Redox - Calculations

Redox titrations are based on redox reactions. Potassium permanganate is widely used in redox titrations since it acts as its own indicator (self-indicating). It is decolourised in a redox reaction and therefore the end-point occurs when a very pale pink colour (slight excess of permanganate) is observed.

Another common redox system uses iodine. This is useful, since traces of iodine give a blue/black colour with starch, which can be used as an indicator.

Other oxidising agents often used are cerium(IV) oxide, Ce^{4+}, and dichromate, $Cr_2O_7^{2-}$.

e.g.

10 cm^3 of 0.02 $mol.l^{-1}$ of acidified potassium permanganate solution is required to completely oxidise 30.0 cm^3 iron(II) ions in iron(II) sulphate solution. What is the concentration of the iron(II) sulphate solution?

Using page 12 of the Data Booklet, the ion-electron equations are;

$$MnO_4^-{}_{(aq)} \quad + \quad 8H^+{}_{(aq)} \quad + \quad 5e^- \quad \rightarrow \quad Mn^{2+}{}_{(aq)} \quad + \quad 4H_2O_{(l)}$$

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

After multiplying the 2nd equation by 5 (to balance the electrons with the 1st equation), the redox equation is;

$$MnO_4^-{}_{(aq)} \quad + \quad 8H^+{}_{(aq)} \quad + \quad 5Fe^{2+}{}_{(aq)} \quad \rightarrow \quad Mn^{2+}{}_{(aq)} \quad + \quad 4H_2O_{(l)} \quad + \quad 5Fe^{3+}{}_{(aq)}$$

0.01 litre   0.03 litre

0.02 $mol.l^{-1}$

$n = c \times v$

$= 0.02 \times 0.01$

$= 0.0002$ mol

From the equation;

1 mol $MnO_4^-{}_{(aq)}$ $\longleftrightarrow$ 5 mol $Fe^{2+}{}_{(aq)}$

0.0002 mol $MnO_4^-{}_{(aq)}$ $\longleftrightarrow$ $\frac{5}{1} \times 0.0002 = 0.001$ mol

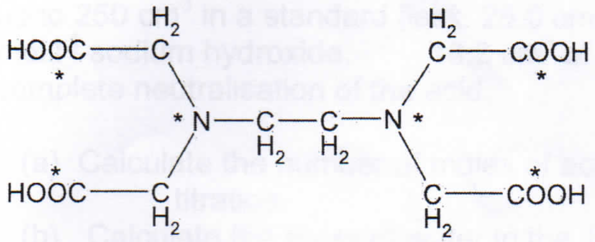
$Fe^{2+}{}_{(aq)}$

$n = 0.001$ mol

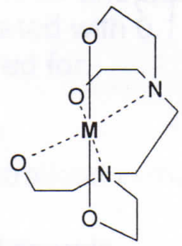
$v = 0.03$ litre $c = \frac{n}{v} = \frac{0.001}{0.03} = 0.033\ mol.l^{-1}$

Complexometric Analysis

Complexometric titrations are based on the formation of a coloured complex by a transition metal ion. This type of analysis is particularly useful for estimating the concentration of metal ions in solution by using their ability to form complex ions with certain organic ligands. EDTA (see Unit 1 page 49, and below) is the most common reagent in complexometric analysis. It has multiple complex forming sites within one molecule, enabling it to form stable 1:1 complexeswith many metals.



* attachment points through lone pairs



M = metal

The end-point of these titrations is indicated by the colour change in an indicator such as murexide or eriochrome black T. Murexide is an excellent indicator for calcium and nickel ions. Complexometric titrations can be used to determine the concentration of metal ions, such as nickel(II), in solutions with very low concentrations (parts per million).

Murexide[metal ion]	+	EDTA	$\rightarrow$	EDTA[metal ion]	+	Murexide
colour (depends on metal ion)						(purple)

WORKED EXAMPLE – complexometric titration calculations

In a complexometric analysis it was found that 20 cm^3 of an unknown solution containing nickel(II) ions required 30.1 cm^3 of 0.1 mol.l^{-1} EDTA to completely react all of the nickel(II) ions present. What is the concentration of the nickel(II) ions in solution?

Most ions react with EDTA in a 1:1 ratio so;

EDTA	+	Ni^{2+}	$\rightarrow$	Complex ion
0.0301 litres		0.02 litres		
0.1 mol.l^{-1}				

n = 0.0301 x 0.1
= 0.00301 mol

1 mol EDTA $\longleftrightarrow$ 1 mol Ni^{2+}

0.00301 mol $\longleftrightarrow$ 0.00301 mol

Ni^{2+}

n = 0.00301 mol
v = 0.02 litres

$$c = \frac{n}{v} = \frac{0.00301}{0.02} = 0.1505 \text{ mol.l}^{-1}$$

Exercise 2

1. Arsenic(V) acid, H_3AsO_4, is a triprotic acid. 25 cm^3 of a solution of the acid required 35.7 cm^3 of 0.1 $mol.l^{-1}$ NaOH solution for complete reaction. What is the concentration of the acid?

2. Anhydrous malonic acid has a relative formula mass of 104. 1.28g of hydrated malonic acid, $CH_2(COOH)_2.nH_2O$, was dissolved in water and made up to 250 cm^3 in a standard flask. 25.0 cm^3 of this acid was titrated with 0.1 $mol.l^{-1}$ sodium hydroxide. 18.2 cm^3 of the alkali was required for complete neutralisation of the acid.

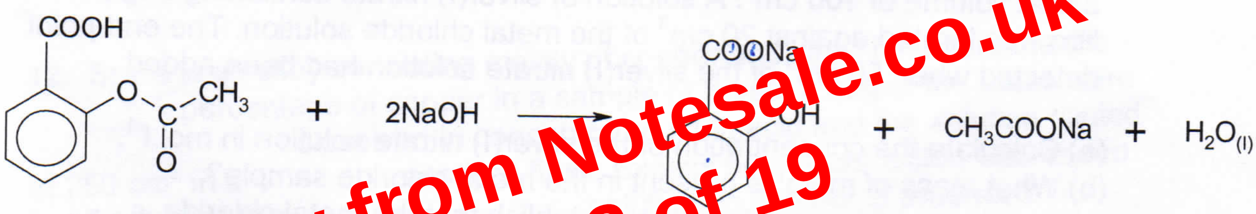
(a) Calculate the number of moles of acid that has been neutralised in the titration.

(b) Calculate the mass of water in the 1.28g of the hydrated sample.

(c) Find the value for **n** in the formula $CH_2(COOH)_2.\mathbf{n}H_2O$.

3. As well as the active ingredient, aspirin tablets contain other substances. In a PPA experiment the aspirin content was determined by the method indicated in steps 1 and 2 below.

Step 1 Crushed tablets were simmered in excess sodium hydroxide solution.



Aspirin
(1 mole = 180g)

Step 2 The excess sodium hydroxide was determined by back titration with a standard solution of sulphuric acid.

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

Three aspirin tablets were added to 25.0 cm^3 of 1.00 $mol.l^{-1}$ sodium hydroxide solution and simmered for 30 minutes. When cooled the reaction mixture was diluted to exactly 250 cm^3 in a standard flask. 25.0 cm^3 samples were then titrated with 0.0500 $mol.l^{-1}$ sulphuric acid until concordant results were obtained. The average titre was 15.2 cm^3.

(a) Calculate the number of moles of sulphuric acid in the average titre.

(b) Calculate the number of moles of excess sodium hydroxide in the standard flask.

(c) Calculate the number of moles of sodium hydroxide which reacted with the aspirin.

(d) Calculate the average mass of pure aspirin in each tablet.