Volumetric Analysis

The Milli-Mole Method

1000 cm^3 xM solution contains x mole solute

⇒ 1 cm^3 xM solution contains x/1000 mole solute

⇒ v cm^3 xM solution contains xv/1000 mole solute
= xv milli-moles

Hence :-

$$\boxed{\text{No.of milli-moles} = \text{volume} \times \text{molarity}}$$

Practice Problem

55.01 cm^3 0.2M Sodium hydroxide were required to neutralise 25.00 cm^3 Nitric acid.

Calculate the molarity of the Nitric acid.

Answer :

No. of m.mols NaOH = 55.01 x 0.2

= 11 m.mols

$NaOH + HNO_3 \rightarrow NaNO_3 + H_2O$

From the above equation :

1 mol NaOH combines with 1 mol HNO_3

=> 11.0 m.mol NaOH combine with 11.0 m. mol HNO_3

=> no. of m.mols HNO_3 in 25.00 cm^3 must be 11.0 m.mols

=> molarity = $\frac{\text{no. of m.mols}}{\text{volume}}$

$= \frac{11}{25}$

$= \underline{0.44 \text{ mol } l^{-1}}$

Preparing a Standard Solution

Our first experiment will be to find the exact molarity of a solution of Sodium hydroxide. To do this, we need to titrate the Sodium hydroxide with a solution of acid of exact concentration - a primary standard.

We will use Oxalic acid $C_2H_2O_4$ for the following reasons:

* It is highly pure
* It is stable
* It is soluble in water
* It is a solid and can therefore be weighed accurately
* It has a high formula mass (126)
  Weighing small masses is innaccurate.

Method:

We need to prepare 250 cm^3 of Oxalic acid solution of approximate molarity 0.05 mol l^{-1}.

1. Calculate the mass of Oxalic acid required.

   No. of m.moles = 250 x 0.05
   = 12.5 m.moles

   => No. of moles = 0.0125 moles

   => Mass = 126 x 0.0125
   = <u>1.575g</u>

2. Weigh out, in a weighing bottle, approximately 1.575g of Oxalic acid to an accuracy of 4 decimal places e.g. 1.5438g.

3. Transfer the Oxalic acid crystals to a 250 cm^3 volumetric flask and make up to 250 cm^3 with water.

4. Calculate the molarity of the primary standard.

   Say we weighed out 1.5438g of Oxalic acid:

   No. of moles of Oxalic acid in 250 cm^3 $= \frac{1.5438}{126}$

   => No. of moles of Oxalic acid in 1000 cm^3 $= \frac{1.5438 \times 4}{126}$

   = 0.0490 mol

   => Molarity = 0.0490 mol l^{-1}

5. Titrate the 0.0490 mol l^{-1} Oxalic acid solution from a burette into 25 cm3 of the Sodium hydroxide solution containing a few drops of Phenolphthalein indicator (pink to colourless at the end point).

Calculation of results

Say 22.65 cm^3 0.0490 mol l^{-1} Oxalic acid are required.

$$2\ NaOH + C_2H_2O_4 \rightarrow Na_2C_2O_4 + 2\ H_2O$$

No. of m.mols Oxalic acid = 22.65 x 0.0490
= 1.10985 m.mols

=> No. of m.mols NaOH = 2.2197 m.mols

=> Molarity of NaOH $= \dfrac{\text{no.of m.mols}}{\text{volume}}$

$= \dfrac{2.2197}{25.00}$

= 0.0888 mol l^{-1}

A solution of accurately known concentration, like the 0.0888 mol l^{-1} solution of Sodium hydroxide, is known as a **standard solution**.

Redox Titration

Object : To find the molarity of a Sodium sulphite solution by titration with 0.02 mol l^{-1} Potassium tetraoxymanganese(VII)

Method :

1. Fill a burette with the Sodium sulphite solution.

2. Pipette 25.00 cm^3 0.02 mol l^{-1} Potassium tetraoxymanganese(VII) into a conical flask then add 10 cm^3 10 mol l^{-1} Sulphuric acid.

3. Titrate till the purple colour of the tetraoxymanganese(VII) ion is discharged. The reaction is self-indicating.

Calculation of results:

Say the volume of Sodium sulphite required was 24.93 cm^3

$$5SO_3^{2-} + 2MnO_4^- + 6H^+ \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 3H_2O$$

No.of m.mols MnO_4^- = 25.00 x 0.02 = 0.5 m.mols

=> No.of m.mols SO_3^{2-} in 24.93 cm^3 = 2.5 x 0.5
= 1.25 m.mols

=> Molarity $= \dfrac{\text{no.of m.mols}}{\text{volume}} = \dfrac{1.25}{24.93} =$ 0.05 mol l^{-1}

Complexometric Titration

Object : To determine the percentage of Nickel in a Nickel(II) salt by titration with 0.1 mol l^{-1} **E**thylene**D**iamine**T**etra**A**cetic acid (**EDTA**)

Method :

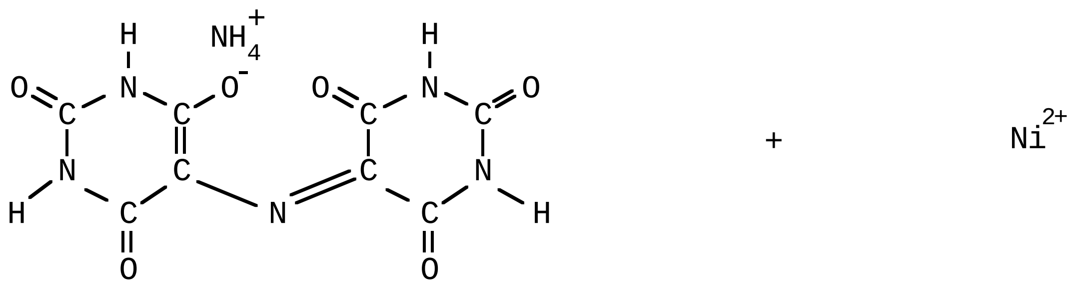
1. Fill a burette with 0.1 mol l^{-1} EDTA.

2. Weigh out accurately, in a weighing bottle, about 2.50g of the Nickel(II) salt.

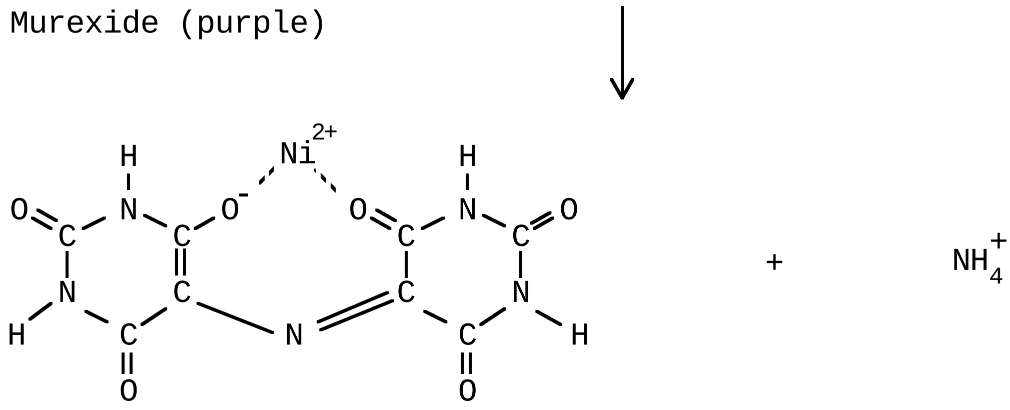
3. Transfer the Nickel(II) salt to a 100 cm^3 volumetric flask and make up the volume of the solution to 100 cm^3 with water.

4. Pipette 25.00 cm^3 of this solution into a conical flask.

5. Add Murexide indicator to the Nickel(II) solution in the conical flask. The indicator forms an unstable yellow complex with Nickel(II) ions :

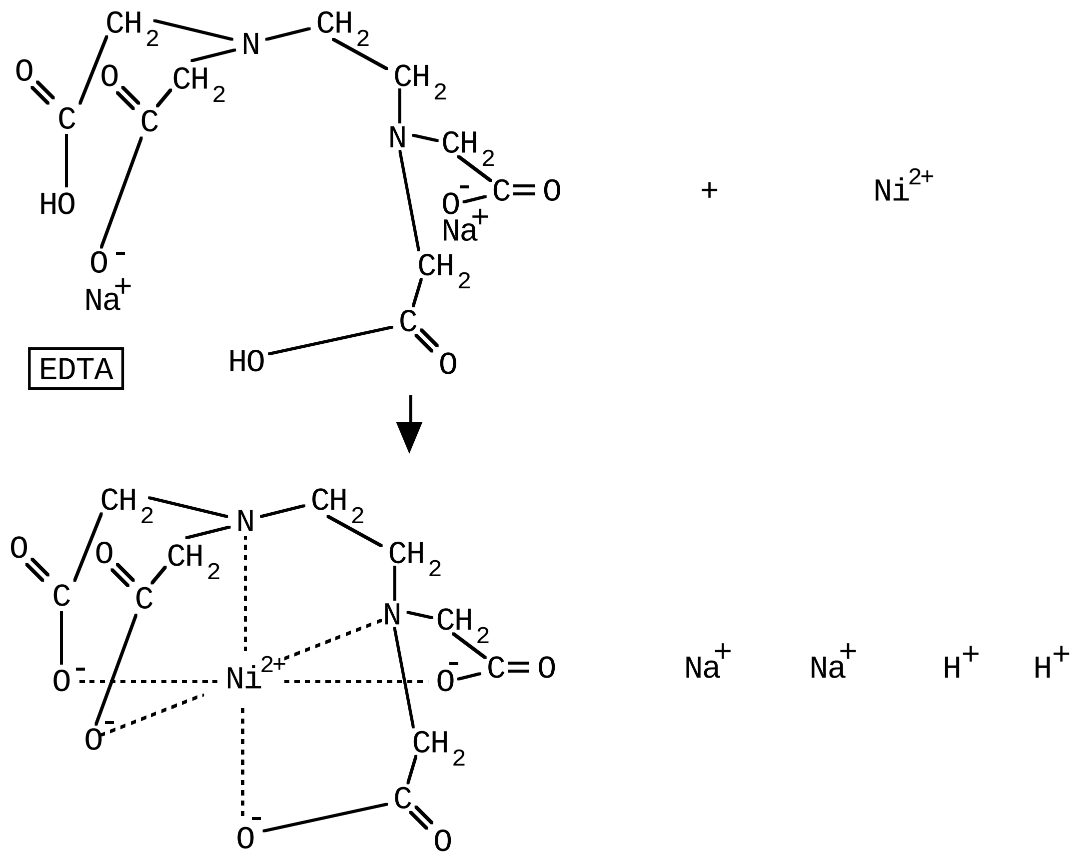


Murexide (purple)



yellow complex

7. Titrate the EDTA solution into the Ni^{2+} solution.
The EDTA reacts with the Ni^{2+} ions in a 1:1 ratio :



Notice that H^{+} ions are produced. If these ions were allowed to build up in solution the reaction would begin to reverse. Addition of about 10 cm^3 0.88 Ammonia just prior to the end point removes these H^{+} ions.

8. Towards the end point the EDTA begins to attack the few remaining Nickel(II) ions which are present in the unstable yellow 'Murexide-Nickel(II)' complex leading to the break down of this complex and the reforming of the purple Murexide indicator. The colour changes from yellow to purple at the end point.

<u>Calculation of results</u>

Say the volume of 0.1 mol l^{-1} EDTA required was 40.49 cm^3 and the weight of Nickel(II) salt was 2.51g.

	No. of m.mols of EDTA = 0.1 x 40.49	=	4.049 m.mols
$\Rightarrow$	No. of m.mols of Ni^{2+} in 25 cm^3	=	4.049 m.mols
$\Rightarrow$	No. of m.mols of Ni^{2+} in 100 cm^3	=	4.049 x 4
		=	16.196 m.mols
$\Rightarrow$	No. of m.mols of Ni^{2+} in 2.51g Ni^{2+} salt	=	16.196 m.mols
$\Rightarrow$	No. of moles of Ni^{2+} in 2.51g Ni^{2+} salt	=	0.016196 moles
$\Rightarrow$	Weight of Ni^{2+} in 2.51g Ni^{2+} salt	=	0.016196 x 59
		=	0.956g
$\Rightarrow$	Percentage of Nickel in Nickel(II) salt	=	$\frac{0.956 \times 100}{2.51}$
		=	<u>38.09 %</u>

Gravimetric Analysis

Object : To determine the number of moles of water of crystallisation in 1 mole of hydrated Barium chloride $BaCl_2.xH_2O$

Method :

1. Weigh out, in a crucible, 2-3g hydrated Barium chloride.

2. Heat the hydrated Barium chloride in the crucible for about 10 minutes. This drives off the water of crystallisation to form anhydrous Barium chloride $BaCl_2$:

   $$BaCl_2.xH_2O \rightarrow BaCl_2 + xH_2O$$

3. Allow the crucible and contents to cool and reweigh.

4. Continue to heat until there is no further loss in mass. This is called 'heating to constant mass'

<u>Calculation of results</u>

Say mass of hydrated Barium chloride was 2.8092g and mass of anhydrous Barium chloride was 2.3955g.

No. of moles of anhydrous Barium chloride $= \dfrac{2.3955}{208.3}$

$= 0.0115$ moles

$\Rightarrow$ Weight of Water removed by heating $= 2.8092 - 2.3955$

$= 0.4137$g

$\Rightarrow$ No. of moles of Water removed $= \dfrac{0.4137}{18}$

$= 0.0230$ mol

Hence 0.0115 mol Barium chloride are combined with 0.0230 mol Water
Hence 1 mol Barium chloride is combined with **2** mol Water

Hence the formula is $\underline{\underline{BaCl_2.\mathbf{2}H_2O}}$