REDOX TITRATIONS

A redox titration involves the titration of an oxidant with a reductant. An aliquot of the sample is usually put into a conical flask, and the standard solution is usually put into the burette. The titration is performed in order to accurately determine the amount, in mole, of the sample. This information is then used to calculate the concentration or mass of the initial sample.

Generally an indicator is not required because a spontaneous colour change occurs at the end point of the titration. This is because transition metals are frequently involved, and transition metals usually change colour with a change in oxidation state. That is, a transition metal will usually change colour during a redox reaction as its oxidation number changes.

PERFORMING REDOX TITRATIONS

As with acid-base titrations, the following procedure should be followed for a redox titration:

1. A **pipette** is used to accurately measure the volume of the sample. This amount of the sample is then known as an **aliquot**. The pipette should be rinsed with the sample itself so that the concentration of the sample does not change.

2. The sample is put into a **conical flask**. The conical flask must be rinsed with distilled water so that the number of moles of the sample does not change.

3. The standard solution is put into a **burette**. The burette must be rinsed with the standard solution so that the concentration of the standard solution does not change.

4. The **equivalence point** of the titration is the point where chemically equivalent amounts of the two solutions, according to the mole ratios shown by the equation, are present. The **end point** of the titration occurs when a permanent colour change is first observed, and the titration is stopped.

5. Several titrations are performed, until there are three concordant results. The average of these volumes is known as the average **titre**.

CALCULATIONS INVOLVING REDOX TITRATIONS

As with acid-base titrations, it is important to have a balanced chemical equation in order to complete the required calculations. In order to write a redox equation, the two half equations must be written and then added together so that the electrons cancel. In order recognise a redox reaction, look for the following clues in the question:

- There is a spontaneous colour change without the addition of an indicator solution.
- There have been changes in oxidation numbers.
- The words **reduced** and **oxidised** might be used.

The following steps are involved in the calculations following a redox titration:

1. A balanced chemical equation is always required.
2. The amount, in mole, of the standard solution must be calculated. The concentration is known accurately, and the volume is usually read from the burette. These values are substituted into the formula $n(s\tan dard\ solution) = C \times V$.
3. Use mole ratios to compare the amount of the standard solution with the amount of the sample. The balanced chemical equation must be used for this.
4. If necessary, use ratios to allow for dilution. Find the amount, in mole, of the unknown in the dilute solution. And therefore also the amount, in mole, of the unknown in the initial concentrated sample.
5. Calculate the concentration of the initial sample by substituting into the formula $C(sample) = \frac{n}{V}$. Or calculate the mass of the initial sample by substituting into the formula: $mass(sample) = n \times M$.

EXAMPLE 1
A student carried out a series of experiments in a school laboratory. From the information given, identify the redox titration. Hence determine the experiment that would require a titration reaction written by first writing the appropriate half equations.

A A sample of sulfuric acid, H_2SO_4, was titrated against a solution of potassium hydroxide, KOH. The products of the reaction were potassium sulphate and water.

B A solution containing Fe^{2+} ions was titrated against a solution of potassium permanganate. The resulting solution of Fe^{3+} and Mn^{2+} ions was almost colourless.

C A sample of vinegar was titrated against a solution of sodium hydroxide. The equation for the reaction was $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COO.Na(aq) + H_2O(l)$.

D A solution containing calcium ions was added to excess sodium oxalate solution. The equation for this reaction was $Ca^{2+}(aq) + C_2O_4{}^{2-}(aq) \rightarrow CaC_2O_4(s)$.

Solution

B is the correct response.

A reaction between iron (II) ions and permanganate ions, MnO_4^-. The conjugate pairs are Fe^{2+}/Fe^{3+} and MnO_4^-/Mn^{2+}. Oxidation numbers have changed and this is a redox reaction. Half reactions would be written in order to write the equation for the titration.

The incorrect responses are:

A A reaction between sulphuric acid and potassium hydroxide. This is an acid-base reaction, not a redox reaction.

C A reaction between vinegar (acetic acid) and sodium hydroxide. Oxidation numbers have not changed in the equation, not a redox reaction.

D A precipitation reaction. Oxidation numbers have not changed in the equation, not a redox reaction.

EXAMPLE 2
The alcohol content of a particular sample of wine was found by titration. A 10.00 ml sample of the wine was pipetted into a conical flask and titrated against a 0.0200 M solution of potassium dichromate, $K_2Cr_2O_7$. An average titre of 18.36 ml was obtained. Calculate the concentration of alcohol in the wine in g L^{-1}, if the equation for the reaction was:

$$3CH_3CH_2OH(aq) + 2Cr_2O_7^{\,2-}(aq) + 16H^+(aq) \rightarrow 3CH_3COOH(aq) + 4Cr^{3+}(aq) + 11H_2O(l)$$

Solution

1. A balanced chemical equation for the titration is required.

$$3CH_3CH_2OH(aq) + 2Cr_2O_7^{\,2-}(aq) + 16H^+(aq) \rightarrow 3CH_3COOH(aq) + 4Cr^{3+}(aq) + 11H_2O(l)$$

2. (a) Calculate the amount of potassium dichromate used in the titration.

$$\begin{aligned} n(K_2Cr_2O_7) &= C \times V \\ &= 0.0200 \times 0.01836 = 3.672 \times 10^{-4}\ mol \end{aligned}$$

(b) Calculate the amount, in mole, of dichromate.

$$K_2Cr_2O_7(aq) \rightarrow 2K^+(aq) + Cr_2O_7^{\,2-}(aq)$$

$$\begin{aligned} n(Cr_2O_7^{\,2-}) &= n(K_2Cr_2O_7) \\ &= 3.672 \times 10^{-4}\ mol \end{aligned}$$

3. Use mole ratios to determine the amount of alcohol, CH_3CH_2OH, in the sample.

$$\begin{aligned} n(CH_3CH_2OH) &= \frac{3}{2} \times n(Cr_2O_7^{\,2-}) \\ &= \frac{3}{2} \times 3.672 \times 10^{-4} = 5.51 \times 10^{-4}\ mol \end{aligned}$$

4. (a) Calculate the mass of alcohol in the 10.00 ml sample.

$$\begin{aligned} mass(CH_3CH_2OH) &= n \times M \\ &= 5.51 \times 10^{-4} \times 46.0 = 0.0253 g\ of\ alcohol in 10.00 ml \end{aligned}$$

(b) Use ratios to calculate the mass of alcohol in 1 L of the wine.

$$\begin{aligned} &0.0253\ g \quad in\ \ 10.00\,ml \\ &x\,mol \quad\ \ in\ \ 1000.00\,ml \end{aligned}$$

$$\begin{aligned} Cross\ multiply: \quad & 10.00 \times x = 0.0253 \times 1000.00 \\ & \therefore x = 2.53\,g\,L^{-1} \end{aligned}$$

EXAMPLE 3

In order to determine the percentage of iron in a piece of wire, a 3.50 g sample of the wire was dissolved in excess hydrochloric acid. The resulting solution containing Fe^{2+} ions was made up to 250.0 ml in a volumetric flask. A pipette was used to transfer 20.00 ml aliquots into four conical flasks, and each aliquot of the dilute solution was titrated against a 0.0500 M solution of potassium permanganate. An average titre of 19.16 ml was obtained, and the resulting solution of Fe^{3+} and Mn^{2+} ions was almost colourless. Calculate the percentage purity of iron in the sample of wire.

Solution

1. Write the two half equations and a balanced chemical equation for the titration reaction.

$$5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + 5e^-$$

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

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

2. (a) Calculate the amount of potassium permanganate used in the titration.

$$n(KMnO_4) = C \times V$$
$$= 0.0500 \times 0.01916 = 9.58 \times 10^{-4}\ mol$$

(b) Calculate the amount, in mole, of permanganate.

$$n(MnO_4^-) = n(KMnO_4)$$
$$= 9.58 \times 10^{-4}\ mol$$

3. Use mole ratios to determine the amount of Fe^{2+} in the dilute solution.

$$n(Fe^{2+}) = \frac{5}{1} \times n(MnO_4^-)$$
$$= \frac{5}{1} \times 9.58 \times 10^{-4} = 0.00479\ mole\ in\ 20.00\ ml\ of\ the\ dilute\ sample$$

4. (a) Use ratios to find the amount, in mole, of Fe^{2+} in 250.00 ml of the dilute solution.

$$0.00479\ mol \quad in \quad 20.00\ ml$$
$$x\ mol \quad in \quad 250.00\ ml$$

$$Cross\ multiply: \quad 20.00 \times x = 0.00479 \times 250.00$$
$$\therefore x = 0.0599\ mol\ of\ Fe^{2+}\ in\ 250.00\ ml\ of\ the\ dilute\ solution$$

(b) During the initial reaction all of the Fe in the wire was oxidised to form Fe^{2+}

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$

$$\therefore n(Fe) = n(Fe^{2+})$$
$$= 0.0599 \text{ mole of Fe in the initial sample of wire}$$

5. (a) Calculate the mass of iron in the initial sample of wire.

$$mass(Fe) = n \times M$$
$$= 0.0599 \times 55.9 = 3.35 \text{ g of Fe in the initial sample}$$

(b) Calculate the percentage by mass of iron in the initial sample of wire.

$$\%(Fe) = \frac{\text{mass of Fe}}{\text{mass of sample}} \times 100 = \frac{3.35}{3.50} \times 100 = 95.6\ \%(m/m)$$