pipette with a safety pump (this is necessary owing to the poisonous properties of the solution) measure out 25.0 mL of the arsenite solution into a 250 mL conical flask, add 25–50 mL of water, 5 g of sodium hydrogencarbonate, and 2 mL of starch solution. Swirl the solution carefully until the hydrogencarbonate has dissolved. Then titrate slowly with the iodine solution, contained in a burette, to the first blue colour.

Alternatively, the arsenite solution may be placed in the burette, and titrated against 25.0 mL of the iodine solution contained in a conical flask. When the solution has a pale yellow colour, add 2 mL of starch solution, and continue the titration slowly until the blue colour is just destroyed.

If it is desired to base the standardisation directly upon arsenic(III) oxide, proceed as follows. Weigh out accurately about 0.20 g of pure arsenic(III) oxide into a conical flask, dissolve it in 10 mL of 1M sodium hydroxide, and add a small excess of dilute sulphuric acid (say, 12–15 mL of 0.5M acid). Mix thoroughly and cautiously. Then add carefully a solution of 2 g of sodium hydrogencarbonate in 50 mL of water, followed by 2 mL of starch solution. Titrate slowly with the iodine solution to the first blue colour. Repeat with two other similar quantities of the oxide.

(B) With standard sodium thiosulphate solution. Sodium thiosulphate solution, which has been recently standardised, preferably against pure potassium iodate, is employed. Transfer 25 mL of the iodine solution to a 250 mL conical flask, dilute to 100 mL and add the standard thiosulphate solution from a burette until the solution has a pale yellow colour. Add 2 mL of starch solution, and continue the addition of the thiosulphate solution slowly until the solution is just colourless.

10.114 PREPARATION OF 0.1M SODIUM THIOSULPHATE

Discussion. Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) is readily obtainable in a state of high purity, but there is always some uncertainty as to the exact water content because of the efflorescent nature of the salt and for other reasons. The substance is therefore unsuitable as a primary standard. It is a reducing agent

potassium hydroxide solution with 0.5 *M* hydrochloric acid using phenolphthalein indicator (record as titration *a* mL).

For the hydrolysis, accurately weigh approximately 2 g of the fat or oil into a 250 mL conical flask with a ground-glass joint and add 25 mL of the potassium hydroxide solution. Attach a reflux condenser and heat the flask contents on a steam bath for 1 h with occasional shaking. While the solution is still hot add phenolphthalein indicator and titrate the excess potassium hydroxide with the 0.5 *M* hydrochloric acid (record as titration *b* mL).

$$\text{The saponification value} = \frac{(a - b) \times 0.5 \times 56.1}{\text{Weight of sample (mg)}}$$

COMPLEXATION TITRATIONS

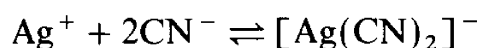
10.43 INTRODUCTION

The nature of complexes, their stabilities and the chemical characteristics of complexones have been dealt with in some detail in Sections 2.21 to 2.27. This particular section is concerned with the way in which complexation reactions can be employed in titrimetry, especially for determining the proportions of individual cations in mixtures.

The vast majority of complexation titrations are carried out using multidentate ligands such as EDTA or similar substances as the complexone. However, there are other more simple processes which also involve complexation using monodentate or bidentate ligands and which also serve to exemplify the nature of this type of titration. This is demonstrated in the determination outlined in Section 10.44.

10.44 A SIMPLE COMPLEXATION TITRATION

A simple example of the application of a complexation reaction to a titration procedure is the titration of cyanides with silver nitrate solution. When a solution of silver nitrate is added to a solution containing cyanide ions (e.g. an alkali cyanide) a white precipitate is formed when the two liquids first come into contact with one another, but on stirring it re-dissolves owing to the formation of a stable complex cyanide, the alkali salt of which is soluble:



When the above reaction is complete, further addition of silver nitrate solution yields the insoluble silver cyanoargentate (sometimes termed insoluble silver cyanide); the end point of the reaction is therefore indicated by the formation of a permanent precipitate or turbidity.

The only difficulty in obtaining a sharp end point lies in the fact that silver cyanide, precipitated by local excess concentration of silver ion somewhat prior to the equivalence point, is very slow to re-dissolve and the titration is time-consuming. In the Dénigès modification, iodide ion (usually as KI, *ca* 0.01 *M*) is used as the indicator and aqueous ammonia (*ca* 0.2 *M*) is introduced to dissolve the silver cyanide.

The iodide ion and ammonia solution are added before the titration is commenced; the formation of silver iodide (as a turbidity) will indicate the

end point:



During the titration any silver iodide which would tend to form will be kept in solution by the excess of cyanide ion always present until the equivalence point is reached:



The method may also be applied to the analysis of silver halides by dissolution in excess of cyanide solution and back-titration with standard silver nitrate. It can also be utilised indirectly for the determination of several metals, notably nickel, cobalt, and zinc, which form stable stoichiometric complexes with cyanide ion. Thus if a Ni(II) salt in ammoniacal solution is heated with excess of cyanide ion, the $[\text{Ni}(\text{CN})_4]^{2-}$ ion is formed quantitatively; since it is more stable than the $[\text{Ag}(\text{CN})_2]^-$ ion, the excess of cyanide may be determined by the Liebig-Dénigès method. The metal ion determinations are, however, more conveniently made by titration with EDTA: see the following sections.

10.45 TITRATION CURVES

If, in the titration of a strong acid, pH is plotted against the volume of the solution of the strong base added, a point of inflexion occurs at the equivalence point (compare Section 10.12). Similarly, in the EDTA titration, if pM (negative logarithm of the 'free' metal ion concentration: $\text{pM} = -\log[\text{M}^{n+}]$) is plotted against the volume of EDTA solution added, a point of inflexion occurs at the equivalence point; in some instances this sudden increase may exceed 10 pM units. The general shape of titration curves obtained by titrating 10.0 mL of a 0.01 M solution of a metal ion M with a 0.01 M EDTA solution is shown in Fig. 10.11. The apparent stability constants (see Sections 2.21, 2.23 and 2.27) of various metal-EDTA complexes are indicated at the extreme right of the

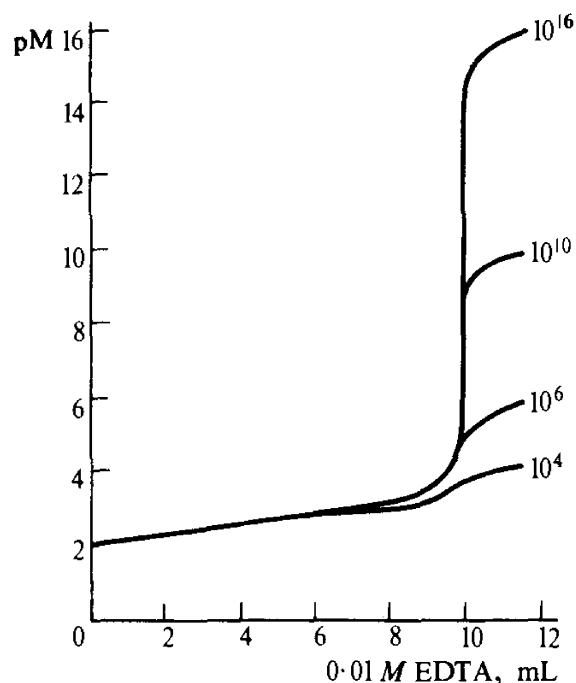


Fig. 10.11

curves. It is evident that the greater the stability constant, the sharper is the end point provided the pH is maintained constant.

In acid–base titrations the end point is generally detected by a pH-sensitive indicator. In the EDTA titration a metal ion-sensitive indicator (abbreviated, to **metal indicator** or **metal-ion indicator**) is often employed to detect changes of pM. Such indicators (which contain types of chelate groupings and generally possess resonance systems typical of dyestuffs) form complexes with specific metal ions, which differ in colour from the free indicator and produce a sudden colour change at the equivalence point. The end point of the titration can also be evaluated by other methods including potentiometric, amperometric, and spectrophotometric techniques.

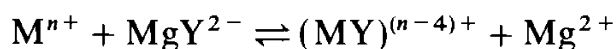
10.46 TYPES OF EDTA TITRATIONS

The most important procedures for the titration of metal ions with EDTA are the following.

A. Direct titration. The solution containing the metal ion to be determined is buffered to the desired pH (e.g. to pH = 10 with NH_4^+ –aq. NH_3) and titrated directly with the standard EDTA solution. It may be necessary to prevent precipitation of the hydroxide of the metal (or a basic salt) by the addition of some auxiliary complexing agent, such as tartrate or citrate or triethanolamine. At the equivalence point the magnitude of the concentration of the metal ion being determined decreases abruptly. This is generally determined by the change in colour of a metal indicator or by amperometric, spectrophotometric, or potentiometric methods.

B. Back-titration. Many metals cannot, for various reasons, be titrated directly; thus they may precipitate from the solution in the pH range necessary for the titration, or they may form inert complexes, or a suitable metal indicator is not available. In such cases an excess of standard EDTA solution is added, the resulting solution is buffered to the desired pH, and the excess of the EDTA is back-titrated with a standard metal ion solution; a solution of zinc chloride or sulphate or of magnesium chloride or sulphate is often used for this purpose. The end point is detected with the aid of the metal indicator which responds to the zinc or magnesium ions introduced in the back-titration.

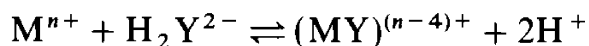
C. Replacement or substitution titration. Substitution titrations may be used for metal ions that do not react (or react unsatisfactorily) with a metal indicator, or for metal ions which form EDTA complexes that are more stable than those of other metals such as magnesium and calcium. The metal cation M^{n+} to be determined may be treated with the magnesium complex of EDTA, when the following reaction occurs:



The amount of magnesium ion set free is equivalent to the cation present and can be titrated with a standard solution of EDTA and a suitable metal indicator.

An interesting application is the titration of calcium. In the direct titration of calcium ions, solochrome black gives a poor end point; if magnesium is present, it is displaced from its EDTA complex by calcium and an improved end point results (compare Section 10.51).

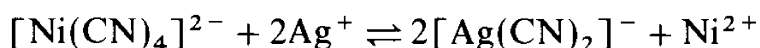
D. Alkalimetric titration. When a solution of disodium ethylenediaminetetraacetate, $\text{Na}_2\text{H}_2\text{Y}$, is added to a solution containing metallic ions, complexes are formed with the liberation of two equivalents of hydrogen ion:



The hydrogen ions thus set free can be titrated with a standard solution of sodium hydroxide using an acid–base indicator or a potentiometric end point; alternatively, an iodate–iodide mixture is added as well as the EDTA solution and the liberated iodine is titrated with a standard thiosulphate solution.

The solution of the metal to be determined must be accurately neutralised before titration; this is often a difficult matter on account of the hydrolysis of many salts, and constitutes a weak feature of alkalimetric titration.

E. Miscellaneous methods. Exchange reactions between the tetracyanonickelate(II) ion $[\text{Ni}(\text{CN})_4]^{2-}$ (the potassium salt is readily prepared) and the element to be determined, whereby nickel ions are set free, have a limited application. Thus silver and gold, which themselves cannot be titrated complexometrically, can be determined in this way.



These reactions take place with sparingly soluble silver salts, and hence provide a method for the determination of the halide ions Cl^- , Br^- , I^- , and the thiocyanate ion SCN^- . The anion is first precipitated as the silver salt, the latter dissolved in a solution of $[\text{Ni}(\text{CN})_4]^{2-}$, and the equivalent amount of nickel thereby set free is determined by rapid titration with EDTA using an appropriate indicator (murexide, bromopyrogallol red).

Fluoride may be determined by precipitation as lead chlorofluoride, the precipitate being dissolved in dilute nitric acid and, after adjusting the pH to 5–6, the lead is titrated with EDTA using xylenol orange indicator.¹⁰

Sulphate may be determined by precipitation as barium sulphate or as lead sulphate. The precipitate is dissolved in an excess of standard EDTA solution, and the excess of EDTA is back-titrated with a standard magnesium or zinc solution using solochrome black as indicator.

Phosphate may be determined by precipitating as $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$, dissolving the precipitate in dilute hydrochloric acid, adding an excess of standard EDTA solution, buffering at pH = 10, and back-titrating with standard magnesium ion solution in the presence of solochrome black.

10.47 TITRATION OF MIXTURES, SELECTIVITY, MASKING AND DEMASKING AGENTS

EDTA is a very unselective reagent because it complexes with numerous doubly, triply and quadruply charged cations. When a solution containing two cations which complex with EDTA is titrated without the addition of a complex-forming indicator, and if a titration error of 0.1 per cent is permissible, then the ratio of the stability constants of the EDTA complexes of the two metals M and N must be such that $K_M/K_N \geq 10^6$ if N is not to interfere with the titration of M. Strictly, of course, the constants K_M and K_N considered in the above expression should be the apparent stability constants of the complexes. If complex-forming indicators are used, then for a similar titration error $K_M/K_N \geq 10^8$.

The following procedures will help to increase the selectivity:

hours or overnight. Filter the precipitate through a sintered-glass crucible (porosity G4) and wash thoroughly with 1 *M* ammonia solution (about 100 mL). Rinse the beaker (in which the precipitation was made) with 25 mL of hot 1 *M* hydrochloric acid and allow the liquid to percolate through the filter crucible, thus dissolving the precipitate. Wash the beaker and crucible with a further 10 mL of 1 *M* hydrochloric acid and then with about 75 mL of water. To the filtrate and washings in the filter flask add 35.0 mL of 0.05 *M* EDTA, neutralise the solution with 1 *M* sodium hydroxide, add 4 mL of buffer solution and a few drops of solochrome black indicator. Back-titrate with standard 0.05 *M* magnesium chloride until the colour changes from blue to wine red.

10.73 DETERMINATION OF SULPHATES

The sulphate is precipitated as barium sulphate from acid solution, the precipitate is filtered off and dissolved in a measured excess of standard EDTA solution in the presence of aqueous ammonia. The excess of EDTA is then titrated with standard magnesium chloride solution using solochrome black as indicator.

Procedure. Prepare a standard magnesium chloride solution (0.05 *M*) and a buffer solution (pH 10); see Section 10.72. Standard EDTA (0.05 *M*) will also be required.

Pipette 25.0 mL of the sulphate solution (0.02–0.03 *M*) into a 250 mL beaker, dilute to 50 mL, and adjust the pH to 1 with 2 *M* hydrochloric acid; heat nearly to boiling. Add 15 mL of a nearly boiling barium chloride solution (*ca* 0.05 *M*) fairly rapidly and with vigorous stirring; heat on a steam bath for 1 hour. Filter with suction through a filter-paper disc (Whatman filter paper No. 42) supported upon a porcelain filter disc or a Gooch crucible, wash the precipitate thoroughly with cold water, and drain. Transfer the filter-paper disc and precipitate quantitatively to the original beaker, add 35.0 mL standard 0.05 *M* EDTA solution and 5 mL concentrated ammonia solution and boil gently for 15–20 minutes; add a further 2 mL concentrated ammonia solution after 10–15 minutes to facilitate the dissolution of the precipitate. Cool the resulting clear solution, add 10 mL of the buffer solution (pH = 10), a few drops of solochrome black indicator, and titrate the excess of EDTA with the standard magnesium chloride solution to a clear red colour.

Sulphate can also be determined by an exactly similar procedure by precipitation as lead sulphate from a solution containing 50 per cent (by volume) of propan-2-ol (to reduce the solubility of the lead sulphate), separation of the precipitate, dissolution in excess of standard EDTA solution, and back-titration of the excess EDTA with a standard zinc solution using solochrome black as indicator.

PRECIPITATION TITRATIONS

10.74 PRECIPITATION REACTIONS

The most important precipitation processes in titrimetric analysis utilise silver nitrate as the reagent (argentimetric processes). Discussion of the theory will, therefore, be confined to argentimetric processes; the same principles can, of

course, be applied to other precipitation reactions. Consider the changes in ionic concentration which occur during the titration of 100 mL of 0.1 M sodium chloride with 0.1 M silver nitrate. The solubility product of silver chloride at the laboratory temperature is 1.2×10^{-10} . The initial concentration of chloride ions, $[\text{Cl}^-]$, is 0.1 mol L^{-1} , or $\text{pCl}^- = 1$ (see Section 2.17). When 50 mL of 0.1 M silver nitrate have been added, 50 mL of 0.1 M sodium chloride remain in a total volume of 150 mL: thus $[\text{Cl}^-] = 50 \times 0.1/150 = 3.33 \times 10^{-2}$, or $\text{pCl}^- = 1.48$. With 90 mL of silver nitrate solution $[\text{Cl}^-] = 10 \times 0.1/190 = 5.3 \times 10^{-3}$, or $\text{pCl}^- = 2.28$.

Now

$$a_{\text{Ag}^+} \times a_{\text{Cl}^-} \approx [\text{Ag}^+] \times [\text{Cl}^-] = 1.2 \times 10^{-10} = K_{\text{sol. AgCl}}$$

or

$$\text{pAg}^+ + \text{pCl}^- = 9.92 = \text{pAgCl}$$

In the last calculation, $\text{pCl}^- = 1.48$, hence $\text{pAg}^+ = 9.92 - 1.48 = 8.44$. In this manner, the various concentrations of chloride and silver ions can be computed up to the equivalence point. At the equivalence point:

$$\text{Ag}^+ = \text{Cl}^- = \sqrt{K_{\text{sol. AgCl}}}$$

$$\text{pAg}^+ = \text{pCl}^- = \frac{1}{2}\text{pAgCl} = 9.92/2 = 4.96$$

and a saturated solution of silver chloride with no excess of silver or chloride ions is present.

With 100.1 mL of silver nitrate solution, $[\text{Ag}^+] = 0.1 \times 0.1/200.1 = 5 \times 10^{-5}$, or $\text{pAg}^+ = 4.30$; $\text{pCl}^- = \text{pAgCl} - \text{pAg}^+ = 9.92 - 4.30 = 5.62$.*

The values calculated in this way up to the addition of 110 mL of 0.1 M silver nitrate are collected in Table 10.7. Similar values for the titration of 100 mL of 0.1 M potassium iodide with 0.1 M silver nitrate are included in the same table ($K_{\text{sol. AgI}} = 1.7 \times 10^{-16}$).

It will be seen by inspecting the silver-ion exponents in the neighbourhood of the equivalence point (say, between 99.8 and 100.2 mL) that there is a marked change in the silver-ion concentration, and the change is more pronounced for silver iodide than for silver chloride, since the solubility product of the latter is about 10^6 larger than for the former. This is shown more clearly in the titration curve in Fig. 10.12, which represents the change of pAg^+ in the range between 10 per cent before and 10 per cent after the stoichiometric point in the titration of 0.1 M chloride and 0.1 M iodide respectively with 0.1 M silver nitrate. An almost identical curve is obtained by potentiometric titration using a silver electrode (see Section 15.20); the pAg^+ values may be calculated from the e.m.f. figures as in the calculation of pH.

* This is not strictly true, since the dissolved silver chloride will contribute silver and chloride ions to the solution; the actual concentration is *ca* $1 \times 10^{-5} \text{ g ions L}^{-1}$. If the excess of silver ions added is greater than 10 times this value, i.e. $> 10\sqrt{K_{\text{sol. AgCl}}}$, the error introduced by neglecting the ionic concentration produced by the dissolved salt may be taken as negligible for the purpose of the ensuing discussion.

Table 10.7 Titration of 100 mL of 0.1M NaCl and 100 mL of 0.1M KI respectively with 0.1M AgNO₃ ($K_{\text{sol. AgCl}} = 1.2 \times 10^{-10}$; $K_{\text{sol. AgI}} = 1.7 \times 10^{-16}$)

Vol. of 0.1M AgNO ₃ (mL)	Titration of chloride		Titration of iodide	
	pCl ⁻	pAg ⁺	pI ⁻	pAg ⁺
0	1.0	—	1.0	—
50	1.5	8.4	1.5	14.3
90	2.3	7.6	2.3	13.5
95	2.6	7.3	2.6	13.2
98	3.0	6.9	3.0	12.8
99	3.3	6.6	3.3	12.5
99.5	3.7	6.2	3.7	12.1
99.8	4.0	5.9	4.0	11.8
99.9	4.3	5.6	4.3	11.5
100.0	5.0	5.0	7.9	7.9
100.1	5.6	4.3	11.5	4.3
100.2	5.9	4.0	11.8	4.0
100.5	6.3	3.6	12.2	3.6
101	6.6	3.3	12.5	3.3
102	6.9	3.0	12.8	3.0
105	7.3	2.6	13.2	2.6
110	7.6	2.3	13.5	2.4

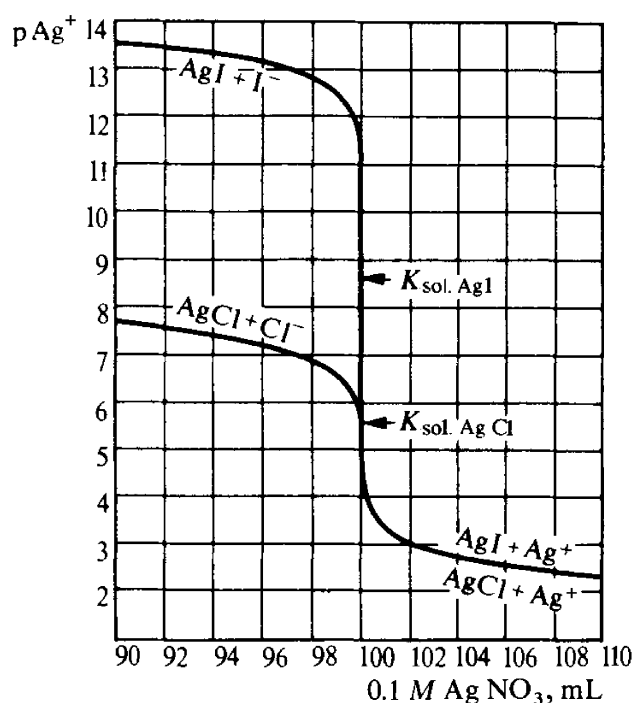


Fig. 10.12 Titration curves of 100 mL of 0.1M NaCl and of 100 mL of 0.1M KI respectively with 0.1M AgNO₃ (calculated).

10.75 DETERMINATION OF END POINTS IN PRECIPITATION REACTIONS

Many methods are utilised in determining end points in these reactions, but only the most important will be mentioned here.

(a) Formation of a coloured precipitate. This may be illustrated by the Mohr procedure for the determination of chloride and bromide. In the titration of a

neutral solution of, say, chloride ions with silver nitrate solution, a small quantity of potassium chromate solution is added to serve as indicator. At the end point the chromate ions combine with silver ions to form the sparingly soluble, red, silver chromate.

The theory of the process is as follows. This is a case of fractional precipitation (Section 2.8), the two sparingly soluble salts being silver chloride ($K_{\text{sol}} 1.2 \times 10^{-10}$) and silver chromate ($K_{\text{sol}} 1.7 \times 10^{-12}$). It is best studied by considering an actual example encountered in practice, viz. the titration of, say, 0.1 *M* sodium chloride with 0.1 *M* silver nitrate in the presence of a few millilitres of dilute potassium chromate solution. Silver chloride is the less soluble salt and the initial chloride concentration is high; hence silver chloride will be precipitated. At the first point where red silver chromate is just precipitated both salts will be in equilibrium with the solution. Hence:

$$[\text{Ag}^+] \times [\text{Cl}^-] = K_{\text{sol. AgCl}} = 1.2 \times 10^{-10}$$

$$[\text{Ag}^+]^2 \times [\text{CrO}_4^{2-}] = K_{\text{sol. Ag}_2\text{CrO}_4} = 1.7 \times 10^{-12}$$

$$[\text{Ag}^+] = \frac{K_{\text{sol. AgCl}}}{[\text{Cl}^-]} = \sqrt{\frac{K_{\text{sol. Ag}_2\text{CrO}_4}}{[\text{CrO}_4^{2-}]}}$$

$$\frac{[\text{Cl}^-]}{\sqrt{[\text{CrO}_4^{2-}]}} = \frac{K_{\text{sol. AgCl}}}{\sqrt{K_{\text{sol. Ag}_2\text{CrO}_4}}} = \frac{1.2 \times 10^{-10}}{\sqrt{1.7 \times 10^{-12}}} = 9.2 \times 10^{-5}$$

At the equivalence point $[\text{Cl}^-] = \sqrt{K_{\text{sol. AgCl}}} = 1.1 \times 10^{-5}$. If silver chromate is to precipitate at this chloride-ion concentration:

$$[\text{CrO}_4^{2-}] = \left(\frac{[\text{Cl}^-]}{9.2 \times 10^{-5}} \right)^2 = \left(\frac{1.1 \times 10^{-5}}{9.2 \times 10^{-5}} \right)^2 = 1.4 \times 10^{-2}$$

or the potassium chromate solution should be 0.014 *M*. It should be noted that a slight excess of silver nitrate solution must be added before the red colour of silver chromate is visible. In practice, a more dilute solution (0.003–0.005 *M*) of potassium chromate is generally used, since a chromate solution of concentration 0.01–0.02 *M* imparts a distinct deep orange colour to the solution, which renders the detection of the first appearance of silver chromate somewhat difficult. The error introduced can be readily calculated, for if $[\text{CrO}_4^{2-}] =$ (say) 0.003, silver chromate will be precipitated when:

$$[\text{Ag}^+] = \sqrt{\frac{K_{\text{sol. Ag}_2\text{CrO}_4}}{[\text{CrO}_4^{2-}]}} = \sqrt{\frac{1.7 \times 10^{-12}}{3 \times 10^{-3}}} = 2.4 \times 10^{-5}$$

If the theoretical concentration of indicator is used:

$$[\text{Ag}^+] = \sqrt{\frac{1.7 \times 10^{-12}}{1.4 \times 10^{-2}}} = 1.1 \times 10^{-5}$$

The difference is $1.3 \times 10^{-5} \text{ mol L}^{-1}$. If the volume of the solution at the equivalence point is 150 mL, then this corresponds to $1.3 \times 10^{-5} \times 150 \times 10^4 / 1000 = 0.02 \text{ mL}$ of 0.1 *M* silver nitrate. This is the theoretical titration error, and is therefore negligible. In actual practice another factor must be considered, viz. the small excess of silver nitrate solution which must be added before the eye

can detect the colour change in the solution; this is of the order of one drop or *ca* 0.05 mL of 0.1 *M* silver nitrate.

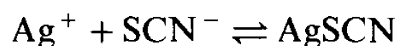
The titration error will increase with increasing dilution of the solution being titrated and is quite appreciable (*ca* 0.4* per cent) in dilute, say 0.01 *M*, solutions when the chromate concentration is of the order 0.003–0.005 *M*. This is most simply allowed for by means of an indicator blank determination, e.g. by measuring the volume of standard silver nitrate solution required to give a perceptible coloration when added to distilled water containing the same quantity of indicator as is employed in the titration. This volume is subtracted from the volume of standard solution used.

It must be mentioned that the titration should be carried out in neutral solution or in very faintly alkaline solution, i.e. within the pH range 6.5–9. In acid solution, the following reaction occurs:

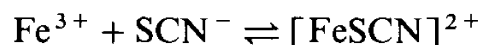


HCrO_4^- is a weak acid; consequently the chromate-ion concentration is reduced and the solubility product of silver chromate may not be exceeded. In markedly alkaline solutions, silver hydroxide ($K_{\text{sol.}} 2.3 \times 10^{-8}$) might be precipitated. A simple method of making an acid solution neutral is to add an excess of pure calcium carbonate or sodium hydrogencarbonate. An alkaline solution may be acidified with acetic acid and then a slight excess of calcium carbonate is added. The solubility product of silver chromate increases with rising temperature; the titration should therefore be performed at room temperature. By using a mixture of potassium chromate and potassium dichromate in proportions such as to give a neutral solution, the danger of accidentally raising the pH of an unbuffered solution beyond the acceptable limits is minimised; the mixed indicator has a buffering effect and adjusts the pH of the solution to 7.0 ± 0.1 . In the presence of ammonium salts, the pH must not exceed 7.2 because of the effect of appreciable concentrations of ammonia upon the solubility of silver salts. Titration of iodide and of thiocyanate is not successful because silver iodide and silver thiocyanate adsorb chromate ions so strongly that a false and somewhat indistinct end point is obtained.

(b) Formation of a soluble coloured compound. This procedure is exemplified by Volhard's method for the titration of silver in the presence of free nitric acid with standard potassium thiocyanate or ammonium thiocyanate solution. The indicator is a solution of iron(III) nitrate or of iron(III) ammonium sulphate. The addition of thiocyanate solution produces first a precipitate of silver thiocyanate ($K_{\text{sol.}} 7.1 \times 10^{-13}$):



When this reaction is complete, the slightest excess of thiocyanate produces a reddish-brown coloration, due to the formation of a complex ion:†

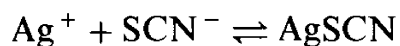
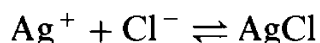


This method may be applied to the determination of chlorides, bromides,

* The errors for 0.1 *M* and 0.01 *M* bromide may be calculated to be 0.04 and 0.4 per cent respectively.

† This is the complex formed when the ratio of thiocyanate ion to iron(III) ion is low; higher complexes, $[\text{Fe}(\text{SCN})_2]^+$, etc., are important only at higher concentrations of thiocyanate ion.

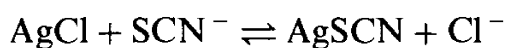
and iodides in acid solution. Excess of standard silver nitrate solution is added, and the excess is back-titrated with standard thiocyanate solution. For the chloride estimation, we have the following two equilibria during the titration of excess of silver ions:



The two sparingly soluble salts will be in equilibrium with the solution, hence:

$$\frac{[\text{Cl}^-]}{[\text{SCN}^-]} = \frac{K_{\text{sol. AgCl}}}{K_{\text{sol. AgSCN}}} = \frac{1.2 \times 10^{-10}}{7.1 \times 10^{-13}} = 169$$

When the excess of silver has reacted, the thiocyanate may react with the silver chloride, since silver thiocyanate is the less soluble salt, until the ratio $[\text{Cl}^-]/[\text{SCN}^-]$ in the solution is 169:



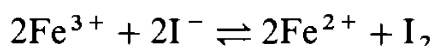
This will take place before reaction occurs with the iron(III) ions in the solution, and there will consequently be a considerable titration error. It is therefore absolutely necessary to prevent the reaction between the thiocyanate and the silver chloride. This may be effected in several ways, of which the first is probably the most reliable:

1. The silver chloride is filtered off before back-titrating. Since at this stage the precipitate will be contaminated with adsorbed silver ions, the suspension should be boiled for a few minutes to coagulate the silver chloride and thus remove most of the adsorbed silver ions from its surface before filtration. The cold filtrate is titrated.
2. After the addition of silver nitrate, potassium nitrate is added as coagulant, the suspension is boiled for about 3 minutes, cooled and then titrated immediately. Desorption of silver ions occurs and, on cooling, re-adsorption is largely prevented by the presence of potassium nitrate.
3. An immiscible liquid is added to 'coat' the silver chloride particles and thereby protect them from interaction with the thiocyanate. The most successful liquid is nitrobenzene (*ca* 1.0 mL for each 50 mg of chloride): the suspension is well shaken to coagulate the precipitate before back-titration.

With bromides, we have the equilibrium:

$$\frac{[\text{Br}^-]}{[\text{SCN}^-]} = \frac{K_{\text{sol. AgBr}}}{K_{\text{sol. AgSCN}}} = \frac{3.5 \times 10^{-13}}{7.1 \times 10^{-13}} = 0.5$$

The titration error is small, and no difficulties arise in the determination of the end point. Silver iodide ($K_{\text{sol.}} 1.7 \times 10^{-16}$) is less soluble than the bromide; the titration error is negligible, but the iron(III) indicator should not be added until excess of silver is present, since the dissolved iodide reacts with Fe^{3+} ions:



(c) Use of adsorption indicators. K. Fajans introduced a useful type of indicator for precipitation reactions as a result of his studies on the nature of adsorption. The action of these indicators is due to the fact that at the equivalence point the indicator is adsorbed by the precipitate, and during the process of

adsorption a change occurs in the indicator which leads to a substance of different colour; they have therefore been termed **adsorption indicators**. The substances employed are either acid dyes, such as those of the fluorescein series, e.g. fluorescein and eosin which are utilised as the sodium salts, or basic dyes, such as those of the rhodamine series (e.g. rhodamine 6G), which are used as the halogen salts.

The theory of the action of these indicators is based upon the properties of colloids, Section 11.3. When a chloride solution is titrated with a solution of silver nitrate, the precipitated silver chloride adsorbs chloride ions (a precipitate has a tendency to adsorb its own ions); this may be termed the primary adsorbed layer. By a process known as secondary adsorption, oppositely charged ions present in solution are held around it (shown diagrammatically in Fig. 10.13a). As soon as the stoichiometric point is reached, silver ions are present in excess and these now become primarily adsorbed; nitrate ions will be held by secondary adsorption (Fig. 10.13b). If fluorescein is also present in the solution, the negative fluorescein ion, which is much more strongly adsorbed than is the nitrate ion, is immediately adsorbed, and will reveal its presence on the precipitate, not by its own colour, which is that of the solution, but by the formation of a pink complex of silver and a modified fluorescein ion on the surface with the first trace of excess of silver ions. An alternative view is that during the adsorption of the fluorescein ion a rearrangement of the structure of the ion occurs with the formation of a coloured substance. It is important to notice that the colour change takes place at the *surface* of the precipitate. If chloride is now added, the suspension remains pink until chloride ions are present in excess, the adsorbed silver ions are converted into silver chloride, which primarily adsorbs chloride ions. The secondary adsorbed fluorescein ions pass back into solution, to which they impart a greenish-yellow colour.

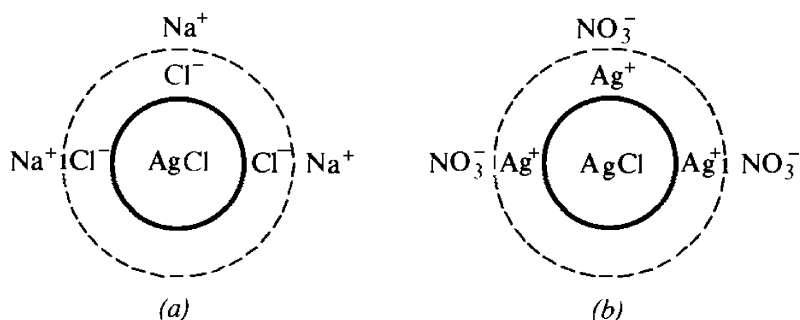


Fig. 10.13 (a) AgCl precipitated in the presence of excess of Cl^- ; (b) AgCl precipitated in the presence of excess of Ag^+ .

The following conditions will govern the choice of a suitable adsorption indicator:

- The precipitate should separate as far as possible in the colloidal condition. Large quantities of neutral salts, particularly of multicharged ions, should be avoided owing to their coagulating effect. The solution should not be too dilute, as the amount of precipitate formed will be small and the colour change far from sharp with certain indicators.
- The indicator ion must be of opposite charge to the ion of the precipitating agent.
- The indicator ion should not be adsorbed before the particular compound

has been completely precipitated, but it should be strongly adsorbed immediately after the equivalence point. The indicator ion should not be too strongly adsorbed by the precipitate; if this occurs, e.g. eosin (tetrabromofluorescein) in the chloride–silver titration, the adsorption of the indicator ion may be a primary process and will take place before the equivalence point.

A disadvantage of adsorption indicators is that silver halides are sensitised to the action of light by a layer of adsorbed dyestuff. For this reason, titrations should be carried out with a minimum exposure to sunlight. When using adsorption indicators, only 2×10^{-4} to 3×10^{-3} mol of dye per mol of silver halide is added; this small concentration is used so that an appreciable fraction of the added indicator is actually adsorbed on the precipitate.

For the titration of chlorides, fluorescein may be used. This indicator is a very weak acid ($K_a = ca\ 1 \times 10^{-8}$); hence even a small amount of other acids reduces the already minute ionisation, thus rendering the detection of the end point (which depends essentially upon the adsorption of the free anion) either impossible or difficult to observe. The optimum pH range is between 7 and 10. Dichlorofluorescein is a stronger acid and may be utilised in slightly acid solutions of pH greater than 4.4; this indicator has the further advantage that it is applicable in more dilute solutions.

Eosin (tetrabromofluorescein) is a stronger acid than dichlorofluorescein and can be used down to a pH of 1–2; the colour change is sharpest in an acetic acid solution (pH < 3). Eosin is so strongly adsorbed on silver halides that it cannot be used for chloride titrations; this is because the eosin ion can compete with chloride ion before the equivalence point and thereby gives a premature indication of the end point. With the more strongly adsorbing ions, Br^- , I^- and SCN^- , the competition is not serious and a very sharp end point is obtained in the titration of these ions, even in dilute solutions. The colour of the precipitate is magenta. Rose Bengal (dichlorotetraiodofluorescein) and dimethyldiiodofluorescein have been recommended for the titration of iodides.

Other dyestuffs have been recommended as adsorption indicators for the titration of halides and other ions. Thus cyanide ion may be titrated with standard silver nitrate solution using diphenylcarbazide as adsorption indicator (see Section 10.44): the precipitate is pale violet at the end point. A selection of adsorption indicators, their properties and uses, is given in Table 10.8.

(d) Turbidity method. The appearance of a turbidity is sometimes utilised to mark the end-point of a reaction, as in Liebig's method for cyanides (see Section 10.44). A method which should be included here is the **turbidity procedure for the determination of silver with chloride**; first introduced by Gay Lussac. A standard solution of sodium chloride is titrated with a solution of silver nitrate or vice versa. Under certain conditions the addition of an indicator is unnecessary, because the presence of a turbidity caused by the addition of a few drops of one of the solutions to the other will show that the end point has not been reached. The titration is continued until the addition of the appropriate solution produces no turbidity. Accurate results are obtained.

The procedure may be illustrated by the following simple experiment, which is a modification of the Gay Lussac–Stas method. The sodium chloride solution is added to the silver solution in the presence of free nitric acid and a small quantity of pure barium nitrate (the latter to assist coagulation of the precipitate).

Table 10.8 Selected adsorption indicators: properties and uses

Indicator	Use
Fluorescein	Cl^- , Br^- , I^- , with Ag^+
Dichlorofluorescein	Cl^- , Br^- , BO_3^{3-} , with Ag^+
Tetrabromofluorescein (eosin)	Br^- , I^- , SCN^- , with Ag^+
Dichloro-tetraiodofluorescein (Rose Bengal)	I^- in presence of Cl^- , with Ag^+
Di-iodo-dimethylfluorescein	I^- , with Ag^+
Tartrazine	Ag^+ , with I^- or SCN^- ; $\text{I}^- + \text{Cl}^-$, with excess Ag^+ , back-titration with I^-
Sodium alizarin sulphonate (alizarin red S)	$[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{MoO}_4]^{2-}$ with Pb^{2+}
Rhodamine 6G	Ag^+ with Br^-
Phenosafranine	Cl^- , Br^- , with Ag^+ Ag^+ , with Br^-

* The colour change is as indicator passes from solution to precipitate, unless otherwise stated.

Weigh out accurately about 0.40 g of silver nitrate into a well-stoppered 200 mL bottle. Add about 100 mL of water, a few drops of concentrated nitric acid, and a small crystal of barium nitrate. Titrate with standard 0.1 M sodium chloride by adding 20 mL at once, stoppering the bottle, and shaking it vigorously until the precipitate of silver chloride has coagulated and settled, leaving a clear solution. The volume of sodium chloride solution taken should leave the silver still in excess. Continue to add the chloride solution, 1 mL at a time, stoppering and shaking after each addition, until no turbidity is produced: note the total volume of sodium chloride solution. Repeat the determination, using a fresh sample of silver nitrate of about the same weight, and run in initially that volume of the 0.1 M sodium chloride, less 1 mL, which the first titration has indicated will be required, and thereafter add the chloride solution dropwise (i.e. in about 0.05 mL portions). It will be found that the end point can be determined within one drop.

The following sections are concerned with the use of standard solutions of reagents such as silver nitrate, sodium chloride, potassium (or ammonium) thiocyanate, and potassium cyanide. Some of the determinations which will be considered strictly involve complex formation rather than precipitation reactions, but it is convenient to group them here as reactions involving the use of standard silver nitrate solutions. Before commencing the experimental work, the theoretical Sections 10.74 and 10.75 should be studied.

10.76 PREPARATION OF 0.1 M SILVER NITRATE

Discussion. Very pure silver can be obtained commercially, and a standard solution can be prepared by dissolving a known weight (say, 10.787 g) in nitric acid in a conical flask having a funnel in the neck to prevent mechanical loss, and making up to a known volume (say, 1 L for a 0.1 M solution). The presence of acid must, however, be avoided in determinations with potassium chromate as indicator or in determinations employing adsorption indicators. It is therefore preferable to employ a neutral solution prepared by dissolving silver nitrate (relative molecular mass, 169.87) in water.

Analytical grade silver nitrate has a purity of at least 99.9 per cent, so that a standard solution can be prepared by direct weighing. If, however, commercial

Standardisation. Use 0.1 *M* silver nitrate, which has been prepared and standardised as described in Section 10.77.

The iron(III) indicator solution consists of a cold, saturated solution of ammonium iron(III) sulphate in water (about 40 per cent) to which a few drops of 6 *M* nitric acid have been added. One millilitre of this solution is employed for each titration.

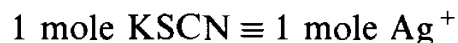
Pipette 25 mL of the standard 0.1 *M* silver nitrate into a 250 mL conical flask, add 5 mL of 6 *M* nitric acid and 1 mL of the iron(III) indicator solution. Run in the potassium or ammonium thiocyanate solution from a burette. At first a white precipitate is produced, rendering the liquid of a milky appearance, and as each drop of thiocyanate falls in, it produces a reddish-brown cloud, which quickly disappears on shaking. As the end point approaches, the precipitate becomes flocculent and settles easily; finally one drop of the thiocyanate solution produces a faint brown colour, which no longer disappears upon shaking. This is the end point. The indicator blank amounts to 0.01 mL of 0.1 *M* silver nitrate. It is essential to shake vigorously during the titration in order to obtain correct results.*

The standard solution thus prepared is stable for a very long period if evaporation is prevented.

Use of tartrazine as indicator. Satisfactory results may be obtained by the use of tartrazine as indicator. Proceed as above, but add 4 drops of tartrazine (0.5 per cent aqueous solution) in lieu of the iron(III) indicator. The precipitate will appear pale yellow during the titration, but the supernatant liquid (best viewed by placing the eye at the level of the liquid and looking through it) is colourless. At the end point, the supernatant liquid assumes a bright lemon-yellow colour. The titration is sharp to one drop of 0.1 *M* thiocyanate solution.

10.83 DETERMINATION OF SILVER IN A SILVER ALLOY

A commercial silver alloy in the form of wire or foil is suitable for this determination. Clean the alloy with emery cloth and weigh it accurately. Place it in a 250 mL conical flask, add 5 mL water and 10 mL concentrated nitric acid; place a funnel in the mouth of the flask to avoid mechanical loss. Warm the flask gently until the alloy has dissolved. Add a little water and boil for 5 minutes in order to expel oxides of nitrogen. Transfer the cold solution quantitatively to a 100 mL graduated flask and make up to the mark with distilled water. Titrate 25 mL portions of the solution with standard 0.1 *M* thiocyanate.



Note. The presence of metals whose salts are colourless does not influence the accuracy of the determination, except that mercury and palladium must be absent since their thiocyanates are insoluble. Salts of metals (e.g. nickel and cobalt) which are coloured must not be present to any considerable extent. Copper does not interfere, provided it does not form more than about 40 per cent of the alloy.

* The freshly precipitated silver thiocyanate adsorbs silver ions, thereby causing a false end point which, however, disappears with vigorous shaking.

Procedure. Pipette 25 mL of the standard 0.1 *M* sodium chloride into a 250 mL conical flask. Add 10 drops of either fluorescein or dichlorofluorescein indicator, and titrate with the silver nitrate solution in a diffuse light, while rotating the flask constantly. As the end point is approached, the silver chloride coagulates appreciably, and the local development of a pink colour upon the addition of a drop of the silver nitrate solution becomes more and more pronounced. Continue the addition of the silver nitrate solution until the precipitate suddenly assumes a pronounced pink or red colour. Repeat the titration with two other 25 mL portions of the chloride solution. Individual titrations should agree within 0.1 mL.

Calculate the molar concentration of the silver nitrate solution.

10.78 DETERMINATION OF CHLORIDES AND BROMIDES

Either the Mohr titration or the adsorption indicator method may be used for the determination of chlorides in neutral solution by titration with standard 0.1 *M* silver nitrate. If the solution is acid, neutralisation may be effected with chloride-free calcium carbonate, sodium tetraborate, or sodium hydrogencarbonate. Mineral acid may also be removed by neutralising most of the acid with ammonia solution and then adding an excess of ammonium acetate. Titration of the neutral solution, prepared with calcium carbonate, by the adsorption indicator method is rendered easier by the addition of 5 mL of 2 per cent dextrin solution; this offsets the coagulating effect of the calcium ion. If the solution is basic, it may be neutralised with chloride-free nitric acid, using phenolphthalein as indicator.

Similar remarks apply to the **determination of bromides**; the Mohr titration can be used, and the most suitable adsorption indicator is **eosin** which can be used in dilute solutions and even in the presence of 0.1 *M* nitric acid, but in general, acetic (ethanoic) acid solutions are preferred. Fluorescein may be used but is subject to the same limitations as experienced with chlorides [Section 10.77(b)]. With eosin indicator, the silver bromide flocculates approximately 1 per cent before the equivalence point and the local development of a red colour becomes more and more pronounced with the addition of silver nitrate solution: at the end point the precipitate assumes a magenta colour.

The indicator is prepared by dissolving 0.1 g eosin in 100 mL of 70 per cent ethanol, or by dissolving 0.1 g of the sodium salt in 100 mL of water.

For the **reverse titration** (bromide into silver nitrate), rhodamine 6G (10 drops of a 0.05 per cent aqueous solution) is an excellent indicator. The solution is best adjusted to 0.05 *M* with respect to silver ion. The precipitate acquires a violet colour at the end point.

Thiocyanates may also be determined using adsorption indicators in exactly similar manner to chlorides and bromides, but an iron(III) salt indicator is usually preferred (Section 10.82).

10.79 DETERMINATION OF IODIDES

Discussion. The Mohr method cannot be applied to the titration of iodides (or of thiocyanates), because of adsorption phenomena and the difficulty of distinguishing the colour change of the potassium chromate. Eosin is a suitable

CHAPTER 11

GRAVIMETRY

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.

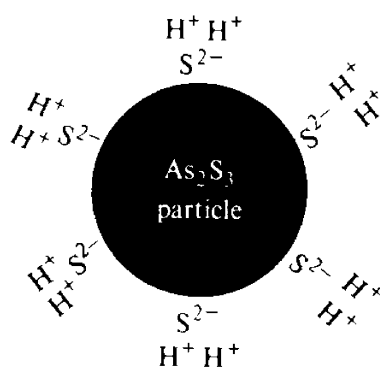


Fig. 11.1

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.^{26,27}

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.

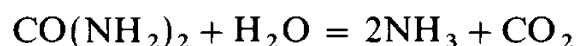
11.7 PRECIPITATION FROM HOMOGENEOUS SOLUTION

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:

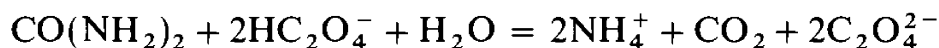
1. the precipitation of barium as barium chromate in the presence of ammonium acetate;
2. the precipitation of large amounts of nickel as the dimethylglyoximate; and
3. the precipitation of aluminium as the oxinate.

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

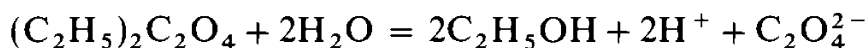
heating gives a dense precipitate of variable composition, which is ignited to and weighed as the dipolyphosphate (pyrophosphate) ZrP_2O_7 .

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 HC_2O_4^- , thus affording a method for the slow generation of oxalate ion. Calcium oxalate may thus be precipitated in a dense form:



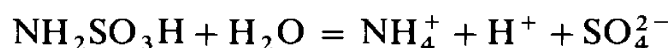
Dimethyl oxalate and diethyl oxalate can also be hydrolysed to yield oxalate ion:



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.

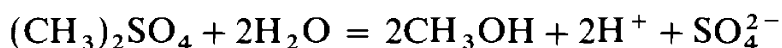
Calcium can be determined as the oxalate by precipitation from homogeneous solution by cation release from the EDTA complex in the presence of oxalate ion.²⁸

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:



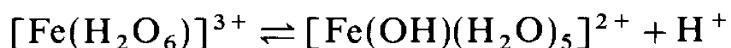
11.8 WASHING THE PRECIPITATE

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 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 2.2×10^{-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.

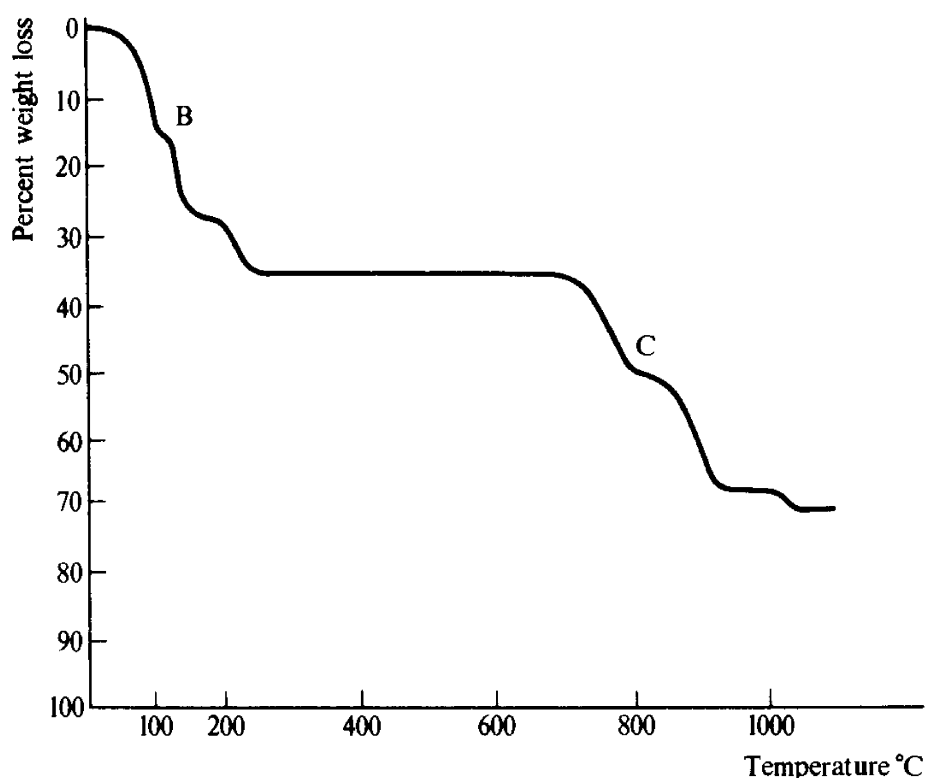


Fig. 11.2

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 Duval²⁹ 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.

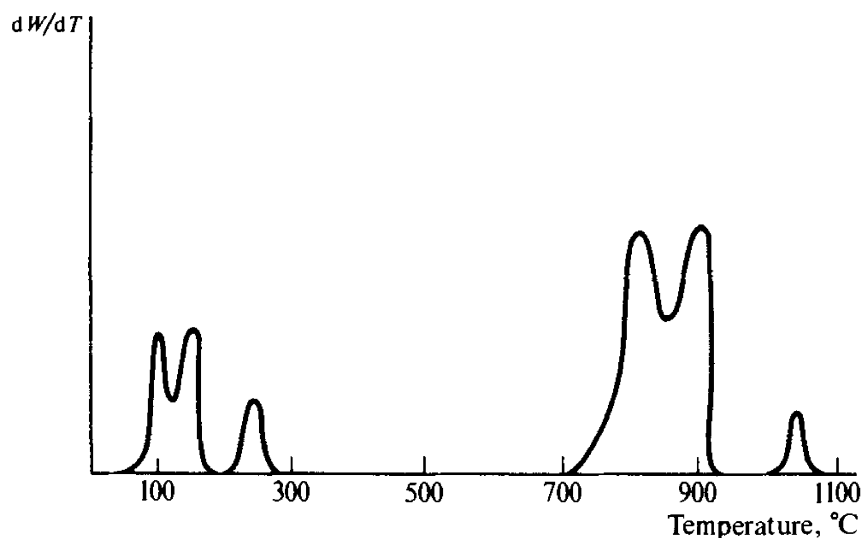


Fig. 11.3

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 Newkirk³⁰ and by Coats and Redfern³¹ 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.

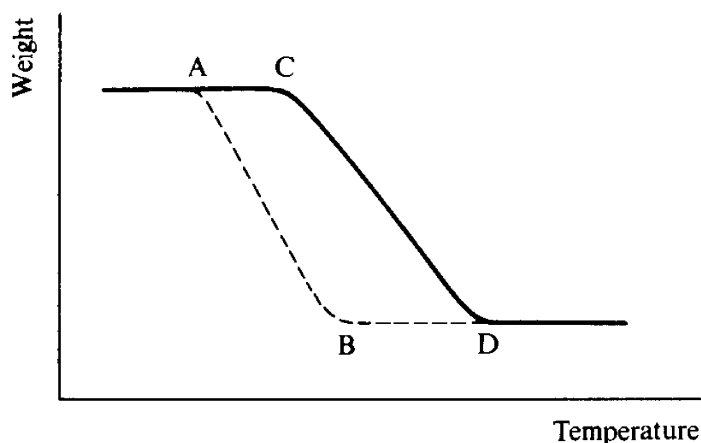


Fig. 11.4

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.³² 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.³³ 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 Knight³⁴ that $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ 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.³⁵

QUANTITATIVE SEPARATIONS BASED UPON PRECIPITATION METHODS

11.10 FRACTIONAL PRECIPITATION

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