REDOX
Reduction-Oxidation Titration

An application method of
Inorganic Pharmaceutical Analysis

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In **acid-base titrations**, the change in pH during titration may be calculated, and the titration curves thus obtained can be used to ascertain the most suitable indicator to be used in a given titration, and 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.

$$E = E^{o} + 0.0591/n \cdot \log [Ox]/[Red] \quad \text{at } 25\ ^{o}C$$

Standard potentials E^{o} 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 may differ from those to which the ideal standard potentials apply.

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

The **formal potential** **Eo’** 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, e.g. 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.

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 titration is the ratio [Ox]/[Red]. We are concerned here with two systems :

1) the Fe^{3+}/Fe^{2+} ion electrode, and

2) the Ce^{4+}/Ce^{3+} ion electrode.

For (1) at 25 °C:

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

For (2), at 25 °C:

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

The equilibrium constant of the reaction is given by

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

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, $[Fe^{3+}]/[Fe^{2+}] = 10/90$ (approximately) and
$E_1 = 0.75 + 0.0591 \log 10/90 = 0.75 - 0.056 =$ 0.69 volt

With 50 mL of the oxidising agent, $E_1 = E^o{}_1 =$ 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 $[Ce^{4+}] = [Fe^{2+}]$

The electrode potential is given by :

$(E_1 + E_2)/2 = (0.75 + 1.45)/2 =$ 1.10 volts

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

Thus :

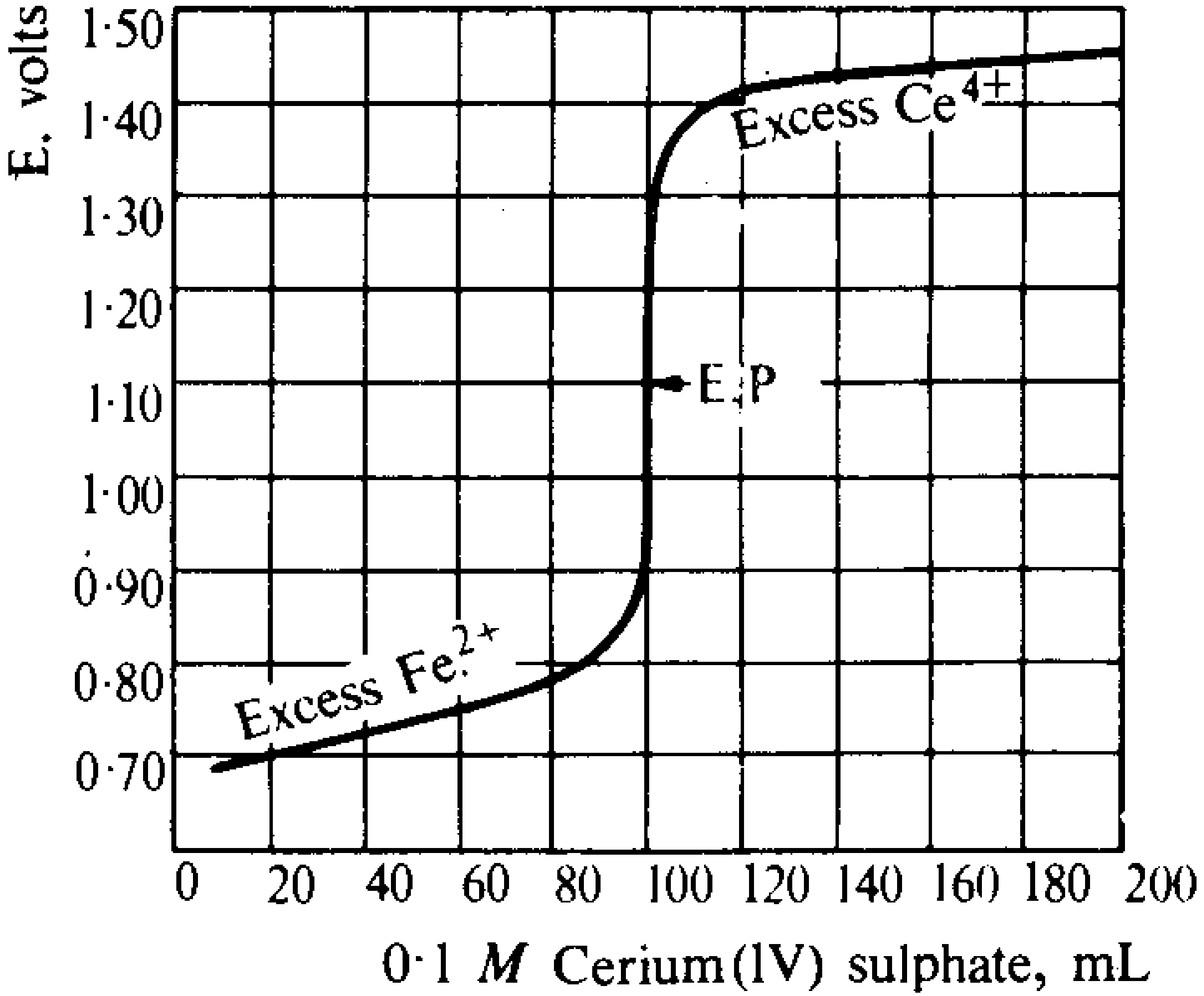
With 100.1 mL, $E_1 = 1.45 + 0.0591 \log 0.1/100 =$ 1.27 volts

With 101 mL, $E_1 = 1.45 + 0.0591 \log 1/100 =$ 1.33 volts

With 110 mL, $E_1 = 1.45 + 0.0591 \log 10/100 =$ 1.39 volts

With 190 mL, $E_1 = 1.45 + 0.0591 \log 90/100 =$ 1.45 volts

Titration of 100 mL of 0.1 M iron(II) with 0.1 M cerium(IV) sulphate



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

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

Now $[Fe^{3+}] = 0.05$ M, 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 is 1.27 volts. The $[Fe^{3+}]$ is practically unchanged at 5×10^{-2} M, and we may calculate $[Fe^{2+}]$ with sufficient accuracy for our purpose from the equation :

$$E = E^{o}_{1} + 0.0591 \log [Fe^{3+}]/[Fe^{2+}]$$

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

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

or

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

Thus pFe^{2+} changes from 4.3 to 10 between 0.1 per cent before and 0.1 percent after the stoichiometric end point.

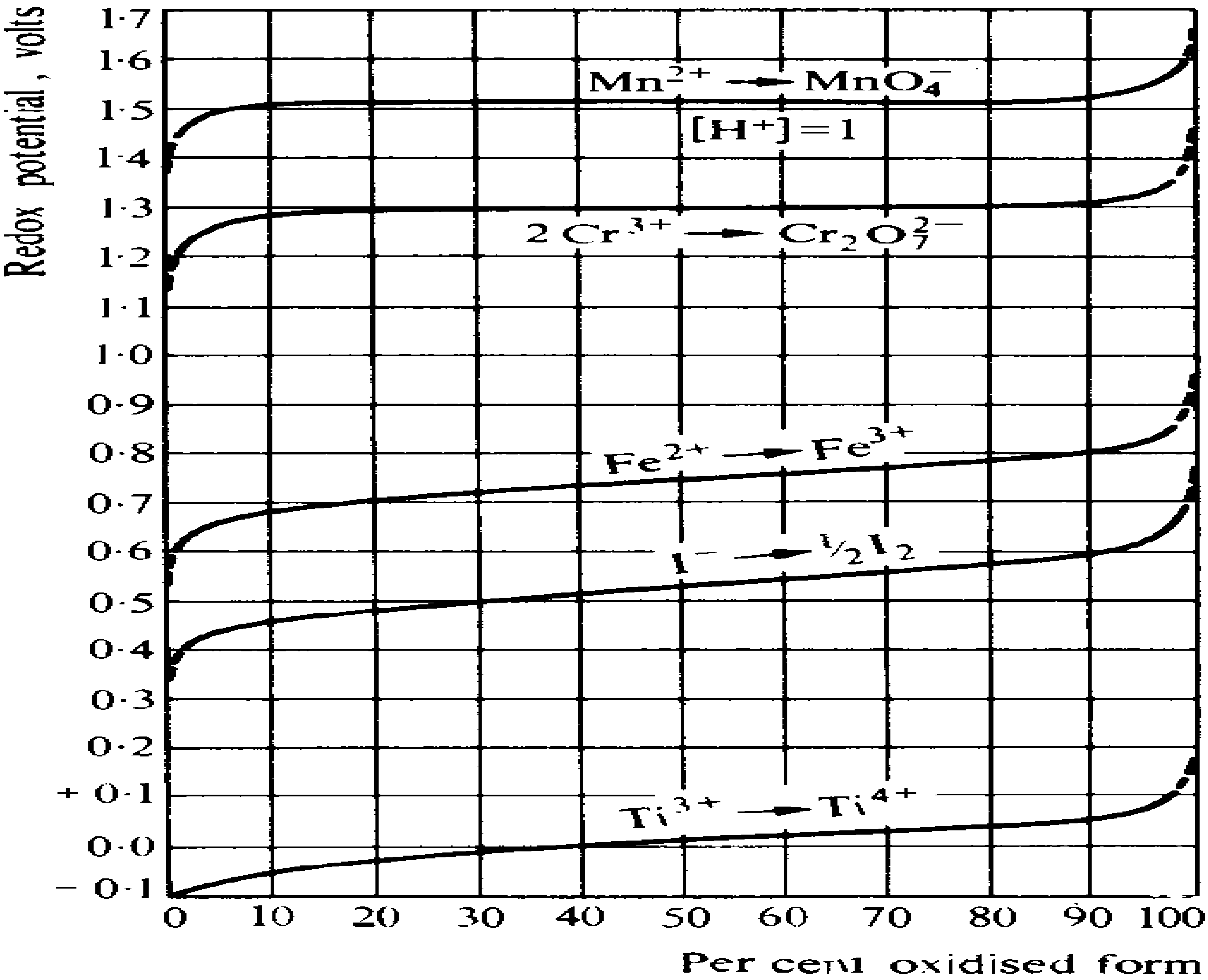
These quantities are of importance in connection with the use of indicators for the detection of the equivalence point.

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 MnO_4/Mn^{2+} system and others which are dependent upon the pH of the solution, the hydrogen-ion concentration is assumed to be molar : lower acidities give lower potentials. The value at 50% 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.


Redox potential, volts
1·7
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
+ 0·1
0·0
− 0·1
$Mn^{2+} \rightarrow MnO_4^-$
$[H^+] = 1$
$2\,Cr^{3+} \rightarrow Cr_2O_7^{2-}$
$Fe^{2+} \rightarrow Fe^{3+}$
$I^- \rightarrow \frac{1}{2} I_2$
$Ti^{3+} \rightarrow Ti^{4+}$
0
10
20
30
40
50
60
70
80
90
100
Per cent oxidised form

Redox Indicators

The ideal oxidation-reduction indicator will be one with an oxidation potential intermediate between that of the solution titrated (analyte) and that of the titrant, and which exhibits a sharp,readily detectable colour change.

An 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 :

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

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

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

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

If the colour intensities of the two forms differ considerably the intermediate colour is attained at potential somewhat removed from E^o, but the error is unlikely to exceed 0.06 volt.

For a sharp colour change at the end point, E^o 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 :

$$\underset{\text{Pale blue}}{[\mathrm{Fe}(\mathrm{C}_{12}\mathrm{H}_8\mathrm{N}_2)_3]^{3+}} + e \rightleftharpoons \underset{\text{Deep red}}{[\mathrm{Fe}(\mathrm{C}_{12}\mathrm{H}_8\mathrm{N}_2)_3]^{2+}}$$

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 the indicator blank is negligible at this or higher concentrations.

The earliest internal indicators 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.

Diphenylamine

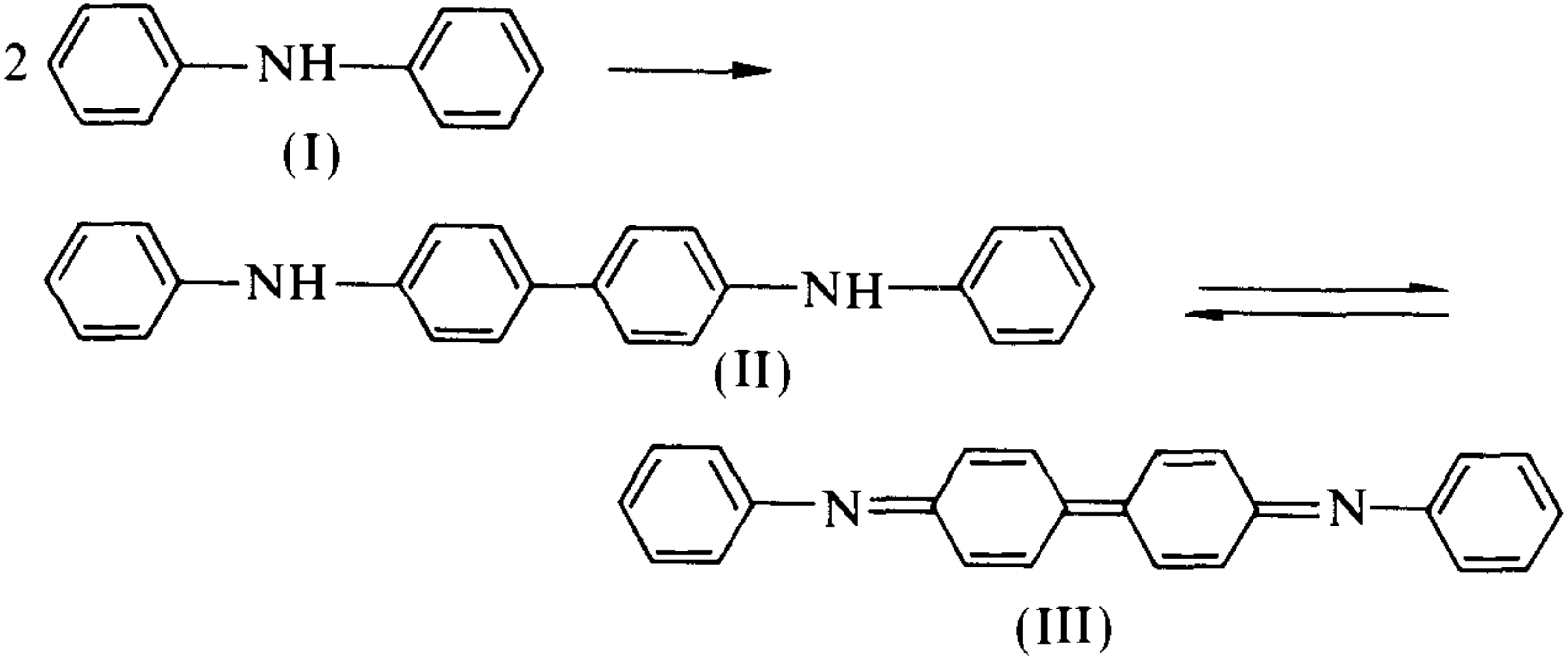


Table 10.9 Some oxidation–reduction indicators

Indicator	Colour change Oxidised form	 Reduced form	Formal potential at pH = 0 (volts)
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

Redox Titration Methods

- Permanganometry
- Dichromatometry
- Cerimetry
- Iodometry & Iodimetry
- Iodatometry
- Bromatometry

1. Permanganometric Titration

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° 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. 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.

Potassium permanganate in strongly alkaline solution can take place two reactions :

(1) In rapid reaction :

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

(2) In slow reaction :

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

Standard potential E° of reaction (1) is 0.56 volt and of reaction (2) is 0.60 volt. By controlling the experimental conditions (e.g. by addition of barium ions to form a fine granular precipitate of sparingly soluble barium manganate) reaction (1) will be the only occured.

In moderate alkaline solution, permanganate will be reduced quantitatively to form manganese dioxide with a half-cell reaction :

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

Standard potential E° is 0.59 volt.

$KMnO_4$ 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 :

$$4\ MnO_4 + 2\ H_2O \rightleftarrows 4\ MnO_2 + 3\ O_2 + 4\ OH$$

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

$$2\ MnO_4 + 3\ Mn^{2+} + 2\ H_2O \rightleftarrows 5\ MnO_2 + 4\ H^+$$

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.

STANDARDIZATION OF $KMnO_4$

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).

$$As_2O_3 + 4OH^- \rightleftharpoons 2\,HAsO_3^{2-} + H_2O$$

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

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 OC, 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 ^{o}C. However with this procedure the results may be 0.1-0.45 percent 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-') to a solution of sodium oxalate in 1 M sulphuric acid at 25-30 OC, the solution is then warmed to 55-60 OC and the titration completed, the last 0.5-1 mL portion being added dropwise.

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

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

DETERMINATION 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.

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

DETERMINATION OF NITRITES

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

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.

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

2. Di(or Bi)chromatometric Titration

Potassium dichromate is not such a powerful oxidising agent as potassium permanganate, but it has several advantages over the latter substance. It can be obtained pure, it is stable up to its fusion point, and it is therefore an excellent primary standard. Standard solutions of exactly known concentration can be prepared by weighing out the pure dry salt and dissolving it in the proper volume of water. Furthermore, the aqueous solutions are stable indefinitely if adequately protected from evaporation. Potassium dichromate is used only in acid solution, and is reduced rapidly at the ordinary temperature to a green chromium(III) salt.

In acid solution :

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ = 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$$

The green colour due to the Cr^{3+} ions formed by the reduction of potassium dichromate makes it impossible to ascertain the end-point of a dichromate titration by simple visual inspection of the solution and so a redox indicator must be employed which gives a strong and unmistakable colour change; this procedure has rendered obsolete the external indicator method which was formerly widely used.

Suitable indicators for use with dichromate titrations include **N-phenylanthranilic acid** (0.1 per cent solution in 0.005 M NaOH) and **sodium diphenylamine sulphonate** (0.2 per cent aqueous solution); the latter must be used in presence of phosphoric (V) acid.

DETERMINATION OF C.O.D

One very important application of potassium dichromate is in a back-titration for the environmental determination of the amount of oxygen required to oxidise all the organic material in a sample of impure water, such as sewage effluent. This is known as the chemical oxygen demand (C.O.D.) and is expressed in terms of milligrams of oxygen required per litre of water, mgL^{-1}.

The analysis of the impure water sample is carried out in parallel with a blank determination on pure, double-distilled water.

Procedure.

Place a 50 mL volume of the water sample in a 250 mL conical flask with a ground-glass neck which can be fitted with a water condenser for refluxing. Add 1 g of mercury(II) sulphate, followed by 80 mL of a silver sulphate/ sulphuric acid solution. Then add 10 mL of approximately 0.00833 M standard potassium dichromate solution, fit the flask with the reflux condenser and boil the mixture for 15 minutes. On cooling rinse the inside of the condenser with 50 mL of water into the flask contents. Add either diphenylamine indicator (1 mL) or ferroin indicator and titrate with 0.025 M ammonium iron(II) sulphate solution. Diphenylamine gives a colour change from blue to green at the end-point, whilst that for ferroin is blue-green to red-brown. Call this titration A mL. Repeat the back-titration for the blank (titration B mL). The difference between the two values is the amount of potassium dichromate used up in the oxidation.

The C.O.D. is calculated from the relationship:

$$\text{C.O.D.} = (A - B) \times 0.2 \times 20 \text{ mgL}^{-1}$$

as a 1 mL difference between the titrations corresponds to 0.2 mg of oxygen required by the 50 mL sample (a correction must, of course, be made if solutions of slightly different molarities are employed).

3. Cerimetric Titration

$$Ce^{4+} + e \rightleftharpoons Ce^{3+}$$

Cerium(IV) sulphate is a powerful oxidising agent; its reduction potential in 0.5-4.0 M sulphuric acid at 25 °C is 1.43 ± 0.05 volts. It can be used only in acid solution, best in 0.5 M or higher concentrations : as the solution is neutralised, cerium(IV) hydroxide [hydrated cerium(IV)oxide] or basic salts precipitate.

The solution has an intense yellow colour, and in hot solutions which are not too dilute the end point may be detected without an indicator.

This procedure, however, necessitates thapplication of a blank correction, and it is therefore preferable to add a suitable indicator.

The advantages of cerium(IV) sulphate as a standard oxidising agent are :

1. Cerium(IV) sulphate solutions are remarkably stable over prolonged periods. They need not be protected from light, and may even be boiled for a short time without appreciable change in concentration. The stability of sulphuric acid solutions covers the wide range of 10-40 mL of concentrated sulphuric acid per litre. It is evident, therefore, that an acid solution of cerium(IV) sulphate surpasses a permanganate solution in stability.
2. Cerium(IV) sulphate may be employed in the determination of reducing agents in the presence of a high concentration of HCl.
3. Cerium(IV) solutions in 0.1 M solution are not too highly coloured to obstruct vision when reading the meniscus in burettes and other titrimetric apparatus.
4. In the reaction of cerium(IV) salts in acid solution with reducing agents, the simple change is assumed to take place. With permanganate, of course, a number of reduction products are produced according to the experimental conditions.

Standardization of Cerium (IV) sulphate

Method A : Standardisation with arsenic(III) oxide.

$$2Ce^{4+} + H_3AsO_3 + H_2O = 2Ce^{3+} + H_3AsO_4 + 2H^+$$

The most trustworthy method for standardising cerium(IV) sulphate solutions is with pure arsenic(III)oxide. The reaction between cerium(IV) sulphate solution and arsenic(III) oxide is very slow at the ambient temperature; it is necessary to add a trace of osmium tetroxide as catalyst. The arsenic(III) oxide is dissolved in sodium hydroxide solution, the solution acidified with dilute sulphuric acid, and after adding 2 drops of an 'osmic acid' solution prepared by dissolving 0.1 g osmium tetroxide in 40 mL of 0.05M sulphuric acid, and the indicator (1-2 drops ferroin or 0.5 mL N-phenylanthranilic acid), it is titrated with the cerium(IV) sulphate solution to the first sharp colour change : orange-red to very pale blue or yellowish-green to purple respectively.

Method B : Standardisation with sodium oxalate.

Standardisation may also be carried out with sodium oxalate; in this case, an indirect procedure must be used as the redox indicators are themselves oxidised at the elevated temperatures which are necessary. The procedure, therefore, is to add an excess of the cerium(IV) solution, and then, after cooling, the excess is determined by back-titration with an iron(II) solution.

It is possible to carry out a direct titration of the sodium oxalate if a potentiometric procedure is used.

Practically all the determinations described under potassium permanganate and potassium dichromate may be carried out with cerium(IV) sulphate. Use is made of the various indicators already detailed and also, in some cases where great accuracy is not required, of the pale yellow colour produced by the cerium(IV) sulphate itself. Only a few determinations will, therefore, be considered in some detail.

Determination of copper :

Copper(II) ions are quantitatively reduced in 2M hydrochloric acid solution by means of the silver reductor to the copper(I) state. The solution, after reduction, is collected in a solution of ammonium iron(III) sulphate, and the Fe^{2+} ion formed is titrated with standard cerium(IV) sulphate solution using ferroin or N-phenylanthranilic acid as indicator.

Determination of nitrites :

Satisfactory results are obtained by adding the nitrite solution to excess of standard 0.1 M cerium(IV) sulphate, and determining the excess of cerium(IV) sulphate with a standard iron(II) solution.

$$2Ce^{4+} + NO_2^- + H_2O = 2Ce^{3+} + NO_3^- + 2H^+$$

For practice, determine the percentage of NO; in potassium nitrite, or the purity of sodium nitrite, preferably of analytical-grade quality.

4. Iodiometric Titration

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:

$$I_{2\ (solid)} + 2e \rightleftharpoons 2\,I^- \quad \text{is 0.5345 volt.}$$

The above equation refers to a saturated aqueous solution in the presence of solid iodine; this half-ce11 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

$$I_2\,(aq.) + I^- \rightleftharpoons I_3^-$$

since iodine is readily soluble in a solution of iodide. The half-ce11 reaction is better written :

$$I_3^- + 2e \rightleftharpoons 3I^-$$

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.

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.

$$I_3^- + 2S_2O_3^{2-} = 3I^- + S_4O_6^{2-}$$

is more accurate than

$$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$$

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.

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.

$$4I^- + O_2 + 4H^+ = 2I_2 + 2H_2O$$

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.

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 :

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$$

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; 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.

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 x 10^{-} M and the iodide concentration is greater than 4 x 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 % ethanol or more. It cannot be used in a strongly acid medium because hydrolysis of the starch occurs.

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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.

Carbon tetrachloride has been used in certain reactions instead of starch solution. One litre of water at 25 OC 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 carbontetrachloride 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.

Standardization of Iodine Solution

(A) With arsenic(III) oxide :

Arsenic(II1) 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 :

$$H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 2I^-$$

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.

(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.

Sodium thiosulphate ($Na_2S_2O_4.5H_20$) 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 by virtue of the half-cell reaction : $2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e$

It is necessary to refer briefly to the stability of thiosulphate solutions. Solutions prepared with conductivity (equilibrium) water are perfectly stable. However, ordinary distilled water usually contains an excess of carbon dioxide; this may cause a slow decomposition to take place with the formation of sulphur:

$$S_2O_3^{2-} + H^+ = HSO_3^- + S$$

Moreover, decomposition may also be caused by bacterial action (e.g. *Thiobacillus thioparus*), particularly if the solution has been standing for some time. For these reasons, the following recommendations are made:

1. Prepare the solution with recently boiled distilled water.

2. Add 3 drops of chloroform or 10mg L^{-1} of mercury(II) iodide; these compounds improve the keeping qualities of the solution. Bacterial activity is least when the pH lies between 9 and 10. The addition of a small amount, 0.1 g L^{-1}, of sodium carbonate is advantageous to ensure the correct pH.

In general, alkali hydroxides, sodium carbonate (> 0.1 g L^{-1}), and sodium tetraborate should not be added, since they tend to accelerate the decomposition:

$$S_2O_3^{2-} + 2O_2 + H_2O \rightleftharpoons 2SO_4^{2-} + 2H^+$$

3. Avoid exposure to light, as this tends to hasten the decomposition.

The standardisation of thiosulphate solutions may be effected with potassium iodate, potassium dichromate, copper and iodine as primary standards, or with potassium permanganate or cerium(IV) sulphate as secondary standards.
Owing to the volatility of iodine and the difficulty of preparation of perfectly pure iodine, this method is not a suitable one for beginners. If, however, a standard solution of iodine is available, this may be used for the standardisation of thiosulphate solutions.

Standardization of sodium thiosulphate solution

(A) With potassium iodate.

Potassium iodate has a purity of at least 99.9 per cent :
it can be dried at 120 ºC . This reacts with potassium iodide in acid solution to liberate iodine :

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$$

Its relative molecular mass is 214.00; a 0.02 M solution therefore contains 4.28 g of potassium iodate per litre.

(B) With potassium dichromate.

Potassium dichromate is reduced by an acid solution of potassium iodide, and iodine is set free :

$$Cr_2O_7^{2-} + 6I^- + 14H^+ = 2Cr^{3+} + 3I_2 + 7H_2O$$

This reaction is subject to a number of errors :

(1) the hydriodic acid (from excess of iodide and acid) is readily oxidised by air, especially in the presence of chromium(III) salts, and

(2) it is not instantaneous. It is accordingly best to pass a current of carbon dioxide through the reaction flask before and during the titration (a more convenient but less efficient method is to add some solid sodium hydrogen carbonate to the acid solution, and to keep the flask covered as much as possible), and to allow 5 minutes for its completion.

Determination of Arsenic(V)

The reaction is the reverse of that employed in the standardisation of iodine with sodium arsenite solution :

$$As_2O_5 + 4H^+ + 4I^- \rightleftharpoons As_2O_3 + 2I_2 + 2H_2O$$

or

$$H_3AsO_4 + 2H^+ + 2I^- \rightleftharpoons H_3AsO_3 + I_2 + H_2O$$

For good results, the following experimental conditions must be observed :

(1) The hydrochloricacid concentration in the final solution should be at least 4 M;

(2) Air should be displaced from the titration mixture by adding a little solid sodium hydrogencarbonate;

(3) The solution must be allowed to stand for at least 5 minutes before the liberated iodine is titrated; and

(4) Constant stirring is essential during the titration to prevent decomposition of the thiosulphate in the strongly acid solution.

5. Iodatometric Titration

Potassium iodate is a powerful oxidising agent, but the course of the reaction is governed by the conditions under which it is employed. The reaction between potassium iodate and reducing agents such as iodide ion or arsenic(III) oxide in solutions of moderate acidity (0.1-2.0 M hydrochloric acid) stops at the stage when the iodate is reduced to iodine :

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$$

$$2IO_3^- + 5H_3AsO_3 + 2H^+ = I_2 + 5H_3AsO_4 + H_2O$$

As already indicated, the first of these reactions is very useful for the generation of known amounts of iodine, and it also serves as the basis of a method for standardising solutions of acids.

With a more powerful reductant, e.g. titanium(III) chloride, the iodate is reduced to iodide :

$$IO_3^- + 6Ti^{3+} + 6H^+ = I^- + 6Ti^{4+} + 3H_2O$$

In more strongly acid solutions (3-6 M hydrochloric acid) reduction occurs to iodine monochloride, and it is under these conditions that it is most widely used.

$$IO_3^- + 6H^+ + Cl^- + 4e \rightleftharpoons ICl + 3H_2O$$

In hydrochloric acid solution, iodine monochloride forms a stable complex ion with chloride ion :

$$ICl + Cl^- \rightleftharpoons ICl_2^-$$

The overall half-cell reaction may therefore be written as:

$$IO_3^- + 6H^+ + 2Cl^- + 4e \rightleftharpoons ICl_2^- + 3H_2O$$

The reduction potential is 1.23 volts; hence under these conditions potassium iodate acts as a very powerful oxidising agent.

Oxidation by iodate ion in a strong hydrochloric acid medium proceeds through several stages :

$$IO_3^- + 6H^+ + 6e \rightleftharpoons I^- + 3H_2O$$

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$$

$$IO_3^- + 2I_2 + 6H^+ = 5I^+ + 3H_2O$$

In the initial stages of the reaction free iodine is liberated : as more titrant is added, oxidation proceeds to iodine monochloride, and the dark colour of the solution gradually disappears.
The overall reaction may be written as :

$$IO_3^- + 6H^+ + 4e \rightleftharpoons I^+ + 3H_2O$$

The reaction has been used for the determination of many reducing agents.

Under these conditions (2.5-9.0 M of HCl) starch cannot be used as indicator because the characteristic blue colour of the st arch-iodine complex is not formed at high concentrations of acid.

In the original procedure, a few millilitres of an immiscible solvent (carbon tetrachloride or chloroform) were added to the solution being titrated contained in a glass-stoppered bottle or conical flask.

The end point is marked by the disappearance of the last trace of violet colour, due to iodine, from the solvent: iodine monochloride is not extracted and imparts a pale yellowish colour to the aqueous phase. The extraction end point is very sharp.

The main disadvantage is the inconvenience of vigorous shaking with the extraction solvent in a stoppered vessel after each addition of the reagent near the end point.

Preparation of 0.025 M Potassium Iodate Solution

Dry some potassium iodate at 120 °C for 1 hour and allow it to cool in a covered vessel in a desiccator. Weigh out exactly 5.350 g of the finely powdered potassium iodate on a watchglass, and transfer it by means of a clean camel-hair brush directly into a dry 1 L graduated flask. Add about 400-500 mL of water, and gently rotate the flask until the salt is completely dissolved. Make up to the mark with distilled water. Shake well. The solution will keep indefinitely. It must be emphasised that this 0.025 M solution is intended for the reaction:

$$IO_3^- + 6H^+ + Cl^- + 4e \rightleftharpoons ICl + 3H_2O$$

but when used in solutions of moderate acidity leading to the liberation of free iodine, ideally the solution then requires 4.28 g L^{-1} potassium iodate; the method of preparation will be as described above with suitable adjustment of the weight of salt taken.

Determination of Arsenic and of Antimony

The determination of arsenic in arsenic(III) compounds is based upon the following reaction :

$$IO_3^- + 2H_3AsO_3 + 2H^+ + Cl^- = ICl + 2H_3AsO_4 + H_2O$$

A similar reaction occurs with antimony(III) compounds. The determination of antimony(III) in the presence of tartrate is not very satisfactory with an immiscible solvent to assist in indicating the end point; amaranth, however, gives excellent results.

$$IO_3^- + 2[SbCl_4]^- + 6H^+ + 5Cl^- = ICl + 2[SbCl_6]^- + 3H_2O$$

6. Bromatometric Titration

Potassium bromate is a powerful oxidising agent which is reduced smoothly to bromide :

$$BrO_3^- + 6H^+ + 6e \rightleftharpoons Br^- + 3H_2O$$

The relative molecular mass is 167.00, and a 0.02 M solution contains 3.34 g L^{-1} potassium bromate. At the end of the titration free bromine appears :

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O$$

The presence of free bromine, and consequently the end-point, can be detected by its yellow colour, but it is better to use indicators such as methyl orange, methyl red, naphthalene black 12B, xylidine ponceau, and fuchsine. These indicators have their usual colour in acid solution, but are destroyed by the first excess of bromine.

With all irreversible oxidation indicators the destruction of the indicator is often premature to a slight extent : a little additional indicator is usually required near the end point. The quantity of bromate solution consumed by the indicator is exceedingly small, and the 'blank' can be neglected for 0.02 M solutions. Direct titrations with bromate solution in the presence of irreversible dyestuff indicators are usually made in hydrochloric acid solution, the concentration of which should be at least 1.5-2 M.

At the end of the titration some chlorine may appear by virtue of the reaction :

$$10Cl^- + 2BrO_3^- + 12H^+ = 5Cl_2 + Br_2 + 6H_2O$$

This immediately bleaches the indicator.

Examples of determinations utilising direct titration with bromate solutions are expressed in the following equations :

$$BrO_3^- + 3H_3AsO_3 \xrightarrow{(HCl)} Br^- + 3H_3AsO_4$$

$$2BrO_3^- + 3N_2H_4 \xrightarrow{(HCl)} 2Br^- + 3N_2 + 6H_2O$$

$$BrO_3^- + NH_2OH \xrightarrow{(HCl)} Br^- + NO_3^- + H^+ + H_2O$$

$$BrO_3^- + 6[Fe(CN)_6]^{4-} + 6H^+ \longrightarrow Br^- + 6[Fe(CN)_6]^{3-} + 3H_2O$$

Various substances cannot be oxidised directly with potassium bromate, but react quantitatively with an excess of bromine. Acid solutions of bromine of exactly known concentration are readily obtainable from a standard potassium bromate solution by adding acid and an excess of bromide :

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O$$

In this reaction 1 mole of bromate yields six atoms of bromine.

Bromine is very volatile, and hence such operations should be conducted at as low a temperature as possible and in conical flasks fitted with ground-glass stoppers. The excess of bromine may be determined iodometrically by the addition of excess of potassium iodide and titration of the liberated iodine with standard thiosulphate solution :

$$2I^{-} + Br_2 = I_2 + 2Br^{-}$$

Potassium bromate is readily available in a high state of purity; the product has an assay value of at least 99.9 per cent. The substance can be dried at 120-150 °C, is anhydrous, and the aqueous solution keeps indefinitely. It can therefore be employed as a primary standard. Its only disadvantage is that one-sixth of the relative molecular mass is a comparatively small quantity.

Determination of Arsenic and of Antimony

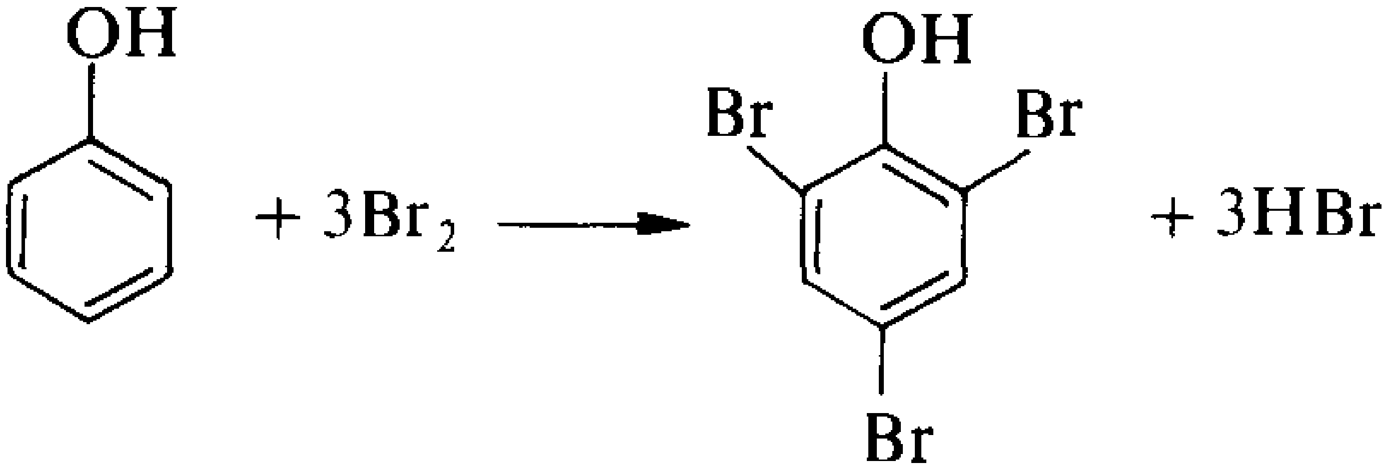
The antimony or the arsenic must be present as antimony(III) or arsenic(III). The reaction of arsenic(III) or antimony(III) with potassium bromate may be written :

$$2KBrO_3 + 3M_2O_3 + 2HCl = 2KCl + 3M_2O_5 + 2HBr \ (M = As \text{ or } Sb)$$

The presence of tin and of considerable quantities of iron and copper interfere with the determinations.

Determination of phenol

A number of phenols can be substituted rapidly and quantitatively with bromine produced from bromate and bromide in acid solution. The determination involves treating phenol with an excess of potassium bromate and potassium bromide; when bromination of the phenol is complete the unreacted bromine is then determined by adding excess potassium iodide and back-titrating the liberated iodine with standard sodium thiosulphate.



End