Mastering Chemistry

Book 8

Topic 15 Analytical Chemistry

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53.1 Volumetric analysis (p.89)

◆ Volumetric analysis is a widely used quantitative analytical method. This is a method of analysis based on titration.

◆ A titration is a technique used to accurately measure the volume of one solution that reacts exactly with another solution.

◆ You must know the concentration of one of the two solutions. Then you can calculate the concentration of the another solution by using the titration results.

◆ Titrations can be used to find out the concentrations of a range of substances, for example, the vitamin C concentration in food and drinks or the chlorine concentration in bleach.

53.1 Volumetric analysis (p.89)

◆ A reaction must fulfill certain conditions so that it can be used in volumetric analysis, including:
  • a significant observable change can easily be detected upon the complete consumption of the chemical species in the conical flask, i.e. a suitable indicator is available;
  • the reaction must be near to completion;
  • the rate of reaction must be fast.

53.1 Volumetric analysis (p.89)

Selection of analytical method

◆ The choice will be determined by several factors such as the sample type, the sample size, the concentration of the chemical species to be analysed, the accuracy required, the availability of instruments, cost and speed.

◆ For example, the dioxin level in air is very low. Hence instrumental analytical method is more appropriate than volumetric analysis for measuring the dioxin level in air.

◆ As in qualitative analysis, it is important to carry out a risk assessment before you carry out quantitative analysis.

53.2 Precipitation methods (p.90)

- Precipitation titrations are based upon reactions that yield precipitates.

- Most practical precipitation titrations today employ silver nitrate as a precipitating agent.

- Precipitation titrations are useful in determining the concentrations of halides.

53.2 Precipitation methods (p.90)

Determining the concentration of chloride ion in water sample

◆ The concentration of chloride ion in a water sample can be determined by titrating the sample with an aqueous solution of silver nitrate. As this silver nitrate solution is slowly added to the sample, a precipitate of silver chloride forms.

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$$

◆ Potassium chromate can serve as an end point indicator for the titration. After all the chloride ion has been precipitated as silver chloride, one drop of excess silver nitrate solution results in the formation of a reddish brown precipitate of silver chromate.

$$2Ag^+(aq) + CrO_4^{2-}(aq) \rightleftharpoons Ag_2CrO_4(s)$$

reddish brown
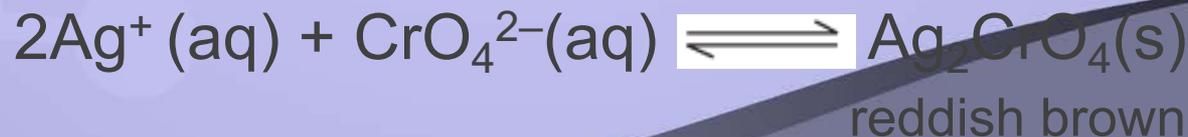
53.2 Precipitation methods (p.90)

◆ The method of performing the titration is as follows:
- Pipette an accurately measured volume, usually 25.00 cm^3, of a water sample into a conical flask. Add 1 cm^3 of the chromate indicator. A clear yellow solution is obtained (a).
- Slowly add standard aqueous solution of silver nitrate from a burette and swirl the mixture. Although the silver chloride that forms is a white precipitate, the chromate indicator initially gives the cloudy solution a faint lemon-yellow colour (b).
- The end point of the titration is identified as the first appearance of a reddish brown colour of silver chromate (c).

(a)   (b)   (c)

53.2 Precipitation methods (p.90)

Q (Example 53.1)

In a certain experiment, a 25.00 cm³ sample of sea water was diluted to make 250.0 cm³ of solution. 25.00 cm³ of the diluted sea water required 15.50 cm³ of 0.0500 mol dm⁻³ aqueous solution of silver nitrate for complete reaction.

Calculate the concentration of chloride ion in the sample of sea water, in g dm⁻³.

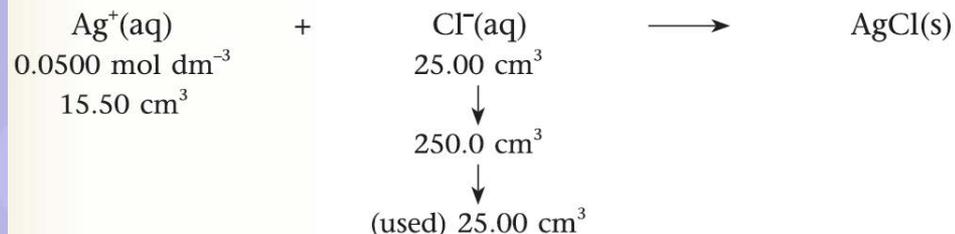(Relative atomic mass: Cl = 35.5)

Determining the concentration of chloride ion in a sea water sample by titration with a standard aqueous solution of silver nitrate *Ref.*

53.2 Precipitation methods (p.90)

Q (Example 53.1) (continued)

A Silver ion and chloride ion react according to the following ionic equation:

$$Ag^+(aq) \quad + \quad Cl^-(aq) \quad \longrightarrow \quad AgCl(s)$$

0.0500 mol dm^{-3} 25.00 cm^3
15.50 cm^3

                   ↓
               250.0 cm^3
                   ↓
        (used) 25.00 cm^3

Number of moles of Ag^+ ion in 15.50 cm^3 solution = 0.0500 mol dm^{-3} x $\dfrac{15.50}{1\ 000}$ dm^3

$$= 7.75 \times 10^{-4} \text{ mol}$$

According to the equation, 1 mole of Ag^+ ion reacts with 1 mole of Cl^- ion.

i.e. number of moles of Cl^- ion in 25.00 cm^3 diluted sea water = 7.75 x 10^{-4} mol

Number of moles of Cl^- ion in 250.0 cm^3 diluted sea water
= 10 x 7.75 x 10^{-4} mol
= 7.75 x 10^{-3} mol
= number of moles of Cl^- ion in 25.00 cm^3 sea water

Concentration of Cl^- ion in sea water = $\dfrac{7.75 \times 10^{-3} \text{ mol}}{\dfrac{25.00}{1\ 000} \text{ dm}^3}$

$$= 0.310 \text{ mol dm}^{-3}$$
$$= 0.310 \text{ mol dm}^{-3} \times 35.5 \text{ g mol}^{-1}$$
$$= 11.0 \text{ g dm}^{-3}$$

∴ the concentration of chloride ion in the sample of sea water is 11.0 g dm^{-3}.

53.3 Redox titrations (p.93)

◆ One way of measuring the concentration of an oxidising agent or a reducing agent is to do a **redox titration (**氧化還原滴定**)**. This is similar in principle to an acid-alkali titration.

◆ Although a wide range of oxidising agents can be used in redox titrations, you will concentrate on two in this unit — potassium permanganate and iodine.

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)

- Potassium permanganate ($KMnO_4$) is a powerful oxidising agent. It is a purple solid and forms a purple aqueous solution.

- Under acidic conditions, the purple permanganate ion is easily reduced to pale pink manganese(II) ion according to the half equation:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$$

Colours of solutions of MnO_4^-(aq) ion (left) and Mn^{2+}(aq) ion (right)

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)
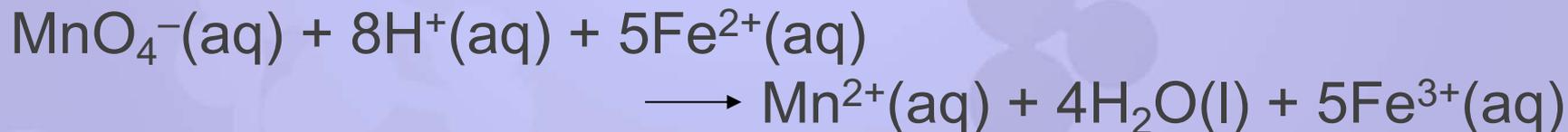
Titration of aqueous solution of potassium permanganate with iron(II) ion

- In this reaction, the iron(II) ion is oxidised and the permanganate ion is reduced.
  The half equations involved are:
  $MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
  $Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$
  The overall equation for the reaction is:
  $MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq)$
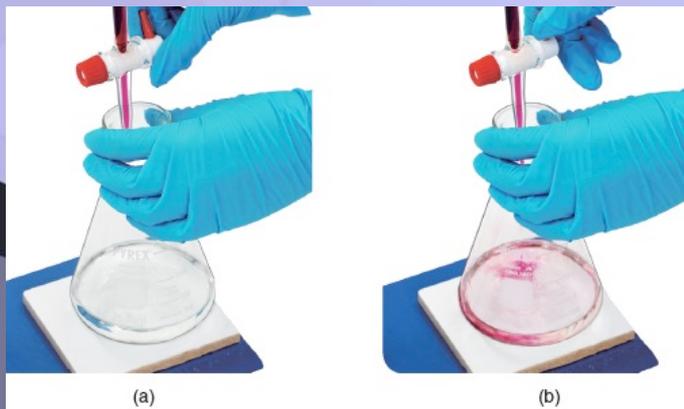 $\longrightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)

- In reasonably concentrated solutions containing Fe^{2+}, Fe^{3+} and Mn^{2+}, the ions have the following colours:
  $Fe^{2+}(aq)$ — pale green
  $Fe^{3+}(aq)$ — yellow
  $Mn^{2+}(aq)$ — pale pink

- The solutions used in titrations are usually so dilute that their colours cannot be identified easily.

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)

◆ The method of performing the titration is as follows:

- Pipette an accurately measured volume, usually 25.00 cm^3, of the iron(II) solution into a conical flask and then add a small volume of dilute sulphuric acid.

- Slowly add standard aqueous solution of potassium permanganate from a burette and swirl the mixture (a).

- The potassium permanganate solution will turn colourless until all of the iron(II) ion has been oxidised.

- Once just enough potassium permanganate solution has been added to react with all the iron(II) ion, one drop of excess permanganate solution gives the contents of the conical flask a persistent pale pink colour (b). This is the end point of the titration.
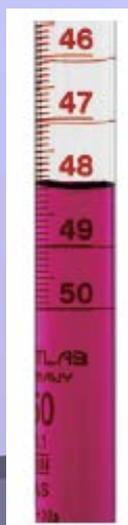

(a)   (b)

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)

Possible sources of error

◆ Some possible sources of error for the above experiment are listed below:
- The burette, pipette and volumetric flask may hold or deliver volumes slightly different from the volumes indicated by the manufacturer.
- The eyes may not be on the same level as the graduation marks of the burette, pipette and volumetric flask when reading the graduation marks and thus leads to reading errors.
- Aqueous solution of potassium permanganate has a deep purple colour and it is very difficult to see the bottom of the meniscus through the intense colour.

The bottom of the meniscus of aqueous solution of potassium permanganate cannot be seen easily

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)

Possible sources of error

- Some possible sources of error for the above experiment are listed below:
  - It is difficult to tell exactly when a persistent pale pink colour in the solution in the conical flask first appears.
  - If the titration is carried out too quickly, the solution may turn brown. This is due to the formation of manganese(IV) oxide. This may lead to inaccurate titration results.
  - Little splashes can cause errors.

Manganese(IV) oxide

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)

Q (Example 53.2)

Iron supplements containing iron(II) sulphate are used to treat iron-deficiency. A 0.305 g iron supplement tablet is crushed and dissolved in 25.00 cm^3 of dilute sulphuric acid. The resulting solution is titrated with 0.00750 mol dm^{-3} KMnO$_4$(aq) and 19.20 cm^3 of KMnO$_4$(aq) are required to reach the end point. Calculate the percentage by mass of iron(II) sulphate in the iron tablet.
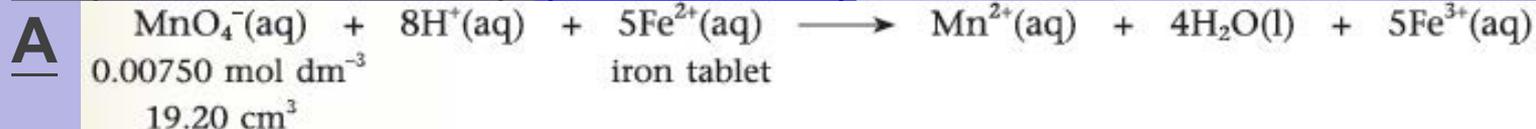
(Molar mass of FeSO$_4$ = 151.9 g mol^{-1})

Determining the percentage by mass of iron(II) sulphate in a brand of iron tablets *Ref.*

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)

Q (Example 53.2) (continued)

A

$$MnO_4^-(aq) \quad + \quad 8H^+(aq) \quad + \quad 5Fe^{2+}(aq) \quad \longrightarrow \quad Mn^{2+}(aq) \quad + \quad 4H_2O(l) \quad + \quad 5Fe^{3+}(aq)$$

0.00750 mol dm^{-3} iron tablet

19.20 cm^3

Number of moles of MnO_4^- ion in 19.20 cm^3 solution $= 0.00750$ mol dm^{-3} x $\dfrac{19.20}{1\ 000}$ dm^3

$$= 1.44 \times 10^{-4}\ mol$$

According to the equation, 1 mole of MnO_4^- ion reacts with 5 moles of Fe^{2+} ion.

i.e. number of moles of Fe^{2+} ion in solution

$= 5 \times 1.44 \times 10^{-4}$ mol

$= 7.20 \times 10^{-4}$ mol

$=$ number of moles of $FeSO_4$ in iron tablet

Mass of $FeSO_4$ in iron tablet $= 7.20 \times 10^{-4}$ mol x 151.9 g mol^{-1}

$$= 0.109\ g$$

Percentage by mass of $FeSO_4$ in iron tablet $= \dfrac{0.109\ g}{0.305\ g}$ x 100%

$$= 35.7\%$$

∴ the percentage by mass of iron(II) sulphate in the iron tablet is 35.7%.

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)

Q (Example 53.3)

Hydroxylammonium chloride (NH_3OHCl) reacts with Fe^{3+}(aq) ion under acidic conditions to form products including Fe^{2+}(aq) ion and an oxide of nitrogen.

An experiment was carried out to deduce the oxidation number of nitrogen in the oxide.

Step 1 100.0 cm³ of 0.130 mol dm⁻³ NH_3OHCl(aq) were added to a solution containing an excess of Fe^{3+}(aq) ion and about 25 cm³ of 1 mol dm⁻³ H_2SO_4(aq). The mixture was boiled. It was then diluted to 250.0 cm³.

Step 2 25.00 cm³ samples of the diluted solution were acidified with excess H_2SO_4(aq) and then titrated with 0.0189 mol dm⁻³ $KMnO_4$(aq) until the end point was reached. The mean titre was 27.50 cm³.

The chemical equation for the reaction involved is as follows:

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$$

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)

Q (Example 53.3) (continued)

a) State the colour change at the end point of the titration.
b) Based on the titration result, calculate the mole ratio of NH_3OH^+ : Fe^{3+} required for the complete reaction in *Step 1*.
c) Given that the oxidation number of N in NH_3OH^+ is –1, and the oxidation numbers of H and O remain unchanged, deduce the oxidation number of N in the oxide.
d) According to (c), suggest an empirical formula for the oxide.
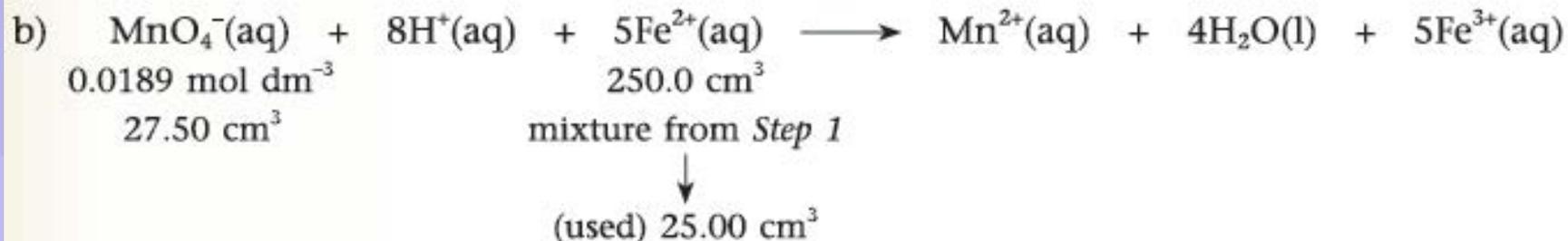e) Write the ionic equation for the reaction between NH_3OH^+ ion and Fe^{3+} ion.

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)

Q (Example 53.3) (continued)

A

a) From yellowish green to pale pink

b) $MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

0.0189 mol dm^{-3}

27.50 cm^3

250.0 cm^3

mixture from *Step 1*

$\downarrow$

(used) 25.00 cm^3

Number of moles of MnO_4^- ion in 27.50 cm^3 solution $= 0.0189$ mol dm^{-3} $\times \dfrac{27.50}{1\ 000}$ dm^3

$= 5.20 \times 10^{-4}$ mol

According to the equation, 1 mole of MnO_4^- ion reacts with 5 moles of Fe^{2+} ion.

i.e. number of moles of Fe^{2+} ion in 25.00 cm^3 solution $= 5 \times 5.20 \times 10^{-4}$ mol

$= 2.60 \times 10^{-3}$ mol

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)

Q (Example 53.3) (continued)

A

Number of moles of Fe^{2+} ion in 250.0 cm^3 solution
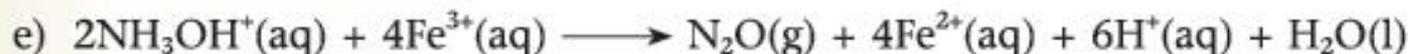
$= 10 \times 2.60 \times 10^{-3}$ mol

$= 0.0260$ mol

$=$ number of moles of Fe^{3+} ion reacted in *Step 1*

Number of moles of NH_3OH^+ ion used in *Step 1* $= 0.130$ mol $dm^{-3} \times \dfrac{100.0}{1\ 000}$ dm^3

$\qquad\qquad\qquad = 0.0130$ mol

Mole ratio of $NH_3OH^+ : Fe^{3+} = 0.0130 : 0.0260$

$\qquad\qquad\qquad\qquad = 1 : 2$

c) The oxidation number of iron decreases from +3 to +2. Since the mole ratio of $NH_3OH^+ :$ Fe^{3+} is 1 : 2, the oxidation number of N would increase by 2, i.e. from −1 to +1.

d) N_2O

e) $2NH_3OH^+(aq) + 4Fe^{3+}(aq) \longrightarrow N_2O(g) + 4Fe^{2+}(aq) + 6H^+(aq) + H_2O(l)$

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)

Practice 53.1

Aqueous solutions of potassium permanganate are unstable, so they are often standardised using solutions of iron(II) ammonium sulphate, freshly prepared from Mohr's salt, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$.

11.17 g of Mohr's salt were dissolved in water and diluted to 250.0 cm^3. 25.00 cm^3 samples of this solution were pipetted into conical flasks with excess sulphuric acid added. Each mixture was titrated against $KMnO_4$(aq). The mean titre was 26.40 cm^3.

a) Describe what you would observe at the end point of the titration.

b) Write the ionic equation for the reaction between MnO_4^-(aq) ion and Fe^{2+}(aq) ion under acidic conditions.

c) Could hydrochloric acid be used instead of sulphuric acid in this experiment? Explain your answer.

d) Calculate the concentration of the aqueous solution of potassium permanganate.

permanganate.

(Molar mass of Mohr's salt = 392.0 g mol^{-1})

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)

Practice 53.1 (continued)

a) From colourless to the appearance of a persistent pale pink colour

b) $MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

c) Not appropriate as $MnO_4^-(aq)$ ion may oxidise the chloride ion in the solution.

d) $MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

? mol dm^{-3} 11.17 g
26.40 cm^3

↓

250.0 cm^3

↓

(used) 25.00 cm^3

Number of moles of Mohr's salt used $= \dfrac{11.17 \text{ g}}{392.0 \text{ g mol}^{-1}} = 0.0285$ mol

Number of moles of Fe^{2+} ion in 25.00 cm^3 solution $= \dfrac{0.0285}{10}$ mol $= 2.85 \times 10^{-3}$ mol

According to the equation, 1 mole of MnO_4^- ion reacts with 5 moles of Fe^{2+} ion.

i.e. number of moles of MnO_4^- ion in 26.40 cm^3 solution $= \dfrac{2.85 \times 10^{-3}}{5}$ mol $= 5.70 \times 10^{-4}$ mol

Concentration of $KMnO_4(aq) = \dfrac{5.70 \times 10^{-4} \text{ mol}}{\dfrac{26.40}{1\,000} \text{ dm}^3} = 0.0216$ mol dm^{-3}

53.4 Redox titrations involving aqueous solution potassium permanganate (p.93)

Titration of aqueous solution of potassium permanganate with ethanedioic acid

◆ Ethanedioic acid and its salts are primary standards and are frequently used to **standardise (**標定**)** aqueous solutions of potassium permanganate.
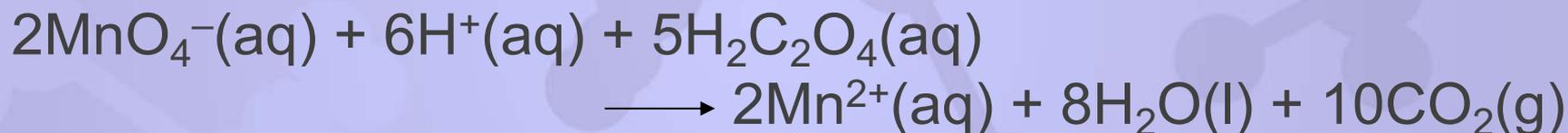

Ethanedioic acid

53.4 Redox titrations involving aqueous solution potassium permanganate (p.93)

- In the reaction with an aqueous solution of potassium permanganate, the ethanedioic acid is oxidised to carbon dioxide. The half equation for this oxidation is:
$$H_2C_2O_4(aq) \longrightarrow 2CO_2(g) + 2H^+(aq) + 2e^-$$
The overall equation for the reaction is:
$$2MnO_4^-(aq) + 6H^+(aq) + 5H_2C_2O_4(aq)$$
$$\longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$$

- Aqueous ethanedioic acid is pipetted into the conical flask and is then acidified with dilute sulphuric acid. Aqueous solution of potassium permanganate is added from the burette. However, the reaction is very slow so the ethanedioic acid is heated to around 60 °C before starting the titration.

53.4 Redox titrations involving aqueous solution potassium permanganate (p.93)

- ◆ Aqueous solution of potassium permanganate can also be used to estimate the amount of ethanedioate ion present in a solution.
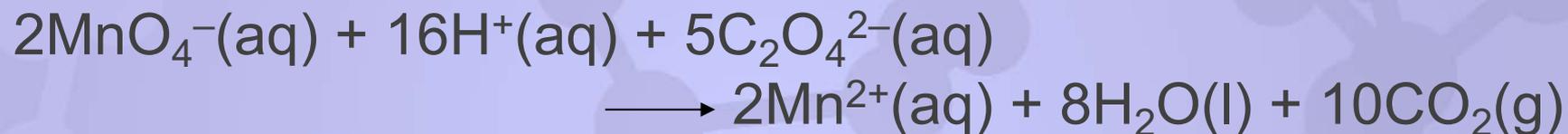
$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq)$

$$\longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$$

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)

Q (Example 53.4)

Hydrated ethanedioic acid has the chemical formula $H_2C_2O_4 \cdot xH_2O$. The value of x can be determined by reacting an aqueous solution of $H_2C_2O_4 \cdot xH_2O$ with $KMnO_4(aq)$.

Procedure

1 Dissolve a 0.1209 g sample of $H_2C_2O_4 \cdot xH_2O$ in 25.0 cm³ of 1.0 mol dm⁻³ $H_2SO_4(aq)$ in a conical flask.

2 Heat the contents of the flask to 60 ℃.

3 Titrate the hot contents of the flask against 0.0161 mol dm⁻³ $KMnO_4(aq)$. 23.85 cm³ of $KMnO_4(aq)$ are required to reach the end point.
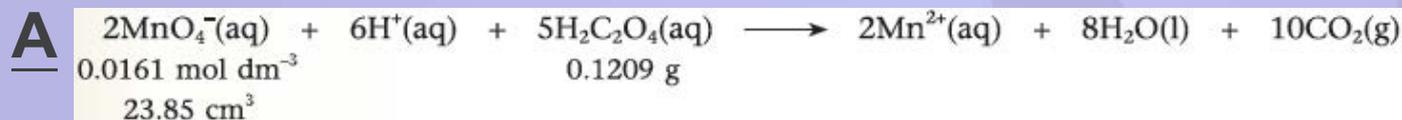
Determine the value of x in the chemical formula of the hydrated ethanedioic acid.

(Relative atomic masses: H = 1.0, C = 12.0, O = 16.0)

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)

Q (Example 53.4)

A

$$2MnO_4^-(aq) + 6H^+(aq) + 5H_2C_2O_4(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$$

0.0161 mol dm^{-3} 0.1209 g

23.85 cm^3

Number of moles of MnO_4^- ion in 23.85 cm^3 solution = 0.0161 mol dm^{-3} x $\dfrac{23.85}{1\ 000}$ dm^3

$$= 3.84 \times 10^{-4} \text{ mol}$$

According to the equation, 2 moles of MnO_4^- ion react with 5 moles of $H_2C_2O_4$.

i.e. number of moles of $H_2C_2O_4$ in solution = $\dfrac{5}{2}$ x 3.84 x 10^{-4} mol

$$= 9.60 \times 10^{-4} \text{ mol}$$

Molar mass of $H_2C_2O_4 \bullet xH_2O$ = [(2 x 1.0 + 2 x 12.0 + 4 x 16.0) + 18x] g mol^{-1}
$$= (90.0 + 18x) \text{ g mol}^{-1}$$

$\therefore$ $\dfrac{0.1209 \text{ g}}{(90.0 + 18x) \text{ g mol}^{-1}}$ = 9.60 x 10^{-4} mol

$(90.0 + 18x)$ g mol^{-1} = $\dfrac{0.1209 \text{ g}}{9.60 \times 10^{-4} \text{ mol}}$

$(90.0 + 18x)$ g mol^{-1} = 126 g mol^{-1}

$$x = \dfrac{36.0}{18}$$

$$= 2$$

$\therefore$ the value of x in the chemical formula of hydrated ethanedioic acid is 2.

53.4 Redox titrations involving aqueous solution potassium permanganate (p.93)

Other redox titrations

◆ The principles of redox titrations can be extended to the analysis of many different substances.

◆ Aqueous solution of potassium dichromate can be used to replace aqueous solution of potassium permanganate.

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)

Practice 53.2

The concentration of an aqueous solution of sodium dichromate can be found by titration with a solution containing Fe^{2+}(aq) ion under acidic conditions.

25.00 cm^3 samples of $Na_2Cr_2O_7$(aq) were acidified with dilute H_2SO_4(aq) and titrated with 0.0500 mol dm^{-3} Fe^{2+}(aq) solution.

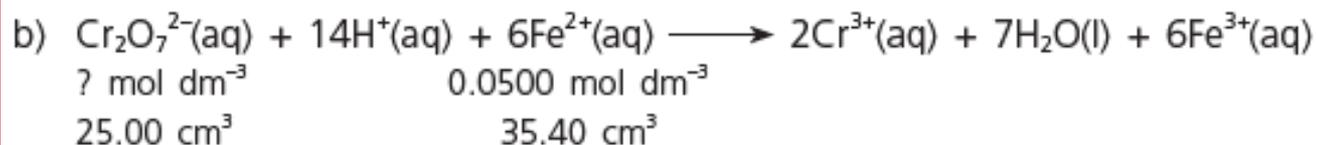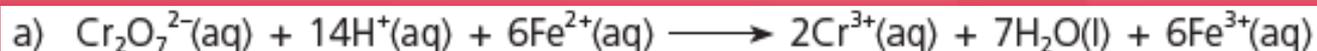An indicator, diphenylamine, was used. This turned an intense violet colour at the end point. The mean titre was 35.40 cm^3.

a) Write the equation for the reaction involved.

b) Calculate the concentration of $Na_2Cr_2O_7$(aq).

c)   Suggest one reason why the indicator diphenylamine is needed, even though the solution in the titration flask changes colour from orange to green when no indicator is used.

53.4 Redox titrations involving aqueous solution of potassium permanganate (p.93)

Practice 53.2 (continued)

a) $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq)$

b) $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq)$
   ? mol dm^{-3} 0.0500 mol dm^{-3}
   25.00 cm^3 35.40 cm^3

Number of moles of Fe^{2+} ion in 35.40 cm^3 solution = 0.0500 mol dm^{-3} x $\dfrac{35.40}{1\,000}$ dm^3

$$= 1.77 \times 10^{-3} \text{ mol}$$

According to the equation, 1 mole of $Cr_2O_7^{2-}$ ion reacts with 6 moles of Fe^{2+} ion.

i.e. number of moles of $Cr_2O_7^{2-}$ ion in solution = $\dfrac{1.77 \times 10^{-3}}{6}$ mol

$$= 2.95 \times 10^{-4} \text{ mol}$$

Concentration of $Na_2Cr_2O_7(aq)$ = $\dfrac{2.95 \times 10^{-4} \text{ mol}}{\dfrac{25.00}{1\,000} \text{ dm}^3}$

$$= 0.0118 \text{ mol dm}^{-3}$$

c) The indicator makes the end point more easier to observe.

53.5 Redox titrations involving iodine (p.101)

◆ Iodine is used as an oxidising agent in many redox titrations and iodide ion is used as a reducing agent in other redox titrations.
The half equation for the reduction of iodine is as follows:
$I_2(aq) + 2e^- \longrightarrow 2I^-(aq)$
The half equation for the oxidation of iodide ion is as follows:
$2I^-(aq) \longrightarrow I_2(aq) + 2e^-$
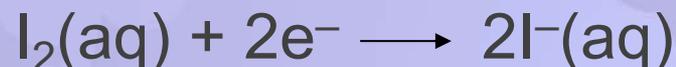
◆ Iodine is a relatively weak oxidising agent. It can react with moderately strong reducing agents.

◆ On the other hand, iodide ion is a strong reducing agent. It can react with many oxidising agents, and the iodide ion is oxidised to iodine in the process.

53.5 Redox titrations involving iodine (p.101)

◆ The concentration of a moderately strong reducing agent in a sample solution can be determined by direct titration with a standard aqueous solution of iodine.

◆ To determine the concentration of a moderately strong oxidizing agent in a sample solution, first treat the sample solution with an excess of iodide ion to form iodine.

oxidising agent in   + I⁻ ———————→ I_2 + other products
a sample solution   excess

Then titrate the iodine formed with a standard aqueous solution of sodium thiosulphate.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

53.5 Redox titrations involving iodine (p.101)

◆ The greater the amount of oxidising agent in the sample solution, the more iodine is formed and the more sodium thiosulphate is needed to react with the iodine.

◆ The indicator that is usually chosen for titrations involving iodine is starch. Starch forms a dark blue complex with iodine.

53.5 Redox titrations involving iodine (p.101)

Determining the vitamin C content in a commercial tablet

◆ Vitamin C (ascorbic acid, $C_6H_8O_6$) is essential to your health.

◆ The human body is unable to synthesise vitamin C on its own and must depend on diet intake for an adequate supply.

◆ Nowadays, tablets, capsules and drink mix packets containing vitamin C are available in the market.

Tablets (left), capsules (middle) and drink mix packets (right) containing vitamin C

53.5 Redox titrations involving iodine (p.101)

◆ Vitamin C (ascorbic acid, $C_6H_8O_6$) is rapidly and quantitatively oxidised by iodine in acidic solution according to the following equation:

vitamin C   + $I_2(aq)$ →   oxidised form of vitamin C   (aq)   + $2H^+(aq)$ + $2I^-(aq)$
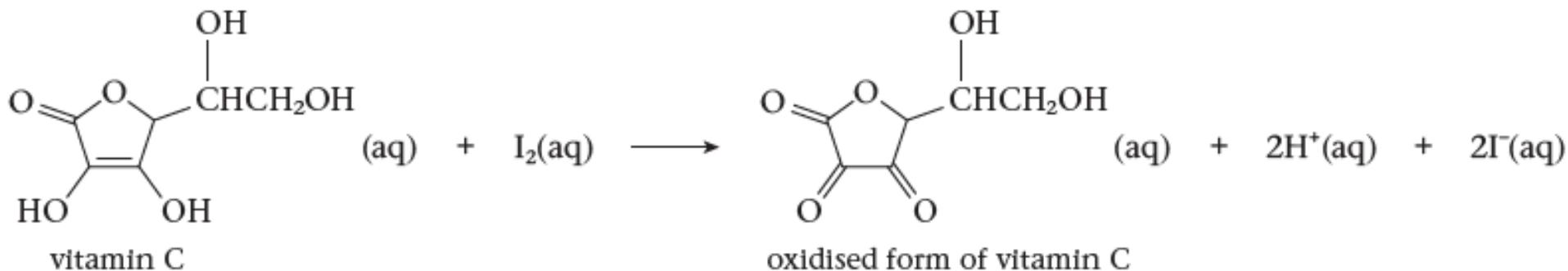
◆ The concentration of vitamin C can be determined in a sample by direct titration with standard aqueous solution of iodine.

Determining the vitamin C content in a sample of commercial tablet by iodometric titration *Ref.*

53.5 Redox titrations involving iodine (p.101)

- Since iodine is not a primary standard, you can generate iodine by mixing an acidified iodate solution with iodide ion:
$$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \longrightarrow 3I_2(aq) + 3H_2O(l)$$

- Iodine is not very soluble in water and is volatile. However, the solubility of iodine is increased in the presence of iodide ion.

53.5 Redox titrations involving iodine (p.101)

◆ Follow the steps below in the titration:

Preparing standard aqueous solution of iodine

• Dissolve a known mass of potassium iodate and excess potassium iodide in deionised water.

• Add sulphuric acid.

• Add deionised water to the mixture to make a solution of volume 250.0 cm^3.

Determining the vitamin C content in a commercial tablet

• Dissolve one vitamin C tablet in deionised water and dilute to make a solution of volume 250.0 cm^3.

• Pipette an accurately measured volume, usually 25.00 cm^3, of the aqueous solution of vitamin C into a conical flask.

• Add 2–3 cm^3 of starch solution.

• Slowly add the standard aqueous solution of iodine from a burette until the first appearance of a persistent dark blue colour in the mixture.

53.5 Redox titrations involving iodine (p.101)

Standard aqueous solution of iodine is run from the burette into the vitamin C solution (left); the first appearance of a persistent dark blue colour indicates the titration end point (right)
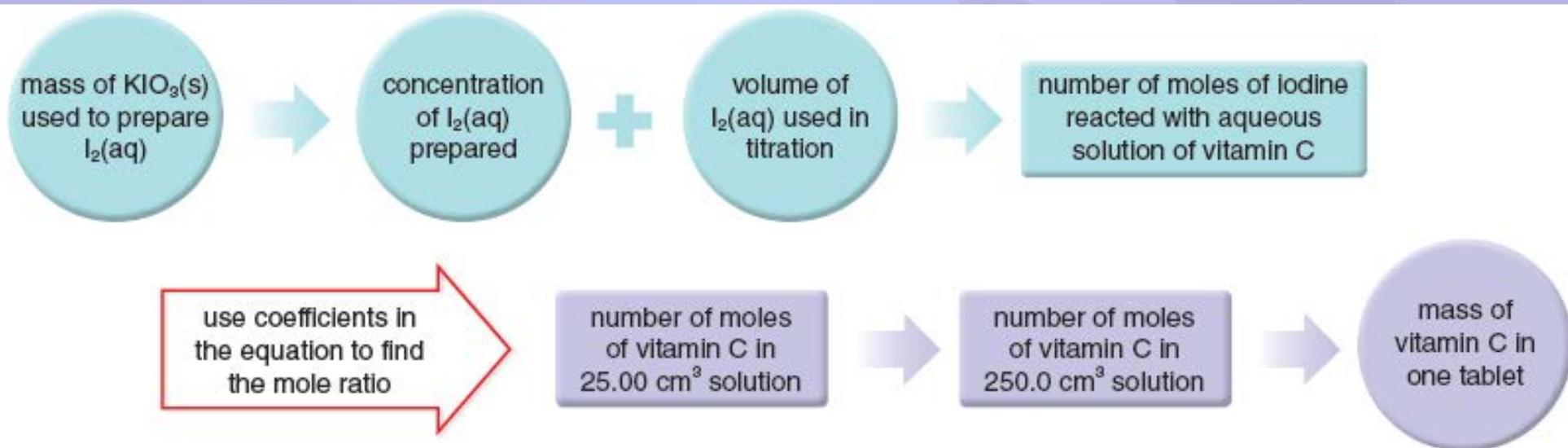
53.5 Redox titrations involving iodine (p.101)

◆ As the aqueous solution of iodine is added to the mixture in the conical flask, it oxidises the vitamin C.

◆ Once all vitamin C has been oxidised, one drop of excess aqueous solution of iodine reacts with the starch to form a dark blue complex. This change indicates the titration end point.

53.5 Redox titrations involving iodine (p.101)

- ◆ The steps you can follow to calculate the vitamin C content in the tablet.

mass of $KIO_3(s)$ used to prepare $I_2(aq)$ → concentration of $I_2(aq)$ prepared ✚ volume of $I_2(aq)$ used in titration → number of moles of iodine reacted with aqueous solution of vitamin C

use coefficients in the equation to find the mole ratio ➡ number of moles of vitamin C in 25.00 cm^3 solution → number of moles of vitamin C in 250.0 cm^3 solution → mass of vitamin C in one tablet

53.5 Redox titrations involving iodine (p.101)

Q (Example 53.5)

A student determined the vitamin C content in a commercial tablet following the steps listed below:

Step 1 Dissolve 0.257 g of potassium iodate and excess potassium iodide in deionised water. Add excess sulphuric acid.

Step 2 Dilute the mixture to a volume of 250.0 cm^3 with deionised water.

Step 3 Dissolve one vitamin C tablet in deionised water and dilute to make a solution of volume 250.0 cm^3.

Step 4 Titrate portions of 25.00 cm^3 of the vitamin C solution with the aqueous solution of iodine prepared, using starch solution as an indicator. The mean titre is 27.85 cm^3.

a) Calculate the molarity of the standard aqueous solution of iodine prepared. (Formula mass of potassium iodate = 214.0)

b) Calculate the vitamin C content in the tablet (in mg). (Relative molecular mass of vitamin C = 176.0)
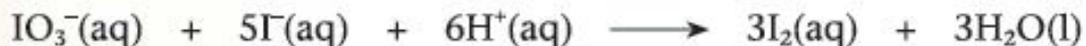
53.5 Redox titrations involving iodine (p.101)

Q (Example 53.5) (continued)

A

a) Iodate reacts with excess iodide to produce iodine according to the equation:

$$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \longrightarrow 3I_2(aq) + 3H_2O(l)$$

Number of moles of KIO_3 used $= \dfrac{0.257\ g}{214.0\ g\ mol^{-1}}$

$$= 1.20 \times 10^{-3}\ mol$$

According to the equation, 1 mole of IO_3^- gives 3 moles of I_2 in the reaction.

i.e. number of moles of I_2 produced $= 3 \times 1.20 \times 10^{-3}\ mol$

$$= 3.60 \times 10^{-3}\ mol$$

Concentration of aqueous solution of iodine $= \dfrac{3.60 \times 10^{-3}\ mol}{\dfrac{250.0}{1\ 000}\ dm^3}$

$$= 0.0144\ mol\ dm^{-3}$$

b) $\quad C_6H_8O_6(aq) + I_2(aq) \longrightarrow C_6H_6O_6(aq) + 2H^+(aq) + 2I^-(aq)$

$\quad$ one tablet $\qquad$ 27.85 cm^3

$\qquad\qquad\downarrow$

250.0 cm^3

$\qquad\qquad\downarrow$

(used) 25.00 cm^3

53.5 Redox titrations involving iodine (p.101)

Q (Example 53.5) (continued)

A

Number of moles of I_2 in 27.85 cm^3 solution = 0.0144 mol dm^{-3} x $\dfrac{27.85}{1\ 000}$ dm^3

$$= 4.01 \times 10^{-4} \text{ mol}$$

According to the equation, 1 mole of vitamin C reacts with 1 mole of I_2.

i.e. number of moles of vitamin C in 25.00 cm^3 solution = 4.01×10^{-4} mol

Number of moles of vitamin C in 250.0 cm^3 solution

= $10 \times 4.01 \times 10^{-4}$ mol

= 4.01×10^{-3} mol

= number of moles of vitamin C in one tablet

Mass of vitamin C in one tablet = 4.01×10^{-3} mol x 176.0 g mol^{-1}

$$= 0.706 \text{ g}$$
$$= 706 \text{ mg}$$

∴ one tablet contains 706 mg of vitamin C.

53.5 Redox titrations involving iodine (p.101)

Practice 53.3

The following experiment was carried out to determine the total concentration of SO_2 in a sample of white wine.

Step 1 25.00 cm^3 of the wine sample were transferred to a conical flask. NaOH(aq) and H_2SO_4(aq) were added to liberate all the SO_2 from the wine.

Step 2 The resulting solution was immediately titrated with 0.00319 mol dm^{-3} I_2(aq), using starch solution as an indicator.

a) State the expected colour change at the end point of the titration.

53.5 Redox titrations involving iodine (p.101)

Practice 53.3 (continued)

b) The experiment was repeated four times and the results are listed below:

Experiment number	1	2	3	4
Volume of I_2(aq) (cm^3)	14.65	13.80	13.85	13.80

i) Calculate a reasonable average of the volume of I_2(aq) used in the titration.

ii) The reaction involved in the titration can be represented by the following equation:

SO_2(g) + I_2(aq) + $2H_2O$(l) $\longrightarrow$ $2HI$(aq) + H_2SO_4(aq)
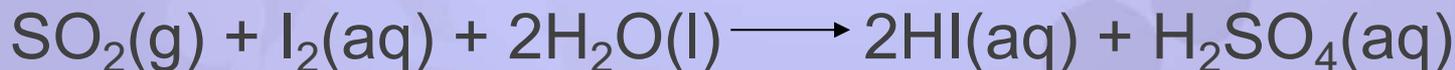
Calculate the total concentration of sulphur dioxide, in mg dm^{-3}, in the sample of white wine.
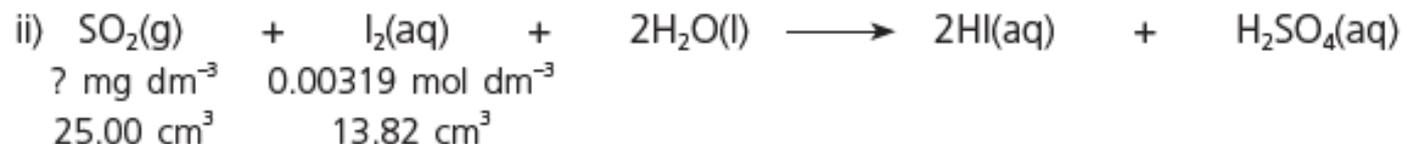
(Relative atomic masses: O = 16.0, S = 32.1)

53.5 Redox titrations involving iodine (p.101)

Practice 53.3 (continued)

a) From colourless to dark blue

b) i) Average volume of I_2(aq) $= \dfrac{13.80 + 13.85 + 13.80}{3}$ cm^3

$= 13.82$ cm^3

ii) SO_2(g) $+$ I_2(aq) $+$ $2H_2O$(l) $\longrightarrow$ $2HI$(aq) $+$ H_2SO_4(aq)

? mg dm^{-3} 0.00319 mol dm^{-3}

25.00 cm^3 13.82 cm^3

Number of moles of I_2 in 13.82 cm^3 solution $= 0.00319$ mol dm^{-3} x $\dfrac{13.82}{1\ 000}$ dm^3

$= 4.41$ x 10^{-5} mol

According to the equation, 1 mole of SO_2 reacts with 1 mole of I_2.

i.e. number of moles of $SO_2 = 4.41$ x 10^{-5} mol

Concentration of $SO_2 = \dfrac{4.41 \times 10^{-5} \text{ mol} \times 64.1 \text{ g mol}^{-1}}{\dfrac{25.00}{1\ 000} \text{ dm}^3}$

$= 0.113$ g dm^{-3}

$= 113$ mg dm^{-3}

53.5 Redox titrations involving iodine (p.101)

Determining the concentration of sodium hypochlorite in a household bleach

◆ The active ingredient in a household bleach is sodium hypochlorite (NaOCl).

◆ Sodium hypochlorite is strong enough to oxidise iodide ion to iodine.

$$OCl^-(aq) + 2H^+(aq) + 2I^-(aq) \longrightarrow Cl^-(aq) + H_2O(l) + I_2(aq)$$

The active ingredient in household bleach is sodium hypochlorite

99.9%

Blea

Active ingredients: Sodium hypochlorite

Net Capacity: 1500ml
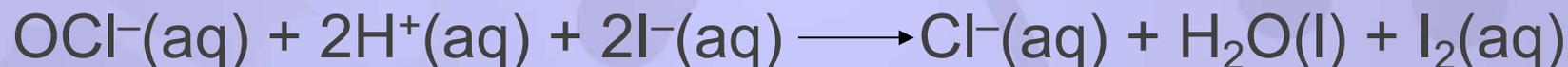
Determining the sodium hypochlorite content in a bleach _Ref._

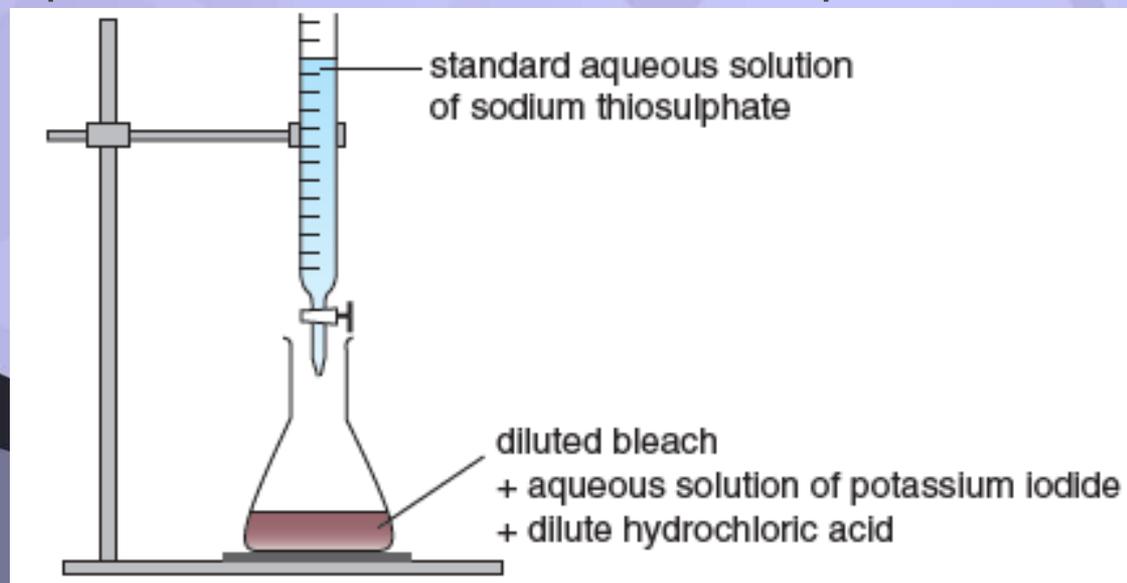# 53.5 Redox titrations involving iodine (p.101)

◆ The concentration of sodium hypochlorite in a household bleach can be determined as follows:

- Pipette 10.00 cm³ of the bleach into a 250.0 cm³ volumetric flask. Add deionised water to prepare 250.0 cm³ of solution.
- Pipette 25.00 cm³ of the diluted bleach into a conical flask. Then add an excess of aqueous solution of potassium iodide followed by sufficient dilute hydrochloric acid to acidify the solution.
- Titrate the iodine in the solution in the conical flask using a standard aqueous solution of sodium thiosulphate from a burette.
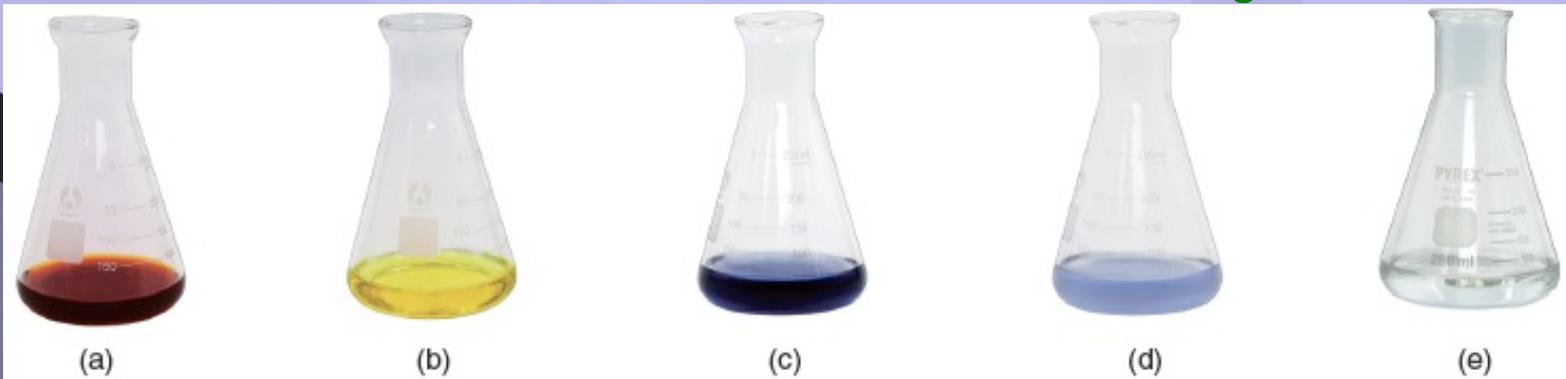
standard aqueous solution
of sodium thiosulphate

diluted bleach
+ aqueous solution of potassium iodide
+ dilute hydrochloric acid

Set-up for titrating the iodine liberated with a standard aqueous solution of sodium thiosulphate

53.5 Redox titrations involving iodine (p.101)

- A brown colour appears when the diluted bleach reacts with the iodide ion to form iodine (a).
- During the titration with the aqueous solution of sodium thiosulphate, the iodine is reduced back to iodide ion and the brown colour fades gradually. When the titration end point is being approached, the iodine colour has faded enough to become a pale straw colour (b).
- At this point, add a small amount of starch solution as an indicator. A dark blue colour mixture forms (c).
- As more aqueous solution of sodium thiosulphate is added, the dark blue colour fades (d).
- At the titration end point, all the iodine has just reacted and the blue colour disappears (e).

Colour changes of the mixture in the conical flask during an iodine-thiosulphate titration

(a)　　　　　(b)　　　　　(c)　　　　　(d)　　　　　(e)

53.5 Redox titrations involving iodine (p.101)

◆ The steps you can follow to calculate the concentration of sodium hypochlorite in the bleach.

concentration and volume of $Na_2S_2O_3(aq)$ used →

number of moles of $S_2O_3^{2-}$ ion reacted with iodine liberated →

use coefficients in the equation to find the mole ratio →

number of moles of iodine liberated from the reaction between diluted bleach and iodide ion →

number of moles of sodium hypochlorite in 25.00 cm^3 of diluted bleach →

number of moles of sodium hypochlorite in 10.00 cm^3 of original bleach →

percentage by mass of sodium hypochlorite in original bleach

53.5 Redox titrations involving iodine (p.101)

Q (Example 53.6)

In an experiment carried out to determine the percentage by mass of sodium hypochlorite in a household bleach, 10.00 cm³ of the diluted bleach were diluted with deionised water and made up to 250.0 cm³ in a volumetric flask. 25.00 cm³ of the diluted bleach were placed in a conical flask. Excess KI(aq) and sufficient dilute HCl(aq) were added.

The iodine formed in the conical flask was titrated with 0.0548 mol dm⁻³(aq), adding starch solution as an indicator at appropriate time. 23.15 cm³ of Na₂S₂O₃(aq) were required to reach the end point.
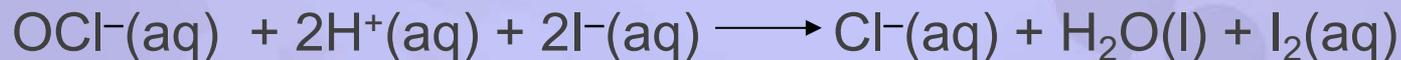
53.5 Redox titrations involving iodine (p.101)

Q (Example 53.6) (continued)

a)   Explain why excess KI(aq) was added to the 25.00 cm^3 diluted bleach.
b)   State the colour change at the titration end point.
c)   In the titration, I_2(aq) reacts with $S_2O_3^{2-}$ (aq) ion according to the equation below.

I_2(aq) + 2$S_2O_3^{2-}$ (aq) $\longrightarrow$ 2I$^-$ (aq) + $S_4O_6^{2-}$ (aq)

From the titration result, calculate the number of moles of iodine formed from the reaction between the diluted bleach and KI(aq).

d)   OCl$^-$(aq) ion from the bleach reacts with I$^-$ (aq) ion to form I_2(aq) according to the equation below.

OCl$^-$(aq) + 2H$^+$(aq) + 2I$^-$(aq) $\longrightarrow$ Cl$^-$(aq) + H_2O(l) + I_2(aq)

Calculate the percentage by mass of sodium hypochlorite in the original bleach.

(Molar mass of NaOCl = 74.5 g mol^{-1};
 density of original bleach = 1.05 g cm^{-3})

53.5 Redox titrations involving iodine (p.101)

Q (Example 53.6) (continued)

A
a) To ensure that all the hypochlorite in the diluted bleach has reacted.

b) From blue to colourless

c) The following reaction occurs in the titration process:

$$I_2(aq) \quad + \quad 2S_2O_3^{2-}(aq) \quad \longrightarrow \quad 2I^-(aq) \quad + \quad S_4O_6^{2-}(aq)$$

$$0.0548 \text{ mol dm}^{-3}$$
$$23.15 \text{ cm}^3$$

Number of moles of $S_2O_3^{2-}$ ion reacted with the iodine formed

$$= 0.0548 \text{ mol dm}^{-3} \times \frac{23.15}{1\ 000} \text{ dm}^3$$

$$= 1.27 \times 10^{-3} \text{ mol}$$

According to the equation, 1 mole of I_2 reacts with 2 moles of $S_2O_3^{2-}$ ion.

i.e. number of moles of I_2 reacted with $S_2O_3^{2-}$ ion

$$= \frac{1.27 \times 10^{-3}}{2} \text{ mol}$$

$$= 6.35 \times 10^{-4} \text{ mol}$$

$$= \text{number of moles of } I_2 \text{ formed from } 25.00 \text{ cm}^3 \text{ of diluted bleach}$$

53.5 Redox titrations involving iodine (p.101)

Q (Example 53.6) (continued)

A

d) $OCl^-(aq) + 2H^+(aq) + 2I^-(aq) \longrightarrow Cl^-(aq) + H_2O(l) + I_2(aq)$
    25.00 cm³ 6.35×10^{-4} mol
    diluted bleach

According to the equation, 1 mole of OCl^- ion reacts with excess I^- ion to form 1 mole of I_2.

i.e. number of moles of OCl^- ion in 25.00 cm³ diluted bleach = 6.35×10^{-4} mol

Number of moles of OCl^- ion in 250.0 cm³ diluted bleach
= $10 \times 6.35 \times 10^{-4}$ mol
= 6.35×10^{-3} mol
= number of moles of OCl^- ion in 10.00 cm³ of original bleach

Number of moles of NaOCl in 1.00 dm³ of original bleach = $6.35 \times 10^{-3} \times \dfrac{1\,000}{10.00}$ mol

= 0.635 mol

Mass of NaOCl in 1.00 dm³ of original bleach = 0.635 mol × 74.5 g mol⁻¹
= 47.3 g

Mass of 1.00 dm³ of original bleach = 1.05 g cm⁻³ × 1 000 cm³
= 1 050 g

Percentage by mass of NaOCl in original bleach = $\dfrac{47.3 \text{ g}}{1\,050 \text{ g}} \times 100\%$

= 4.50%

∴ the percentage by mass of sodium hypochlorite in the bleach is 4.50%.

53.5 Redox titrations involving iodine (p.101)

Practice 53.4

Ozone is important not only for its protective effects from harm caused by ultraviolet radiation, but also for water and sewage treatment. It is usually produced as a mixture with oxygen called ozonised oxygen.

The amount of ozone in ozonised oxygen can be determined by using the ozone to oxidise iodide ion and titrating the iodine formed with a standard aqueous solution of sodium thiosulphate.

$$O_3(g) + 2I^-(aq) + H_2O(l) \longrightarrow O_2(g) + I_2(aq) + 2OH^-(aq)$$

10.0 dm^3 of ozonised oxygen were shaken repeatedly with an aqueous solution of potassium iodide. The iodine formed required 40.00 cm^3 of 1.00 mol dm^{-3} aqueous solution of sodium thiosulphate for reduction.

a) Write the ionic equation for the reaction between the iodine formed and the aqueous solution of sodium thiosulphate.

b) Briefly describe how the end point of the titration can be determined.

c) Calculate the percentage by volume of ozone in the ozonised oxygen.

(Molar volume of gas at temperature and pressure of the experiment = 24.0 dm^3 mol^{-1})

53.5 Redox titrations involving iodine (p.101)

Practice 53.4 (continued)

a) $I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

b) Add $Na_2S_2O_3(aq)$ to the reaction mixture until the mixture changes to a pale straw colour.
   Add starch solution.
   Add $Na_2S_2O_3(aq)$ dropwise until the mixture changes from dark blue to colourless.

c) Number of moles of $S_2O_3^{2-}$ ion reacted with I_2 = 1.00 mol dm^{-3} x $\dfrac{40.00}{1\ 000}$ dm^3
   = 0.0400 mol

Number of moles of I_2 formed = $\dfrac{0.0400}{2}$ mol
   = 0.0200 mol

$$O_3(g)\ +\ 2I^-(aq)\ +\ H_2O(l) \longrightarrow O_2(g)\ +\ I_2(aq)\ +\ 2OH^-(aq)$$
10.0 dm^3 0.0200 mol

According to the equation, O_3 reacts with KI to produce 0.0200 mole of I_2.
i.e. number of moles of O_3 = 0.0200 mol
Volume of O_3 = 0.0200 mol x 24.0 dm^3 mol^{-1}
   = 0.480 dm^3

Percentage by volume of O_3 in the ozonised oxygen = $\dfrac{0.480 \text{ dm}^3}{10.0 \text{ dm}^3}$ x 100%

   = 4.80%

Key terms (p.112)

redox titration	氧化還原滴定	standardise	標定

Summary (p.113)

1 Volumetric analysis is a widely used quantitative analytical method. This is a method of analysis based on titration.

2 a) Precipitation titrations are based upon reactions that yield precipitates. They are useful in determining the concentrations of halides.

b) The concentration of chloride ion in a sample solution can be determined by precipitation titration with standard $AgNO_3$(aq), using a chromate indicator.

3 Determine the iron content in a commercial iron tablet by titration with standard $KMnO_4$(aq).

The first appearance of a persistent pale pink colour indicates the titration end point.

Summary (p.113)

4 To determine the vitamin C in a commercial tablet:

    Step 1 Prepare $I_2(aq)$ from a known mass of KIO_3 with excess $KI(aq)$ and $H^+(aq)$.

        $IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \longrightarrow 3I_2(aq) + 3H_2O(l)$
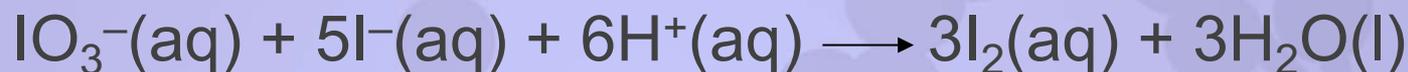
    Step 2 Determine the vitamin C content in a commercial tablet by titration with $I_2(aq)$, using starch solution as an indicator.
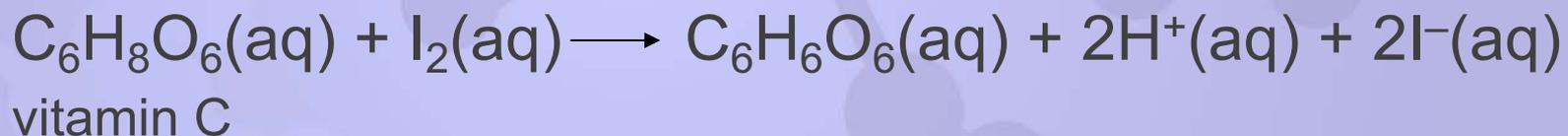
        $C_6H_8O_6(aq) + I_2(aq) \longrightarrow C_6H_6O_6(aq) + 2H^+(aq) + 2I^-(aq)$

        vitamin C

        The first appearance of a persistent dark blue colour indicates the titration end point.

Summary (p.113)

5 To determine the concentration of sodium hypochlorite in a household bleach:

Step 1 Liberate iodine from a diluted household bleach sample by the addition of excess KI(aq) and H^+(aq).

$$OCl^-(aq) + 2H^+(aq) + 2I^-(aq) \longrightarrow Cl^-(aq) + H_2O(l) + I_2(aq)$$
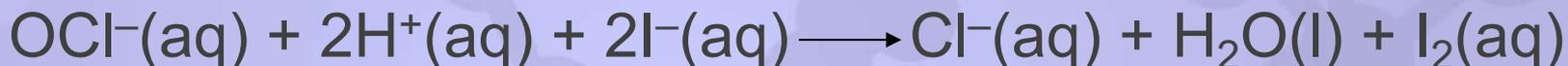
Step 2 Titration the iodine liberated with standard $Na_2S_2O_3$(aq).

$$I_2(aq) + 2S_2O_3{}^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6{}^{2-}(aq)$$

Add starch solution to the mixture when the titration end point is being approached. The blue colour disappears at the end point.

Unit Exercise (p.114)

Note: Questions are rated according to ascending level of difficulty (from 1 to 5):

👍 **question targeted at level 3 and above;**
👍👍 **question targeted at level 4 and above;**
👍👍👍 **question targeted at level 5.**

Unit Exercise (p.114)

PART I KNOWLEDGE AND UNDERSTANDING

1 Complete the following concept map.
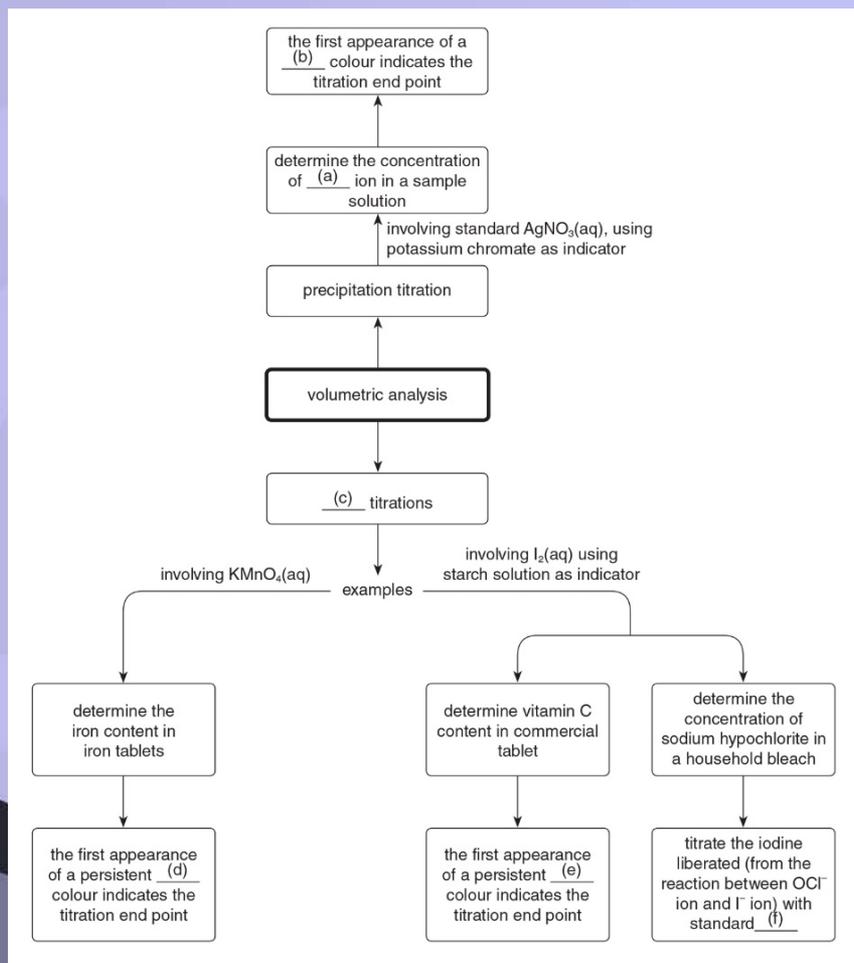
a) chloride
b) reddish brown
c) redox
d) pale pink
e) dark blue
f) aqueous solution of sodium thiosulphate

Unit Exercise (p.114)

PART II MULTIPLE CHOICE QUESTIONS

Directions: Questions 2–4 refer to the following experiment carried out to determine the concentration of chloride ion in a sample of sea water. 25.00 cm^3 of sea water were diluted to make 250.0 cm^3 of solution. 25.00 cm^3 of the diluted sea water were measured with apparatus X and placed in apparatus Y. The diluted sea water in Y was then titrated with 0.0860 mol dm^{-3} AgNO$_3$(aq), using a chromate indicator. 16.85 cm^3 of AgNO$_3$(aq) were required to reach the titration end point. (Relative atomic mass: Cl = 35.5)

2   Which of the following combinations concerning X and Y is correct?

	X	Y
A	measuring cylinder	conical flask
B	measuring cylinder	volumetric flask
C	pipette	conical flask
D	pipette	volumetric flask

Answer: C

Unit Exercise (p.114)

3 What would be observed at the titration end point?

A   A lemon yellow solution formed.
B   A reddish brown solution formed.
C   A lemon yellow precipitate formed.
D   A reddish brown precipitate formed.

Answer: D

Unit Exercise (p.114)

4 What is the concentration of chloride ion in the sample of sea water?

A 16.3 g dm^{-3}

B 20.6 g dm^{-3}

C 29.3 g dm^{-3}

D 36.9 g dm^{-3}

Explanation:

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

0.0860 mol dm^{-3} 25.00 cm^3

16.85 cm^3

250.0 cm^3

(used) 25.00 cm^3

Number of moles of Ag$^+$ ion in 16.85 cm^3 solution

$$= 0.0860 \text{ mol dm}^{-3} \times \frac{16.85}{1\,000} \text{ dm}^3$$

$$= 1.45 \times 10^{-3} \text{ mol}$$

According to the equation, 1 mole of Ag$^+$ ion reacts with 1 mole of Cl$^-$ ion.

i.e. number of moles of Cl$^-$ ion in 25.00 cm^3 diluted sea water = 1.45 x 10^{-3} mol

Number of moles of Cl$^-$ ion in 250.0 cm^3 diluted sea water

= 10 x 1.45 x 10^{-3} mol

= 1.45 x 10^{-2} mol

= number of moles of Cl$^-$ ion in 25.00 cm^3 sea water

Concentration of Cl$^-$ ion in sea water = $\dfrac{1.45 \times 10^{-2} \text{ mol} \times 35.5 \text{ g mol}^{-1}}{\frac{25.00}{1\,000} \text{ dm}^3}$

= 20.6 g dm^{-3}

Answer: B

Unit Exercise (p.114)

5 A titration using potassium permanganate in dilute sulphuric acid can be used to determine the percentage of

A   aspirin in aspirin tablets.
B   chlorine in bleach.
C   copper in an alloy.
D   iron(II) sulphate in iron tablets.

Answer: D

Unit Exercise (p.114)

Directions: Questions 6–7 refer to the following experiment carried out to determine the mass of a sample of potassium ethanedioate crystals $(K_2C_2O_4 \cdot H_2O)$.

A student dissolved a sample of potassium ethanedioate crystals in deionised water and the volume made up to 100.0 cm^3.

25.00 cm^3 of this solution were titrated with 0.0500 mol dm^{-3} $KMnO_4$(aq).

18.40 cm^3 of $KMnO_4$(aq) were required to reach the end point.

The equation for the reaction taking place is given below.

$5C_2O_4^{2-}$(aq) + $2MnO_4^-$(aq) + $16H^+$(aq) $\longrightarrow$ $10CO_2$(g) + $2Mn^{2+}$(aq) + $8H_2O$(l)
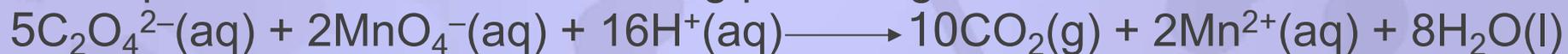
6 What colour change indicated the titration end point?

A   From colourless to pale pink
B   From colourless to yellow
C   From yellow to colourless
D   From pale pink to colourless

Answer: A

Unit Exercise (p.114)

7 What is the mass of the sample of potassium ethanedioate crystals ($K_2C_2O_4 \cdot H_2O$)?
(Molar mass of $K_2C_2O_4 \cdot H_2O$ = 184.2 g mol^{-1})

A 1.69 g

B 2.12 g

C 4.24 g

D 8.47 g

Answer: A

Explanation:
$5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \longrightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$
25.00 cm^3 0.0500 mol dm^{-3}
                18.40 cm^3
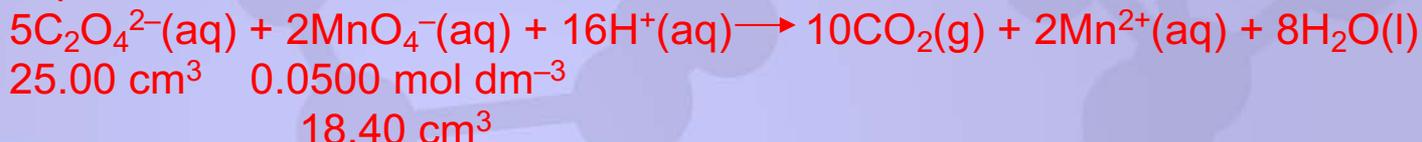
Number of moles of MnO_4^- ion in 18.40 cm^3 solution
= 0.0500 mol dm^{-3} x $\dfrac{18.40}{1\,000}$ dm^3
= 9.20 x 10^{-4} mol

According to the equation, 2 moles of MnO_4^- ion react with 5 moles of $C_2O_4^{2-}$ ion. i.e. number of moles of $C_2O_4^{2-}$ ion in 25.00 cm^3 solution

= $\dfrac{5}{2}$ x 9.20 x 10^{-4} mol

= 2.30 x 10^{-3} mol

Number of moles of $C_2O_4^{2-}$ ion in 100.0 cm^3 solution = 4 x 2.30 x 10^{-3} mol
                                              = 9.20 x 10^{-3} mol

Mass of $K_2C_2O_4 \cdot H_2O$ = 9.20 x 10^{-3} mol x 184.2 g mol^{-1}
                        = 1.69 g

Unit Exercise (p.114)

Directions: Questions 8–10 refer to the following experiment carried out to determine the concentration of an iodine solution.

An iodine solution was prepared by dissolving solid iodine and potassium iodide in deionised water, and making the volume up to 1.00 dm^3.

25.00 cm^3 of this solution were titrated with 0.0780 mol dm^{-3} $Na_2S_2O_3$(aq), using starch solution

as an indicator. 29.50 cm^3 of $Na_2S_2O_3$(aq) were required to reach the end point.

8 During the titration, the starch solution should NOT be added until nearly all the iodine has reacted. This is because when the concentration of iodine is high,

    A   the starch decomposes.

    B   the starch reacts with the thiosulphate ion added.

    C   the dark blue complex formed between starch and iodine becomes colourless.

    D   the starch adsorbs some of the iodine.

Answer: D

Unit Exercise (p.114)

9 What colour change would be observed at the titration end point?

A   From colourless to yellow
B   From colourless to blue
C   From blue to colourless
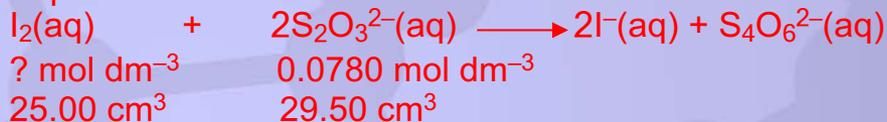D   From blue to yellow

Answer: C

Unit Exercise (p.114)

10 I_2(aq) reacts with $Na_2S_2O_3$(aq) according to the equation below:

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$
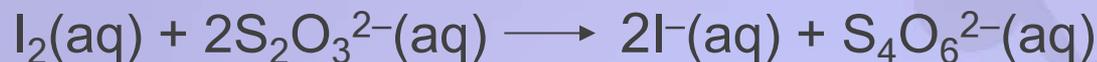
What is the concentration of the iodine solution?

Explanation:

$$I_2(aq) \quad + \quad 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

? mol dm⁻³	0.0780 mol dm⁻³
25.00 cm³	29.50 cm³

A   0.0920 mol dm^{-3}
B   0.0661 mol dm^{-3}
C   0.0460 mol dm^{-3}
D   0.0331 mol dm^{-3}

Number of moles of $S_2O_3^{2-}$ ion in 29.50 cm³ solution

$= 0.0780$ mol dm^{-3} x $\dfrac{29.50}{1\,000}$ dm³

$= 2.30$ x 10^{-3} mol

According to the equation, 1 mole of I_2 reacts with 2 moles of $S_2O_3^{2-}$ ion.

i.e. number of moles of I_2 = $\dfrac{2.30 \times 10^{-3}}{2}$ mol

$= 1.15$ x 10^{-3} mol

Answer: C

Concentration of iodine solution = $\dfrac{1.15 \times 10^{-3} \text{ mol}}{\frac{25.00}{1\,000} \text{dm}^3}$

$= 0.0460$ mol dm^{-3}

Unit Exercise (p.114)

PART III **STRUCTURED QUESTIONS**

11 Sodium chloride is added to a particular meat product. The amount of chloride in the meat product can be found by titration with aqueous solution of silver nitrate.

The chloride from 100.0 g of the meat product was extracted into water and the solution made up to 1.00 dm^3 in a volumetric flask. 10.0 cm^3 portions of the solution were titrated with 0.0200 mol dm^{-3} AgNO$_3$(aq), using a chromate indicator. The mean titre was 15.50 cm^3.

Unit Exercise (p.114)

11 (continued)

a) State and explain the colour change at the end point.

The first appearance of a reddish brown colour indicates the end point. (1)
After all the chloride ion has been precipitated as silver chloride, one drop of excess silver nitrate solution results in the formation of a reddish brown precipitate of silver chromate. This signals the end point of the titration. (1)

Unit Exercise (p.114)

11 <u>(continued)</u>

b) Calculate the percentage by mass of sodium chloride in the meat product. (Relative atomic masses: Na = 23.0, Cl = 35.5)

$Ag^+(aq)$ + $Cl^-(aq)$ ⟶ $AgCl(s)$
0.0200 mol dm^{-3} 1.00 dm^3
15.50 cm^3 (used)   (used) 10.00 cm^3

Number of moles of Ag^+ ion in 15.50 cm^3 solution

= 0.0200 mol dm^{-3} x $\dfrac{15.50}{1\,000}$ dm^3

= 3.10×10^{-4} mol (1)

According to the equation, 1 mole of Cl^- ion reacts with 1 mole of Ag^+ ion.

i.e. number of moles of Cl^- ion in 10.00 cm^3 solution = 3.10×10^{-4} mol (1)

Number of moles of Cl^- ion in 1.00 dm^3 solution = $100 \times 3.10 \times 10^{-4}$ mol
= 0.0310 mol

Mass of NaCl in 100.0 g of meat product = 0.0310 mol x 58.5 g mol^{-1}
= 1.81 g (1)

Percentage by mass of NaCl in meat product = $\dfrac{1.81 \text{ g}}{100.0 \text{ g}}$ x 100%

∴ the percentage by mass of sodium chloride in the meat product is 1.81%.
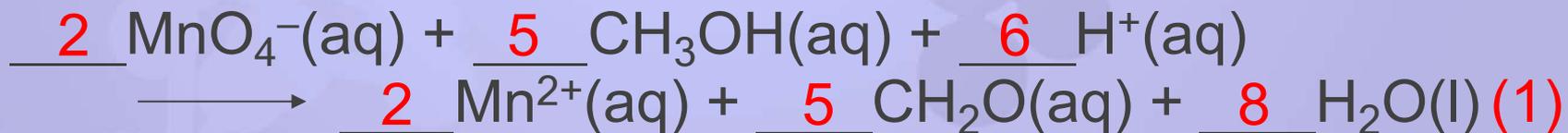
Unit Exercise (p.114)

12 A technician tested the concentration of methanol in diluted windshield washer fluid using a redox reaction.
   25.00 cm^3 of the sample were acidified and titrated with 0.0200 mol dm^{-3} KMnO$_4$(aq). 14.50 cm^3 of KMnO$_4$(aq) were required to reach the titration end point.
   a) State the colour change at the end point.

   From colourless to persistent pale pink (1)

   b) The equation below represents the reaction between KMnO$_4$(aq) and methanol in acidic solution.
   __2__ MnO$_4^-$(aq) + __5__ CH$_3$OH(aq) + __6__ H$^+$(aq)
   $\longrightarrow$ __2__ Mn^{2+}(aq) + __5__ CH$_2$O(aq) + __8__ H$_2$O(l) (1)
   Balance this equation by putting the appropriate numbers.

Unit Exercise (p.114)

12 (continued)

c) Calculate the concentration of methanol, in mol dm^{-3}, in the diluted windshield washer fluid.

$2MnO_4^-(aq) \quad + \quad 5CH_3OH(aq) + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5CH_2O(aq) + 8H_2O(l)$
0.0200 mol dm^{-3} $\quad$? mol dm^{-3}
14.50 cm^3 $\quad\quad\quad\quad$ 25.00 cm^3
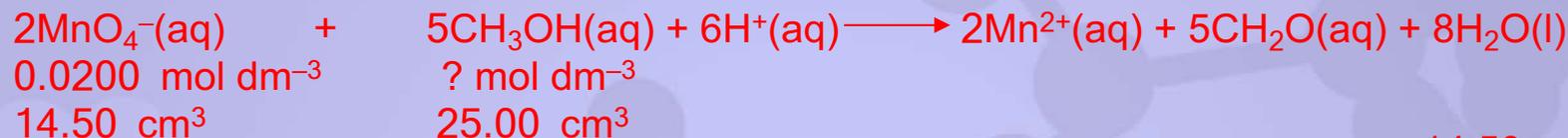
Number of moles of MnO$_4^-$ ion in 14.50 cm^3 solution = 0.0200 mol dm^{-3} x $\frac{14.50}{1\,000}$ dm^3

$\qquad\qquad\qquad\qquad\qquad\qquad =2.90 \times 10^{-4}$ mol (1)

According to the equation, 5 moles of CH$_3$OH react with 2 moles of MnO$_4^-$ ion.

i.e. number of moles of CH$_3$OH in 25.00 cm^3 solution = $\frac{5}{2}$ x 2.90 x 10^{-4} mol

$\qquad\qquad\qquad\qquad = 7.25 \times 10^{-4}$ mol (1)

Concentration of CH$_3$OH in diluted windshield washer fluid = $\dfrac{7.25 \times 10^{-4} \text{ mol}}{\frac{25.00}{1\,000} \text{ dm}^3}$

$\qquad\qquad\qquad\qquad = 0.0290$ mol dm^{-3} (1)

∴ the concentration of methanol in the diluted windshield washer fluid is 0.0290 mol dm^{-3}.

Unit Exercise (p.114)

13 Iron(II) ethanedioate dihydrate ($FeC_2O_4 \cdot 2H_2O$) reacts with acidified $KMnO_4(aq)$. Both the iron(II) ion and the ethanedioate ion are oxidised by the permanganate ion.

   1.232 g of iron(II) ethanedioate were dissolved in excess dilute sulphuric acid and made up to 250.0 cm^3 solution. 25.00 cm^3 portions of this solution were titrated with 0.0192 mol dm^{-3} $KMnO_4(aq)$.

   Four trials of the titration were carried out and the results were listed below:

Trial	1	2	3	4
Volume of $KMnO_4(aq)$ used (cm^3)	22.35	21.40	21.40	21.45

Unit Exercise (p.114)

13

a) Calculate a reasonable average of the volume of $KMnO_4(aq)$ used in the titration.

Average volume of $KMnO_4(aq)$ = $\dfrac{21.40 + 21.40 + 21.45}{3}$ cm^3

= 21.42 cm^3 (1)

b) Based on the experimental results, calculate the mole ratio of iron(II) ethanedioate to permanganate ion for the reaction taking place in the titration. (Molar mass of $FeC_2O_4 \cdot 2H_2O$ = 179.8 g mol^{-1})

Number of moles of MnO_4^- ion in 21.42 cm^3 solution = 0.0192 mol dm^{-3} x $\dfrac{21.42}{1\,000}$ dm^3

= 4.11 x 10^{-4} mol (1)

Number of moles of MnO_4^- ion required to react with 250.0 cm^3 solution of iron(II) ethanedioate

= 10 x 4.11 x 10^{-4} mol

= 4.11 x 10^{-3} mol

Number of moles of iron(II) ethanedioate = $\dfrac{1.232 \text{ g}}{179.8 \text{ g mol}^{-1}}$

= 6.85 x 10^{-3} mol (1)

Mole ratio of iron(II) ethanedioate to permanganate ion = $\dfrac{6.85 \times 10^{-3} \text{ mol}}{4.11 \times 10^{-3} \text{ mol}}$

= 1.67 = $\dfrac{5}{3}$ (1)

∴ the mole ratio of iron(II) ethanedioate to permanganate ion for the reaction is 5 : 3.

Unit Exercise (p.114)

14 Tin forms an oxide, A, that contains the metal in both oxidation states II and IV. The formula of A can be found by the following method.

Step 1   A sample of A was dissolved in H_2SO_4(aq), producing solution B, which was a mixture of tin(II) sulphate and tin(IV) sulphate.

Step 2   25.00 cm^3 of solution B were titrated against 0.0150 mol dm^{-3} $KMnO_4$(aq). 18.00 cm^3 of $KMnO_4$(aq) were required to reach the titration end point.

Step 3   Another 25.00 cm^3 sample of solution B was treated with an excess of powdered zinc. This converted all the tin into tin(II) ion. The excess of zinc powder was filtered off. The filtrate was titrated against 0.0150 mol dm^{-3} $KMnO_4$(aq). 27.15 cm^3 of $KMnO_4$(aq) were required to reach the titration end point.

The equation for the reaction occurring during the titration is as follows.

$2MnO_4^-$(aq) + $16H^+$(aq) + $5Sn^{2+}$(aq) $\longrightarrow$ $2Mn^{2+}$(aq) + $8H_2O$(l) + $5Sn^{4+}$(aq)

Unit Exercise (p.114)

14

a) Write the ionic equation for the reaction between $Zn(s)$ and $Sn^{4+}(aq)$.

$Zn(s) + Sn^{4+}(aq) \longrightarrow Zn^{2+}(aq) + Sn^{2+}(aq)$
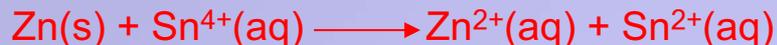
b) Use the results of the two titrations to calculate

i) the number of moles of Sn^{2+} in the titration sample in *Step 2*;

$2MnO_4^-(aq) \quad + \quad 16H^+(aq) + 5Sn^{2+}(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Sn^{4+}(aq)$
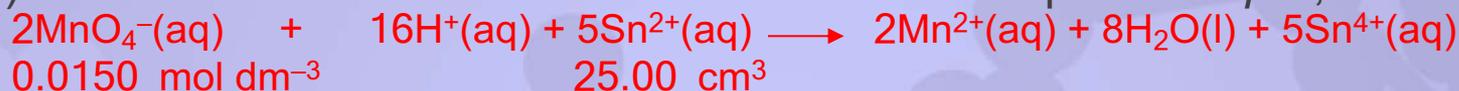
0.0150 mol dm^{-3} $\qquad\qquad 25.00$ cm^3

18.00 cm^3

Number of moles of MnO_4^- ion in 18.00 cm^3 solution $= 0.0150$ mol dm^{-3} x $\dfrac{18.00}{1\ 000}$ dm^3

$= 2.70$ x 10^{-4} mol (1)

According to the equation, 5 moles of Sn^{2+} ion react with 2 moles of MnO_4^- ion.

i.e. number of moles of Sn^{2+} in titration sample $= \dfrac{5}{2}$ x 2.70 x 10^{-4} mol

$= 6.75$ x 10^{-4} mol (1)

ii) the number of moles of Sn^{2+} in the titration sample in *Step 3*.

Number of moles of MnO_4^- ion in 27.15 cm^3 solution $= 0.0150$ mol dm^{-3} x $\dfrac{27.15}{1\ 000}$ dm^3

$= 4.07$ x 10^{-4} mol (1)

Number of moles of Sn^{2+} in titration sample $= \dfrac{5}{2}$ x 4.07 x 10^{-4} mol

$= 1.02$ x 10^{-3} mol (1)

Unit Exercise (p.114)

14

c) Use the results of your calculation in (b) to deduce the ratio of Sn^{2+} / Sn^{4+} in the oxide A, and hence suggest the chemical formula of A.

Number of moles of Sn^{4+} ion in 25.00 cm^3 sample = $(1.02 \times 10^{-3} - 6.75 \times 10^{-4})$ mol
$$= 3.45 \times 10^{-4} \text{ mol}$$

Mole ratio of Sn^{2+} / Sn^{4+} in oxide A = $\dfrac{6.75 \times 10^{-4} \text{ mol}}{3.45 \times 10^{-4} \text{ mol}}$

$$= 2 \text{ (1)}$$

Chemical formula of A is $2SnO + SnO_2$, i.e. Sn_3O_4. (1)

Unit Exercise (p.114)

15 A student carried out the following experiment to investigate the oxidation states of vanadium.

Step 1   A 0.631 g sample of vanadium metal was completely reacted with acid to form a yellow solution. The solution was made up to 250.0 cm^3 in a volumetric flask. The yellow solution contained VO_3^- ion.

Step 2   The yellow solution containing VO_3^- ion was reduced to a violet solution containing V^{n+} ion.

Step 3   25.00 cm^3 of the violet solution were titrated with 0.0554 mol dm^{-3} KMnO$_4$(aq). 13.45 cm^3 of KMnO$_4$(aq) were required to reach the titration end point.

In the titration, V^{n+} ion was oxidised back to VO_3^- ion.
MnO$_4^-$ ion was reduced:
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$

Unit Exercise (p.114)

15 (continued)

a) Why was the colour change at the titration end point difficult to observe?

$KMnO_4$ is pink in colour and V^{n+} / V^{2+} is violet in colour. (1)

b) Based on the experimental results, calculate the mole ratio of $V^{n+}(aq)$: $MnO_4^-(aq)$ in the titration. (Relative atomic mass: V = 50.9)

Number of moles of MnO_4^- ion in 13.45 cm^3 solution

= 0.0554 mol dm^{-3} x $\dfrac{13.45}{1\ 000}$ dm^3

= 7.45 x 10^{-4} mol (1)

Number of moles of VO_3^- ion in 250.0 cm^3 solution = $\dfrac{0.631\ g}{50.9\ g\ mol^{-1}}$

= 0.0124 mol (1)

Number of moles of VO_3^- ion in 25.00 cm^3 solution = $\dfrac{0.0124}{10}$ mol

= 0.00124 mol

Mole ratio of V^{n+} : MnO_4^- in titration = $\dfrac{0.00124\ mol}{7.45\ x\ 10^{-4}mol}$

= 1.66

= $\dfrac{5}{3}$ (1)

Unit Exercise (p.114)

15

c) Deduce the value of n in the V^{n+} ion formed in *Step 2*.

The oxidation number of Mn changes from +7 to +2, and the oxidation number of V in VO_3^- ion is +5.
The mole ratio of V^{n+} : MnO_4^- is 5 : 3.
i.e. $n + 3 = +5$
$n = +2$ (1)

d) Construct the ionic equation for the reaction that takes place during the titration.

$5V^{2+}(aq) + 3MnO_4^-(aq) + 3H_2O(l) \longrightarrow 5VO_3^-(aq) + 3Mn^{2+}(aq) + 6H^+(aq)$ (1)

Unit Exercise (p.114)

16 a) The following method was used to estimate the concentration of ethanol in an aqueous solution, Q, prepared by the fermentation of sucrose.

25.00 cm^3 of Q was measured using a pipette and transferred to a 250.0 cm^3 volumetric flask; the flask was made up to the mark with distilled water and mixed thoroughly, forming a diluted solution, R.

25.00 cm^3 samples of R were mixed with an equal volume of a 0.200 mol dm^{-3} potassium dichromate solution and excess dilute sulphuric acid

The mixture was allowed to stand for several hours and then the amount of unreacted potassium dichromate was determined by titration against a 0.255 mol dm^{-3} iron(II) ammonium sulphate solution. The mean titre was 23.85 cm^3.

Unit Exercise (p.114)

a) i) Use the half equations below to write the full ionic equation for the reaction between potassium dichromate and iron(II) ammonium sulphate.

$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$$

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq) \quad (1)$$

ii) Calculate the number of moles of potassium dichromate that remained unreacted after standing for several hours with solution R.

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq)$$
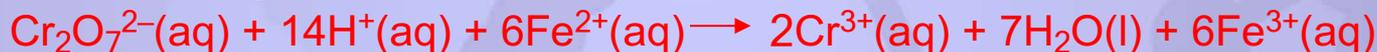
? mol   0.255 mol dm^{-3}
                                          23.85 cm^3

Number of moles of Fe^{2+} ion in 23.85 cm^3 solution = 0.255 mol dm^{-3} x $\dfrac{23.85}{1\ 000}$ dm^3

$$= 6.08 \times 10^{-3} \text{ mol (1)}$$

According to the equation, 1 mole of Cr$_2$O$_7^{2-}$ ion reacts with 6 moles of Fe^{2+} ion.

i.e. number of moles of Cr$_2$O$_7^{2-}$ ion remained = $\dfrac{6.08 \times 10^{-3}}{6}$ mol

$$= 1.01 \times 10^{-3} \text{ mol}$$

Unit Exercise (p.114)

16 (continued)

a) iii) Calculate the number of moles of potassium dichromate that reacted with the ethanol while standing for several hours with solution R.

Number of moles of $Cr_2O_7^{2-}$ ion at start = 0.200 mol dm^{-3} x $\dfrac{25.00}{1\ 000}$ dm^3

= 5.00 x 10^{-3} mol

Number of moles of $Cr_2O_7^{2-}$ ion reacted with ethanol = (5.00 − 1.01) x 10^{-3} mol

= 3.99 x 10^{-3} mol (1)

iv) Write the half equation for the oxidation of ethanol to ethanoic acid.
Use your half equation, and the half equation for the reduction of dichromate ions, to show that 3 moles of ethanol are oxidised by 2 moles of potassium dichromate.

$CH_3CH_2OH + H_2O \longrightarrow CH_3COOH + 4H^+ + 4e^-$ (1)

3 moles of CH_3CH_2OH require 12 moles of electrons supplied by 2 moles of $K_2Cr_2O_7$. (1)

v) Calculate the concentration of ethanol (in mol dm^{-3}) in solution Q.

Number of moles of ethanol reacted with $K_2Cr_2O_7$ = $\dfrac{3}{2}$ x 3.99 x 10^{-3} mol

= 5.99 x 10^{-3} mol (1)

Concentration of ethanol in solution Q = 10 x $\dfrac{5.99\ \times\ 10^{-3}\ \text{mol}}{\dfrac{25.00}{1\ 000}\ \text{dm}^3}$

= 2.40 mol dm^{-3} (1)

∴ the concentration of ethanol in solution Q is 2.40 mol dm^{-3}.

Unit Exercise (p.114)

16 (continued)

b) This method of determining ethanol concentration does not give very reliable results, although the titration is very accurate.

Suggest ONE reason why this might be the case, explaining how the measured concentration would differ from the actual concentration of the ethanol.

(Edexcel Advanced GCE, Unit 5, 6CH05/01, Jun. 2014, 21(a), (c))

Any one of the following:
- Difficult to know when all the ethanol has been oxidised to ethanoic acid. / Some ethanol may only be oxidised to ethanal.   (1)
  So less potassium dichromate will be used up and ethanol concentration will appear low.   (1)
- Other compounds in the fermented solution (e.g. aldehydes) are oxidised also. (1)
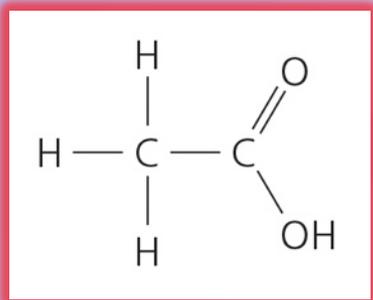 So more potassium dichromate will be used up and ethanol concentration will appear high.   (1)

Unit Exercise (p.114)

17 E300 is an antioxidant used in white wines. It prevents dissolved oxygen reacting with the ethanol to form an acid, X, which would produce a sour-tasting wine.

a) Draw the structural formula of the acid, X, responsible for the wine's sour taste.

(1)

b) The maximum allowed concentration of E300 in drinks is 150 mg dm^{-3}. A student performed the following redox titration procedure to find out if a drink containing E300 was within this limit.

The student prepared an aqueous solution of iodine by dissolving 0.132 g of potassium iodate (KIO_3) and excess potassium iodide in deionised water. Dilute sulphuric acid was added. The mixture was diluted to a volume of 250.0 cm^3.

25.00 cm^3 portions of the drink were titrated with the aqueous solution of iodine prepared, using starch solution as an indicator. The mean titre was 6.35 cm^3.

Unit Exercise (p.114)

17

b) i) Potassium iodate reacts with excess potassium iodide to produce iodine according to the equation:

$$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \longrightarrow 3I_2(aq) + 3H_2O(l)$$

Calculate the concentration of the aqueous solution of iodine prepared. (Formula mass of potassium iodate = 214.0)

Number of moles of KIO_3 = $\dfrac{0.132 \text{ g}}{214.0 \text{ g mol}^{-3}}$

$= 6.17 \times 10^{-4} \text{ mol}$ (1)

According to the equation, 1 mole of KIO_3 reacts with KI to give 3 moles of I_2.
i.e. number of moles of I_2 = $3 \times 6.17 \times 10^{-4}$ mol
$= 1.85 \times 10^{-3}$ mol

Concentration of I_2 solution = $\dfrac{1.85 \times 10^{-3} \text{ mol}}{\dfrac{250.0}{1\ 000} \text{ dm}^3}$

$= 7.40 \times 10^{-3} \text{ mol dm}^3$ (1)

Unit Exercise (p.114)

17

b) ii) State the expected colour change at the end point of the titration.

From colourless to dark blue (1)
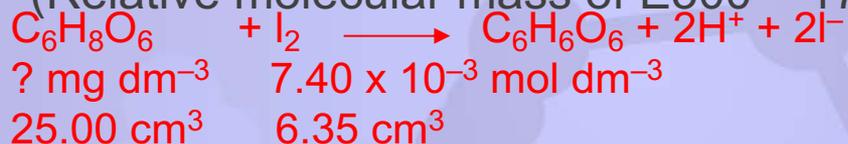
iii) E300 reacts with iodine according to the equation below:

$$C_6H_8O_6 + I_2 \longrightarrow C_6H_6O_6 + 2H^+ + 2I^-$$
   E300

Determine the concentration of E300 in the drink and hence whether the drink is within the limited allowed.

(Relative molecular mass of E300 = 176.0)

$$C_6H_8O_6 \qquad + I_2 \longrightarrow C_6H_6O_6 + 2H^+ + 2I^-$$
? mg dm^{-3} 7.40 x 10^{-3} mol dm^{-3}
25.00 cm^3 6.35 cm^3

Number of moles of I$_2$ in 6.35 cm^3 solution = 7.40 x 10^{-3} mol dm^{-3} x $\dfrac{6.35}{1\ 000}$ dm^3

= 4.70 x 10^{-5} mol   (1)

According to the equation, 1 mole of E300 reacts with 1 mole of I$_2$.
i.e. number of moles of E300 in 25.00 cm^3 drink = 4.70 x 10^{-5} mol   (1)

Concentration of E300 in drink = $\dfrac{4.70\ \text{x}\ 10^{-5}\ \text{mol}}{\dfrac{25.00}{1\ 000}\ \text{dm}^3}$

= 1.88 x 10^{-3} mol dm^{-3} x 176.0 g mol^{-1}
= 0.331 g dm^{-3}
= 331 mg dm^{-3} (1)

The concentration of E300 in the drink exceeds the limit.

Unit Exercise (p.114)

18 Iodine can be extracted from the ash of burnt seaweed. The ash is washed with water. The remaining solid is heated with manganese(IV) oxide and concentrated sulphuric acid, forming iodine.

$$2I^- + MnO_2 + 4H^+ \longrightarrow Mn^{2+} + 2H_2O + I_2$$

a) A student extracts iodine from seaweed ash. The student suspects that the water which has been used to wash the ash contains a mixture of salts, including sodium chloride.
The student tests this water to see if it contains chloride ion.

i) What reagent would the student need to add to the water?
Aqueous solution of silver nitrate   (1)

ii) Give the result of the test for chloride ion and name the compound formed.

A white precipitate forms.   (1)
Silver chloride   (1)

Unit Exercise (p.114)

18 (continued)

a) iii) Suggest why the student might NOT get the expected test result.

Any one of the following:
- Water may contain low concentration of chloride ion or no chloride ion, so would not give a precipitate.   (1)
- Water may contain iodide ion which would give a yellow precipitate.   (1)
- Water may contain bromide ion which would give a creamy precipitate.   (1)
- Water may contain chromate ion which would give a reddish brown precipitate.   (1)
- Water may contain hydroxide ion / sulphide ion which would give a black precipitate.   (1)

b) The student collected 0.920 g of impure iodine, I_2, and decided to determine its purity.

The student dissolved the impure iodine in potassium iodide solution.

This iodine solution was then titrated with sodium thiosulphate solution.
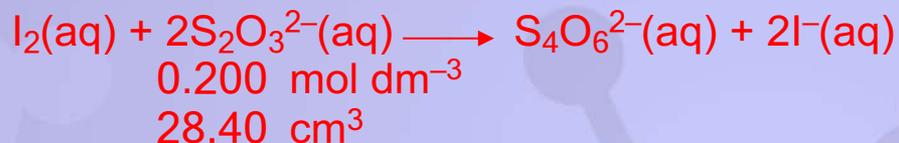
The equation for the reaction is shown below.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

Unit Exercise (p.114)

18 (continued)

b) i) The titration required 28.40 cm^3 of 0.200 mol dm^{-3} sodium thiosulphate solution.

Calculate the number of moles of thiosulphate ion, $S_2O_3^{2-}$, used.

$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$
                0.200 mol dm^{-3}
                28.40 cm^3

Number of moles of $S_2O_3^{2-}$ ion in 28.40 cm^3 solution = 0.200 mol dm^{-3} x $\dfrac{28.40}{1\ 000}$ dm^3

$= 5.68 \times 10^{-3}$ mol (1)

ii) Give the number of moles of iodine, I_2, in the iodine solution.

According to the equation, 1 mole of I_2 reacts with 2 moles of $S_2O_3^{2-}$ ion.

i.e. number of moles of $I_2 = \dfrac{5.68 \times 10^{-3}}{2}$ mol

$= 2.84 \times 10^{-3}$ mol   (1)

Unit Exercise (p.114)

18

b) iii) Calculate the percentage purity of the iodine.
(Relative atomic mass: I = 126.9)

(OCR Advanced Subsidiary GCE, Chem. B (Salters), F332/01, Jun. 2014, 1(f), (h))

Mass of I_2 = 2.84 x 10^{-3} mol x 253.8 g mol^{-1}
= 0.721 g

Percentage purity of iodine = $\dfrac{0.721 \text{ g}}{0.920 \text{ g}}$ x 100%

= 78.4 %   (1)

∴ the percentage purity of the iodine is 78.4%.

Unit Exercise (p.114)

19 An experiment was performed to determine the percentage by mass of $NaClO_3(s)$ in a sample. 1.63 g of the sample was dissolved in deionised water and then made up to 250.0 cm³. 10.00 cm³ of the solution was transferred to a conical flask. Then 10 cm³ of 1 M KI(aq) and 20 cm³ of 6 M HCl(aq) were added in the flask. The resulting mixture was titrated with 0.112 M $Na_2S_2O_3(aq)$, adding starch solution as an indicator at appropriate time. The titration was repeated several times, and the mean volume of $Na_2S_2O_3(aq)$ required to reach the end point was 27.88 cm³.

a) Describe how the sample dissolved in deionised water can be made up to 250.0 cm³.

b) It is known that in the conical flask, $ClO^{3-}(aq)$ reacted with $I^-(aq)$ in the presence of $H^+(aq)$ to form $I_2(aq)$ and $Cl^-(aq)$. Write an ionic equation for the reaction.

c) State the colour change at the end point of the titration.

d) The chemical equation for the titration reaction is as follows:

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

Assuming that no other species in the sample would react with $I^-(aq)$, calculate the percentage by mass of $NaClO_3(s)$ in the sample.

(Relative atomic masses: O = 16.0, Na = 23.0, Cl = 35.5)

(HKDSE, Paper 2, 2018, 3(b))

Answers for the questions of the public examinations in Hong Kong are not provided (if applicable).

Unit Exercise (p.114)

20 Iodine pentoxide is used as a reagent to determine the concentration of carbon monoxide in a gaseous sample.

Step 1 2.00 m^3 sample of gas were passed over heated iodine pentoxide, producing carbon dioxide and iodine.

Step 2 The iodine produced was added to 25.00 cm^3 of 0.0400 mol dm^{-3} $Na_2S_2O_3(aq)$ (excess).

Step 3 The resulting solution was titrated with 0.00800 mol dm^{-3} $I_2(aq)$. 22.50 cm^3 of $I_2(aq)$ were required for complete reaction.

The equations for the reactions involved are as follows:

$I_2O_5(s) + 5CO(g) \longrightarrow I_2(s) + 5CO_2(g)$

$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

a) i) Suggest a suitable indicator for the titration.

Starch solution   (1)

ii) State the colour change you expect at the end point.

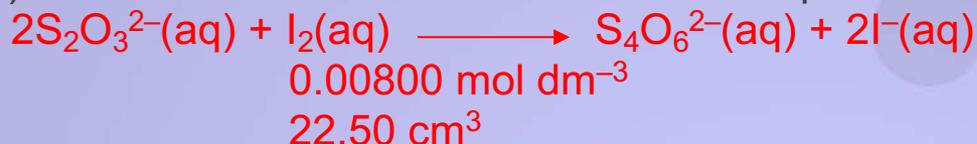From colourless to dark blue   (1)

Unit Exercise (p.114)

20

b) Calculate the number of moles of thiosulphate ion left after the reaction in *Step 2*.

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

0.00800 mol dm^{-3}

22.50 cm^3

Number of moles of I_2 = 0.00800 mol dm^{-3} x $\dfrac{22.50}{1\ 000}$ dm^3

= 1.80 x 10^{-4} mol (1)

According to the equation, 2 moles of $S_2O_3^{2-}$ ion react with 1 mole of I_2.

i.e. number of moles of $S_2O_3^{2-}$ ion left = 2 x 1.80 x 10^{-4} mol

= 3.60 x 10^{-4} mol   (1)

c) Calculate the number of moles of iodine produced in *Step 1*.

Number of moles of $S_2O_3^{2-}$ ion at start = 0.0400 mol dm^{-3} x $\dfrac{25.00}{1\ 000}$ dm^3

= 1.00 x 10^{-3} mol (1)

Number of moles of $S_2O_3^{2-}$ ion reacted with I_2 produced = (1.00 x 10^{-3} – 3.60 x 10^{-4}) mol

= 6.40 x 10^{-4} mol

Number of moles of I_2 produced = $\dfrac{6.40 \times 10^{-4}}{2}$ mol

= 3.20 x 10^{-4} mol   (1)

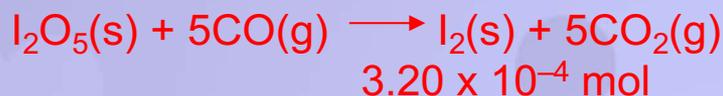# Unit Exercise (p.114)

20

d) Calculate the volume of carbon monoxide, in dm^3, in the original gaseous sample.

(Molar volume of gas under the experimental conditions = 24.0 dm^3 mol^{-1})

$I_2O_5(s) + 5CO(g) \longrightarrow I_2(s) + 5CO_2(g)$
3.20×10^{-4} mol

According to the equation, 5 moles of CO react with I_2O_5 to produce 1 mole of I_2.
i.e. number of moles of CO = $5 \times 3.20 \times 10^{-4}$ mol
$= 1.60 \times 10^{-3}$ mol   (1)

Volume of CO in the original gaseous sample = 1.60×10^{-3} mol x 24.0 dm^3 mol^{-1}
$= 0.0384$ dm^3 (1)

∴ the volume of carbon monoxide in the original gaseous sample is 0.0384 dm^3.

e) Suggest how the procedure could be amended to produce more reliable results.
Any one of the following:
- Repeat the experiment to obtain concordant titres.   (1)
- Divide the solution into equal portions before carrying out the titration.   (1)
- Divide the gas into equal samples before carrying out the titration.   (1)