indicators (1,10-phenanthroline–iron(II) ion or N-phenylantranilic 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:

\[
\text{MnO}_4^- + 8H^+ + 5e^- \rightleftharpoons \text{Mn}^{2+} + 4H_2O
\]

The standard potential in acid solution, \(E^0\), 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:

\[
2\text{MnO}_4^- + 10\text{Cl}^- + 16H^+ = 2\text{Mn}^{2+} + 5\text{Cl}_2 + 8H_2O
\]

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 (\(\text{MnSO}_4 \cdot 4\text{H}_2\text{O}\)) 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 \(\text{MnO}_4^- - \text{Mn}^{2+}\) 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$_4$)$_2$]$^{3+}$, 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:
   \[ \text{MnO}_4^- + e^- \rightleftharpoons \text{MnO}_2^{2-} \]

2. The relatively slow reaction:
   \[ \text{MnO}_2^{2-} + 2\text{H}_2\text{O} + 2e^- \rightleftharpoons \text{MnO}_2 + 4\text{OH}^- \]

The standard potential $E^\circ$ 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:

\[ \text{MnO}_4^- + 2\text{H}_2\text{O} + 3e^- \rightleftharpoons \text{MnO}_2 + 4\text{OH}^- \]

and the standard potential $E^\circ$ 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:

\[ 4\text{MnO}_4^- + 2\text{H}_2\text{O} = 4\text{MnO}_2 + 3\text{O}_2 + 4\text{OH}^- \]

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

\[ 2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} = 5\text{MnO}_2 + 4\text{H}^+ \]

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.

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$_2$H$_4$(NH$_3$)$_2$SO$_4$, 4H$_2$O. 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).

\[
\text{As}_2\text{O}_3 + 4\text{OH}^- = 2\text{HAsO}_3^- + \text{H}_2\text{O}
\]

\[
5\text{H}_3\text{AsO}_4 + 2\text{MnO}_4^- + 6\text{H}^+ = 5\text{H}_3\text{AsO}_4 + 2\text{Mn}^{2+} + 3\text{H}_2\text{O}
\]

**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 decolourised 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 250 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
KIO₃ 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.

\[
2\text{Na}^+ + \text{C}_2\text{O}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4 \text{} + 2\text{Na}^+ \]

\[
2\text{MnO}_4^- + 5\text{H}_2\text{C}_2\text{O}_4 + 6\text{H}^+ = 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O} \]

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: