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:

$$Ce^{4+} + Fe^{2+} \rightleftharpoons Ce^{3+} + Fe^{3+}$$

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

For (1) at 25 °C:

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

For (2), at 25 °C:

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

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

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

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 $[Fe^{3+}]/[Fe^{2+}]$. When 10 mL of the oxidising agent have been added, $[Fe^{3+}]/[Fe^{2+}] = 10/90$ (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, $E_1 = E_1^{\ominus} = 0.75$ volt
With 90 mL, $E_1 = 0.75 + 0.0591\log 90/10 = 0.81$ volt
With 99 mL, $E_1 = 0.75 = 0.0591\log 99/1 = 0.87$ volt
With 99.9 mL, $E_1 = 0.75 + 0.0591\log 99.9/0.1 = 0.93$ volt

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

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 $[Ce^{4+}]/[Ce^{3+}]$. Thus:

With 100.1 mL, $E_2 = 1.45 + 0.059\,1 \log 0.1/100 = 1.27$ volts
With 101 mL, $E_2 = 1.45 + 0.059\,1 \log 1/100 = 1.33$ volts
With 110 mL, $E_2 = 1.45 + 0.059\,1 \log 10/100 = 1.39$ volts
With 190 mL, $E_2 = 1.45 + 0.059\,1 \log 90/100 = 1.45$ volts

These results are shown in Fig. 10.14.

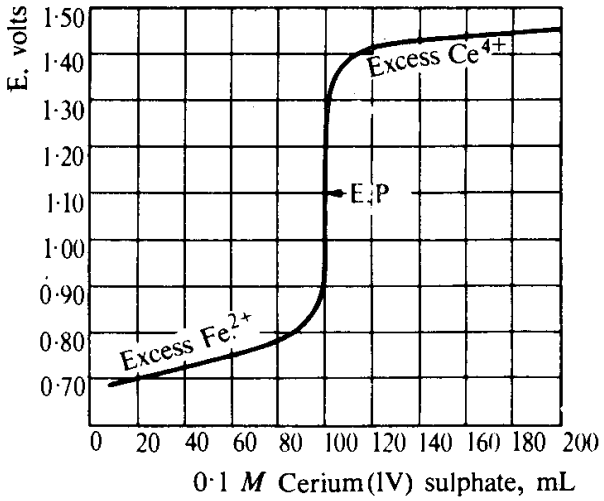


Fig. 10.14 Titration of 100 mL of 0.1*M* iron(II) with 0.1*M* cerium(IV) sulphate (calculated).

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, $[Fe^{2+}] = 0.1 \times 0.1/199.9 = 5 \times 10^{-5}$, or $pFe^{2+} = 4.3$. The concentration at the equivalence point is given by (Section 2.33):

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

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

$a\,Ox_I + b\,Red_{II} \rightleftharpoons b\,Ox_{II} + a\,Red_I$

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 Ox_I, Red_I, and $E_2^{\ominus}$ to Ox_{II}, Red_{II}.

purpose from the equations:

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

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

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

or

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

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

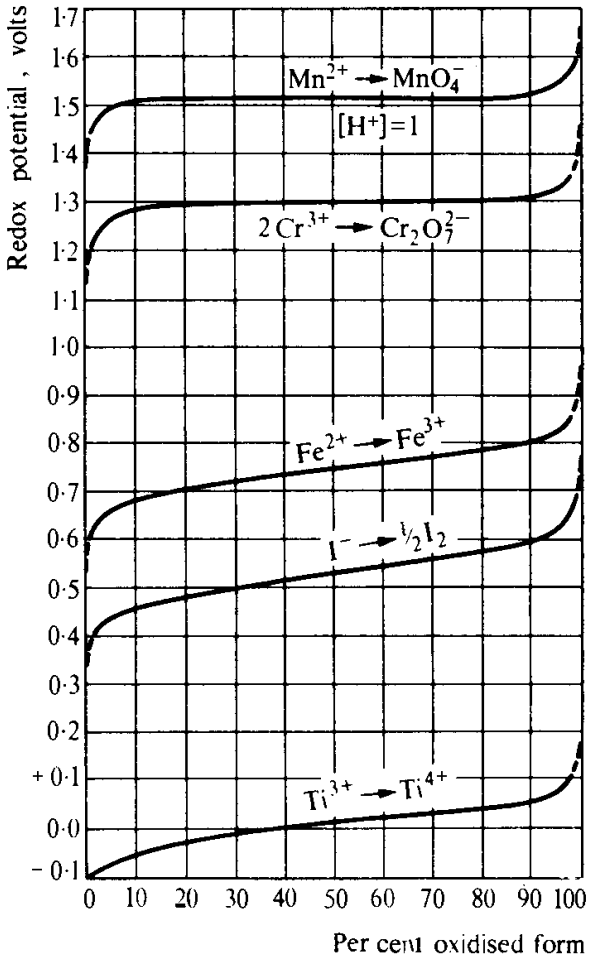


Fig. 10.15 Variation of redox potentials with oxidant/reductant ratio.

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 $Cr_2O_7^{2-}/Cr^{3+}$ 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:

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

where $E^{\ominus\prime}$ 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 $E^{\ominus\prime}$ 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:

$[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-}$; $E^{\ominus} = +0.36$ volt

$I_2 + 2e \rightleftharpoons 2I^-$; $E^{\ominus} = +0.54$ volt

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

$$2[Fe(CN)_6]^{4-} + I_2 = 2[Fe(CN)_6]^{3-} + 2I^-$$

In fact $[Fe(CN)_6]^{4-}$ 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 $H_4Fe(CN)_6$ are weaker than those derived from $H_3Fe(CN)_6$; the activity of the $[Fe(CN)_6]^{4-}$ ion is decreased to a greater extent than that of the $[Fe(CN)_6]^{3-}$ 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, $E^{\ominus\prime} = +0.73$ 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 $E^{\ominus\prime} = +1.44$ 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:

$$In_{Ox} + ne \rightleftharpoons In_{Red}$$

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:

$$E = E^{\ominus}_{In} + \frac{RT}{nF} \ln a_{In.ox}/a_{In.Red}$$

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

where $E^{\ominus}_{In}$ 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 $[In_{Ox}]/[In_{Red}]$ from 10 to $\frac{1}{10}$, this leads to an interval of potential of:

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

If the colour intensities of the two forms differ considerably the intermediate colour is attained at potential somewhat removed from $E^{\ominus}_{In}$, but the error is unlikely to exceed 0.06 volt. For a sharp colour change at the end point, $E^{\ominus}_{In}$ 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:

$$\underset{\text{Pale blue}}{[Fe(C_{12}H_8N_2)_3]^{3+}} + e \rightleftharpoons \underset{\text{Deep red}}{[Fe(C_{12}H_8N_2)_3]^{2+}}$$

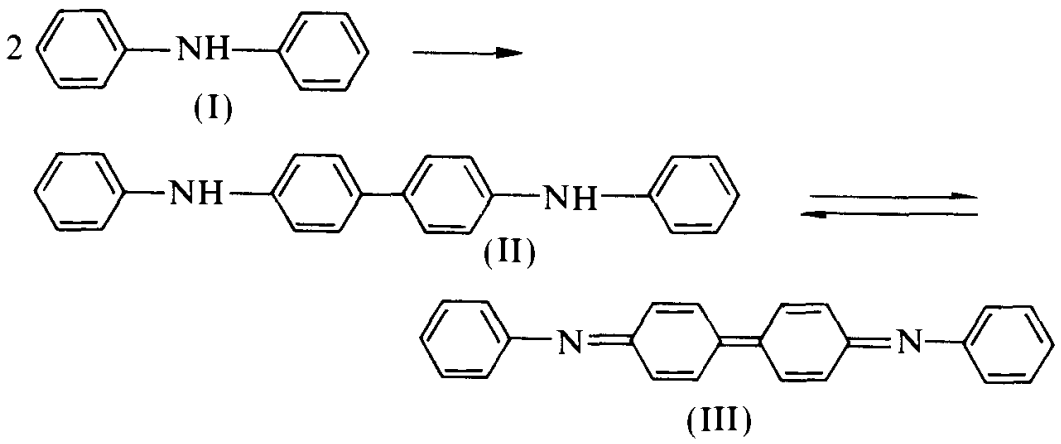
The standard redox potential is 1.14 volts; the formal potential is 1.06 volts in 1 M hydrochloric acid solution. The colour change, however, occurs at about 1.12 volts, because the colour of the reduced form (deep red) is so much more intense than that of the oxidised form (pale blue). The indicator 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 ($E^{\ominus}_{\text{In}}$) 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,	Purple red	Colourless	0.89
4,7-Dimethyl-1,10-phenanthroline iron(II) sulphate (4,7-dimethylferroin)	Pale blue	Red	0.88
Diphenylaminesulphonic acid	Red–violet	Colourless	0.85
Diphenylbenzidine	Violet	Colourless	0.76
Diphenylamine	Violet	Colourless	0.76
3,3′-Dimethylnaphthidine	Purplish-red	Colourless	0.71
Starch–I_3^-,KI	Blue	Colourless	0.53
Methylene blue	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:

$$M^{+} + Ce^{4+} \rightarrow M^{2+} + Ce^{3+}$$

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:

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$$

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:

$$2MnO_4^- + 10Cl^- + 16H^+ = 2Mn^{2+} + 5Cl_2 + 8H_2O$$

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 ($MnSO_4,4H_2O$) 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 MnO_4^- – 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)

sulphate is to supply an adequate concentration of Mn^{2+} ions to react with any local excess of permanganate ion. Mn(III) is probably formed in the reduction of permanganate ion to manganese(II); the Mn(II), and also the orthophosphoric acid, exert a depressant effect upon the potential of the Mn(III)–Mn(II) couple, so that Mn(III) is reduced by Fe^{2+} ion rather than by chloride ion. The phosphoric(V) acid combines with the yellow Fe^{3+} ion to form the complex ion $[Fe(HPO_4)]^+$, thus rendering the end point more clearly visible. The phosphoric(V) acid lowers the reduction potential of the Fe(III)–Fe(II) system by complexation, and thus tends to increase the reducing power of the Fe^{2+} ion. Under these conditions permanganate ion oxidises iron(II) rapidly and reacts only slowly with chloride ion.

For the titration of colourless or slightly coloured solutions, the use of an indicator is unnecessary, since as little as 0.01 mL of 0.02*M* potassium permanganate imparts a pale-pink colour to 100 mL of water. The intensity of the colour in dilute solutions may be enhanced, if desired, by the addition of a redox indicator (such as sodium diphenylamine sulphonate, *N*-phenylanthranilic acid, or ferroin) just before the end point of the reaction; this is usually not required, but is advantageous if more dilute solutions of permanganate are used.

Potassium permanganate may also be used in *strongly* alkaline solutions. Here two consecutive partial reactions take place:
(1) the relatively rapid reaction:

$$MnO_4^- + e \rightleftharpoons MnO_4^{2-}$$

and (2) the relatively slow reaction:

$$MnO_4^{2-} + 2H_2O + 2e \rightleftharpoons MnO_2 + 4OH^-$$

The standard potential $E^\ominus$ of reaction (1) is 0.56 volt and of reaction (2) 0.60 volt. By suitably controlling the experimental conditions (e.g. by the addition of barium ions, which form the sparingly soluble barium manganate as a fine, granular precipitate), reaction (1) occurs almost exclusively. In *moderately alkaline* solutions permanganate is reduced quantitatively to manganese dioxide. The half-cell reaction is:

$$MnO_4^- + 2H_2O + 3e \rightleftharpoons MnO_2 + 4OH^-$$

and the standard potential $E^\ominus$ is 0.59 volt.

Potassium permanganate is not a primary standard. It is difficult to obtain the substance perfectly pure and completely free from manganese dioxide. Moreover, ordinary distilled water is likely to contain reducing substances (traces of organic matter, etc.) which will react with the potassium permanganate to form manganese dioxide. The presence of the latter is very objectionable because it catalyses the auto-decomposition of the permanganate solution on standing:

$$4MnO_4^- + 2H_2O = 4MnO_2 + 3O_2 + 4OH^-$$

Permanganate is inherently unstable in the presence of manganese(II) ions:

$$2MnO_4^- + 3Mn^{2+} + 2H_2O = 5MnO_2 + 4H^+$$

This reaction is slow in acid solution, but it is very rapid in neutral solution. For these reasons, potassium permanganate solution is rarely made up by dissolving weighed amounts of the purified solid in water; it is more usual to

heat a freshly prepared solution to boiling and keep it on the steam bath for an hour or so, and then filter the solution through a non-reducing filtering medium, such as purified glass wool or a sintered-glass filtering crucible (porosity No. 4). Alternatively, the solution may be allowed to stand for 2–3 days at room temperature before filtration. The glass-stoppered bottle or flask should be carefully freed from grease and prior deposits of manganese dioxide: this may be done by rinsing with dichromate–sulphuric acid cleaning mixture* and then thoroughly with distilled water. Acidic and alkaline solutions are less stable than neutral ones. Solutions of permanganate should be protected from unnecessary exposure to light: a dark-coloured bottle is recommended. Diffuse daylight causes no appreciable decomposition, but bright sunlight slowly decomposes even pure solutions.

Potassium permanganate solutions may be standardised using arsenic(III) oxide or sodium oxalate as primary standards: secondary standards include metallic iron, and iron(II) ethylenediammonium sulphate (or ethylenediamine iron(II) sulphate), $FeSO_4,C_2H_4(NH_3)_2SO_4,4H_2O$. Full details of the first two methods are given in Section 10.93 below. Standardisation using metallic iron is similar to that for potassium dichromate given in Section 10.100.

10.93 PREPARATION OF 0.02 *M* POTASSIUM PERMANGANATE

Weigh out about 3.2–3.25 g potassium permanganate on a watchglass, transfer it to a 1500 mL beaker, add 1 L water, cover the beaker with a clockglass, heat the solution to boiling, boil gently for 15–30 minutes and allow the solution to cool to the laboratory temperature. Filter the solution through a funnel containing a plug of purified glass wool, or, more simply, through a sintered-glass or porcelain filtering crucible or funnel. Collect the filtrate in a vessel which has been cleaned with chromic acid mixture* and then thoroughly washed with distilled water. The filtered solution should be stored in a clean, glass-stoppered bottle, and kept in the dark or in diffuse light except when in use: alternatively, it may be kept in a dark brown glass bottle.

10.94 STANDARDISATION OF PERMANGANATE SOLUTIONS

Method A: With arsenic(III) oxide. This procedure, which utilises arsenic(III) oxide as a primary standard and potassium iodide or potassium iodate as a catalyst for the reaction, is convenient in practice and is a trustworthy method for the standardisation of permanganate solutions. Analytical grade arsenic(III) oxide has a purity of at least 99.8 per cent, and the results by this method agree to within 1 part in 3000 with the sodium oxalate procedure (Method B, below).

$$As_2O_3 + 4OH^- = 2HAsO_3^{2-} + H_2O$$

$$5H_3AsO_3 + 2MnO_4^- + 6H^+ = 5H_3AsO_4 + 2Mn^{2+} + 3H_2O$$

Procedure. Dry some arsenic(III) oxide at 105–110 °C for 1–2 hours, cover the container, and allow to cool in a desiccator. Accurately weigh approximately

* **Caution:** This is a very powerful reagent and should only be used by experienced chemists.

0.25 g of the dry oxide, and transfer it to a 400 mL beaker. Add 10 mL of a cool solution of sodium hydroxide, prepared from 20 g sodium hydroxide and 100 mL water (Note 1). Allow to stand for 8–10 minutes, stirring occasionally. When solution is complete, add 100 mL water, 10 mL pure concentrated hydrochloric acid, and 1 drop 0.0025*M* potassium iodide or potassium iodate (Note 2). Add the permanganate solution from a burette until a faint pink colour persists for 30 seconds. Add the last 1–1.5 mL dropwise, allowing each drop to become decolorised before the next drop is introduced. For the most accurate work it is necessary to determine the volume of permanganate solution required to duplicate the pink colour at the end point. This is done by adding permanganate solution to a solution containing the same amounts of alkali, acid, and catalyst as were used in the test. The correction should not be more than 0.03 mL. Repeat the determination with two other similar quantities of oxide. Calculate the concentration of the potassium permanganate solution. Duplicate determinations should agree within 0.1 per cent.

Notes. (1) For *elementary students*, it is sufficient to weigh out accurately about 1.25 g of arsenic(III) oxide, dissolve this in 50 mL of a cool 20 per cent solution of sodium hydroxide, and make up to 250 mL in a graduated flask. Shake well. Measure 25.0 mL of this solution by means of a burette and **not** with a pipette (**caution — the solution is highly poisonous**) into a 500 mL conical flask, add 100 mL water, 10 mL pure concentrated hydrochloric acid, one drop potassium iodide solution, and titrate with the permanganate solution to the first permanent pink colour as detailed above. Repeat with two other 25 mL portions of the solution. Successive titrations should agree within 0.1 mL.

(2) 0.0025*M* Potassium iodide = 0.41 g KI L^{-1}. 0.0025*M* Potassium iodate = 0.54 g KIO_3 L^{-1}.

Calculation. It is evident from the equation given above that if the weight of arsenic(III) oxide is divided by the number of millilitres of potassium permanganate solution to which it is equivalent, as found by titration, we have the weight of primary standard equivalent to 1 mL of the permanganate solution.

Method B: With sodium oxalate. This reagent is readily obtained pure and anhydrous, and the ordinary material has a purity of at least 99.9 per cent. In the experimental procedure originally employed a solution of the oxalate, acidified with dilute sulphuric acid and warmed to 80–90 °C, was titrated with the permanganate solution slowly (10–15 mL min^{-1}) and with constant stirring until the first permanent faint pink colour was obtained; the temperature near the end-point was not allowed to fall below 60 °C. However with this procedure the results may be 0.1–0.45 per cent high; the titre depends upon the acidity, the temperature, the rate of addition of the permanganate solution, and the speed of stirring. Because of this it is best to make *a more rapid* addition of 90–95 per cent of the permanganate solution (about 25–35 mL min^{-1}) to a solution of sodium oxalate in 1 *M* sulphuric acid at 25–30 °C, the solution is then warmed to 55–60 °C and the titration completed, the last 0.5–1 mL portion being added dropwise. The method is accurate to 0.06 per cent. Full experimental details are given below.

$$2Na^+ + C_2O_4^{2-} + 2H^+ \rightleftharpoons H_2C_2O_4 + 2Na^+$$

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ = 2Mn^{2+} + 10CO_2 + 8H_2O$$

It should be mentioned that if oxalate is to be determined it is often not convenient to use the room temperature technique for unknown amounts of

oxalate. The permanganate solution may then be standardised against sodium oxalate at about 80 °C using the same procedure in the standardisation as in the analysis.

Procedure. Dry some analytical grade sodium oxalate at 105–110 °C for 2 hours, and allow it to cool in a covered vessel in a desiccator. Weigh out accurately from a weighing bottle about 0.3 g of the dry sodium oxalate into a 600 mL beaker, add 240 mL of recently prepared distilled water, and 12.5 mL of concentrated sulphuric acid (**caution**) or 250 mL of 1 *M* sulphuric acid. Cool to 25–30 °C and stir until the oxalate has dissolved (Note 1). Add 90–95 per cent of the required quantity of permanganate solution from a burette at a rate of 25–35 mL min^{-1} while stirring slowly (Note 2). Heat to 55–60 °C (use a thermometer as stirring rod), and complete the titration by adding permanganate solution until a faint pink colour persists for 30 seconds. Add the last 0.5–1 mL dropwise, with particular care to allow each drop to become decolorised before the next is introduced. For the most exact work, it is necessary to determine the excess of permanganate solution required to impart a pink colour to the solution. This is done by matching the colour produced by adding permanganate solution to the same volume of boiled and cooled dilute sulphuric acid at 55–60 °C. This correction usually amounts to 0.03–0.05 mL. Repeat the determination with two other similar quantities of sodium oxalate.

Notes. (1) For *elementary students*, it is sufficient to weigh out accurately about 1.7 g of sodium oxalate, transfer it to a 250 mL graduated flask, and make up to the mark. Shake well, Use 25 mL of this solution per titration and add 150 mL of *ca* 1 *M* sulphuric acid. Carry out the titration rapidly at the ordinary temperature until the *first* pink colour appears throughout the solution, and allow to stand until the solution is colourless. Warm the solution to 50–60 °C and continue the titration to a permanent faint pink colour. It must be remembered that oxalate solutions attack glass, so that the solution should not be stored more than a few days.

(2) An approximate value of the volume of permanganate solution required can be computed from the weight of sodium oxalate employed. In the first titration about 75 per cent of this volume is added, and the determination is completed at 55–60 °C. Thereafter, about 90–95 per cent of the volume of permanganate solution is added at the laboratory temperature.

Provided that it is stored with due regard to the precautions referred to in Section 10.92 the standardised permanganate solution will keep for a long time, but it is advisable to re-standardise the solution frequently to confirm that no decomposition has set in.

10.95 ANALYSIS OF HYDROGEN PEROXIDE

Hydrogen peroxide is usually encountered in the form of an aqueous solution containing about 6 per cent, 12 per cent or 30 per cent hydrogen peroxide, and frequently referred to as '20-volume', '40-volume', and '100-volume' hydrogen peroxide respectively; this terminology is based upon the volume of oxygen liberated when the solution is decomposed by boiling. Thus 1 mL of '100-volume' hydrogen peroxide will yield 100 mL of oxygen measured at standard temperature and pressure.

The following reaction occurs when potassium permanganate solution is added to hydrogen peroxide solution acidified with dilute sulphuric acid:

$$2MnO_4^- + 5H_2O_2 + 6H^+ = 2Mn^{2+} + 5O_2 + 8H_2O$$

This forms the basis of the method of analysis given below.

It is good practice to use a fairly high concentration of acid and a reasonably low rate of addition in order to reduce the danger of forming manganese dioxide, which is an active catalyst for the decomposition of hydrogen peroxide. For slightly coloured solutions or for titrations with dilute permanganate, the use of ferroin as indicator is recommended. Organic substances may interfere. A fading end point indicates the presence of organic matter or other reducing agents, in which case the iodometric method is better (Section 10.118).

Procedure. Transfer 25.0 mL of the '20-volume' solution by means of a burette to a 500 mL graduated flask, and dilute with water to the mark. Shake thoroughly. Pipette 25.0 mL of this solution to a conical flask, dilute with 200 mL water, add 20 mL dilute sulphuric acid (1:5), and titrate with standard 0.02*M* potassium permanganate to the first permanent, faint pink, colour. Repeat the titration; two consecutive determinations should agree within 0.1 mL.

Calculate: (i) the weight of hydrogen peroxide per L of the original solution and (ii) the 'volume strength', i.e. the number of millilitres of oxygen at s.t.p. that can be obtained from 1 mL of the original solution.

Analysis of metallic peroxides. A metallic peroxide, such as **sodium peroxide**, can be analysed in similar manner, provided that care is taken to avoid loss of oxygen during the dissolution of the peroxide. This may be done by working in a medium containing boric acid which is converted to the relatively stable 'perboric acid' upon the addition of the peroxide.

Procedure. To 100 mL of distilled water, add 5 mL of concentrated sulphuric acid, cool and then add 5 g of pure boric acid; when this has dissolved cool the mixture in ice. Transfer gradually from a weighing bottle about 0.5 g (accurately weighed) of the sodium peroxide sample (**handle with care**) to the well-stirred, ice-cold solution. When the addition is complete, transfer the solution to a 250 mL graduated flask, make up to the mark, and then titrate 50 mL portions of the solution with standard 0.02*M* permanganate solution.

10.96 DETERMINATION OF NITRITES

Discussion. Nitrites react in warm acid solution (*ca* 40 °C) with permanganate solution in accordance with the equation:

$$2MnO_4^- + 5NO_2^- + 6H^+ = 2Mn^{2+} + 5NO_3^- + 3H_2O$$

If a solution of a nitrite is titrated in the ordinary way with potassium permanganate, poor results are obtained, because the nitrite solution has first to be acidified with dilute sulphuric acid. Nitrous acid is liberated, which being volatile and unstable, is partially lost. If, however, a measured volume of standard potassium permanganate solution, acidified with dilute sulphuric acid, is treated with the nitrite solution, added from a burette, until the permanganate is just decolorised, results accurate to 0.5–1 per cent may be obtained. This is due to the fact that nitrous acid does not react instantaneously with the permanganate. This method may be used to determine the purity of commercial potassium nitrite.