CHE 1000 e-LEARNING

RECAP ON TITRATIONS

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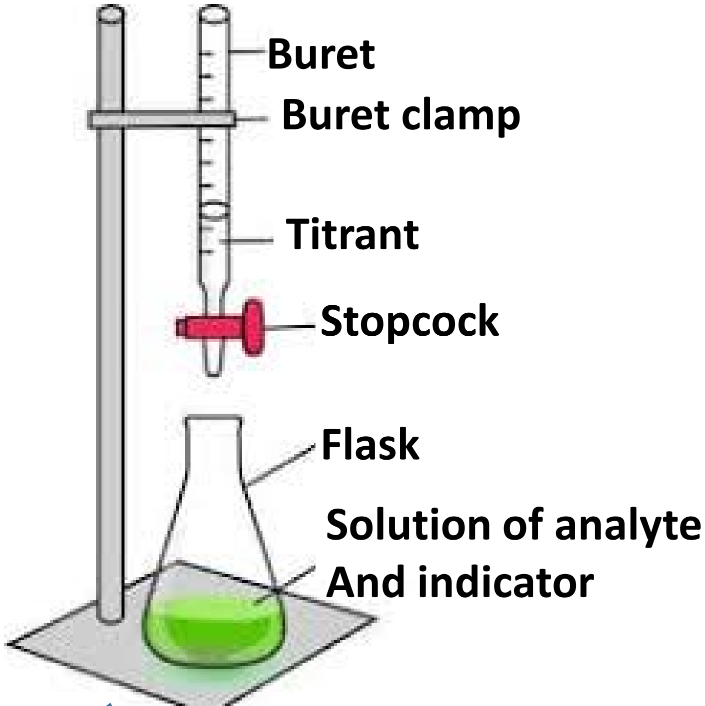
- Titration is a chemical analysis method in which the quantity of the sample (analyte) is determined by placing it in the conical flask and by stepwise addition of a standardized solution from the burette until the end-point is reached.
- The end point is determined by adding an indicator to the analyte solution.
- Some redox titration is self-indicating.
- The molarity of the standardized solution, M_s, is known, and the volume of the titre, V_s, is found at the end-point.

Remember this statement please

- In **titration,** a solution of accurately known concentration, called a **standard solution,** is added gradually to another solution of unknown concentration, until the chemical reaction between the two solutions is complete.

- If we know the volumes of the standard and unknown solutions used in the titration, along with the concentration of the standard solution, we can calculate the concentration of the unknown solution.

This is the main objective of any titration



Typical Titration setup

Standardization of solutions

- Before we use a solution in titrations, it must be standardized.
- There are two types of standard solutions in titrations:
  - Primary standard
    - A **primary standard** is a reference chemical used to measure an unknown concentration of another known chemical. It can be used directly when performing **titrations** or used to calibrate **standard** solutions. A **primary standard** is of **known purity and stability** that can be measured accurately and used in its entirety requiring no additional measurements.
  - Secondary standard
    - A **secondary standard** is a chemical that has been standardized (whose concentration has been accurately determined) against a **primary standard** for use in a specific analysis. **Secondary standards** are commonly used to calibrate analytical methods.

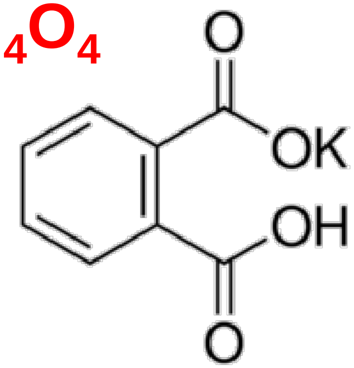
Four Characteristics of a Primary Standard

- It must be pure (99.999 % purity)
- It must be cheap and readily available
- It must be very stable (remain unchanged during storage and weighing)
- It must have a known formula

Remember these characteristics

Example of a primary standard that fits these characteristics a white crystalline acidic chemical compound called **Potassium hydrogen phthalate** (KHP) which **$KHC_8H_4O_4$**

It has the following structural formula



Examples of primary and secondary standards

- **Standardization of a secondary standard using a primary standard**
- This is the titration of secondary standard using accurate concentration (Molarity) of a primary standard
- Primary std/ secondary std

  Na_2CO_3(aq)/HCl(aq) 1:2 rxn

  KHP(aq)/NaOH(aq) 1:1 rxn
- KHP ($KHC_8H_4O_4$, 204.23 g/mol)

Example:

How do you prepare 0.1000 M Na_2CO_3 in a 250.00 mL volumetric flask

Solution

First calculate the number of moles using the formula or relationship between moles, volume and concentration

- n_{Na2CO3} = 0.1000 mol/L x 0.2500L=0.02500 mol

Remember M is moles per liter so volume must be in liters

Next, convert the moles to mass. Recall that n= m/mol/g

- m_{Na2CO3} = 0.02500 mol x 105.99 g/mol =2.6498 g

- So finally weigh 2.6498 g Na_2CO_3 and dissolve all of it in a little water and transfer into 250 mL volumetric flask and add more water up to the lower meniscus of the mark.

Types of titrations

There are two main types of titration: Forward or Normal Titration and Back Titration

Forward or Normal Titration

They are of two types:

1. Single reaction

   Here the analyte and the titrant are in a single reaction

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

standard Analyte

2. Sequence of reactions

Here the analyte and the titrant are in separate reaction reactions

$$Mn_2O_7\,(l) + H_2O(\mathit{l}) \rightarrow 2MnO_4^-(\mathit{aq}) + 2H^+(\mathit{aq})$$

Analyte

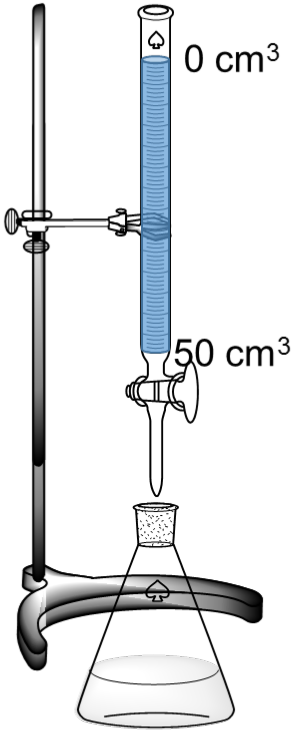
$$2MnO_4^-(\mathit{aq}) + 5C_2O_4^{2-}(\mathit{aq}) + 16H^+(\mathit{aq}) \rightarrow 2Mn^{2+}(aq) + 8H_2O(\mathit{l}) + 10CO_2(\mathit{g})$$

Standard

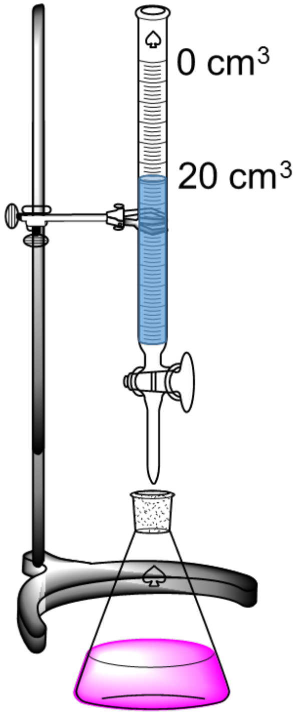
Example

A 5.00 g sample of manganese (VII)oxide (di-manganese heptoxide- a very volatile liquid) was dissolved in distilled water and volume made up to 250 cm^3. 25.0 cm^3 of this solution required exactly 20 cm^3 of a 0.5 molar oxalic acid at the phenolphthalein end point. Calculate the percent manganese in the original sample.

NOTE that the molarity of the standard $M_{C_2O_4^{2-}}$ is known and the volume of the titre $V_{C_2O_4^{2-}}$ is found at the end of the titration by reading off the buret



Before titration
Initial volume= 0 cm^3



After titration
Final volume= 20 cm^3

To calculate the volume of the titrant used in the titration, subtract initial volume from final volume 20 cm^3 – 0 cm^3= 20 cm^3 = titre

Steps in the Calculations in Sequence rxns

- First calculate the number of moles of titrant. Why are we first calculating these moles? Its because we know the concentration of the titrant and now after titration, we know the volume hence its easy to calculate the moles.

REMEMBER THAT IN CHEMISTRY, ALL REACTIONS OCCUR ON A MOLE TO MOLE RATIO HENCE THINK IN TERMS OF MOLES NOT VOLUMES OR MASSES n $_{C_2O_4^{2-}}$ =M$_{C_2O_4^{2-}}$ x V$_{C_2O_4^{2-}}$ remembering that volume must be in Liters

n $_{C_2O_4^{2-}}$ $= 0.5\ {}^{mol}/_{L} \times 20\ cm^3 \times \frac{1\ L}{1000\ cm^3} = 0.01\ mol$

Next check the reaction ratio in the balanced equation.

5 mol $C_2O_4^{2-}$ reacts with 2 mol MnO_4^{2-}

0.01 mol $C_2O_4^{2-}$ $\longrightarrow$ x

Cross multiply and solve for x.

5 mol $C_2O_4^{2-}$ reacts with 2 mol MnO_4^{2-}

0.01 mol $C_2O_4^{2-}$ $\longrightarrow$ x

$$0.01\ mol\ C_2O_4^{2-}\ \times 2\ mol\ MnO_4^-\ = x\ \times 5\ mol\ C_2O_4^{2-}$$

$$x = \frac{0.01\ mol\ C_2O_4^{2-}\ \times 2\ mol\ MnO_4^-}{5\ mol\ C_2O_4^{2-}}$$

$$x = \frac{0.01\ \cancel{mol\ C_2O_4^{2-}}\ \times 2\ mol\ MnO_4^-}{5\ \cancel{mol\ C_2O_4^{2-}}}$$

Cancel out common items

$$x = 0.004\ mol\ MnO_4^-$$

Now, these moles are in 25 cm^3 so in 250 cm^3 we have

$$\frac{250\ cm^3 \times 0.004\ molMnO_4^-}{25\ cm^3} = 0.04\ molMnO_4^-.$$

Next check the reaction ratio in the balanced equation.

2 mol MnO_4^- are produced by 1 mol Mn_2O_7

0.04 mol MnO_4^- $\longrightarrow$ y

Cross multiply and solve for y as in the previous step.

$$y = 0.02\, mol\ Mn_2O_7$$

Now 1 mol Mn_2O_7 contains 2 mol Mn

0.02 mol Mn_2O_7 will have 0.02 x 2 mol Mn = 0.04 Mn

Now 1 mol Mn weighs 54.94 g

So 0.04 mol Mn will weigh 0.04 x 54.94 g= 2.1992 g

$$Percent\ Mn = \frac{2.1992\ g}{5.0\ g} \times 100\% = 43.98\% = 44.0\ \%$$

Back Titration

- Back titration is carried on the excess moles of the excess reagent left after the completion of the reaction.
- Here the analyte is the limiting reagent.
- The excess reagent left after the completion of the reaction is titrated using a suitable standard.

Example

A 1.25 g sample OF LIMESTONE was added to 50.00 mL of 1.00 M HCl. When reaction stopped, the solution was made up to 250 mL with distilled water. A 25.00 mL of this sample was pippetted into a conical flask and titrated with 0.100 M NaOH in presence of Methyl orange indicator. It required exactly 30.00 mL of NaOH. Determine percent $CaCO_3$ in the sample.

The reaction involved is

$$CaCO_3(s) + 2HCl(aq) = CaCl_2(aq) + 2H_2O(l)$$

The titration reaction is

$$HCl(aq) + NaOH(aq) = NaCl(aq) + H_2O(l)$$

Solution

Start the calculation from the titration reaction (last or back reaction)
As usual, check the reaction or mol ratio. In this case its 1mol HCl reacts with 1 mol NaOH = 1:1

$$n_{HCl,in\ 25cm^3} = n_{NaOH} = 0.100\frac{mol}{\cancel{L}} \times 30\ \cancel{cm}^3 \times \frac{1\cancel{L}}{1000\ \cancel{cm}^3} = 3.00 \times 10^{-3}\ mol$$

$$n_{HCl,in\ 250cm^3} = 3.00 \times 10^{-3}\ mol\ \times \frac{250cm^3}{25cm^3} = 3.00 \times 10^{-2}\ mol$$

$$n_{HCl,initial\ or\ original} = 1.0\frac{mol}{L} \times 50\ cm^3 \times \frac{1L}{1000\ cm^3} = 5.00 \times 10^{-2}\ mol$$

Mol of HCl that reacted with limestone = initial – excess mol in 250 cm^3

$$= 5.00 \times 10^{-2}\ mol - 3.00 \times 10^{-2}\ mol = 2.00 \times 10^{-2}\ mol$$

Next calculate the amount of calcium carbonate. Remember that in back titration, analyte is limiting. Check the equation and make appropriate mol ratios.

2 mol HCl reacts with 1 mol $CaCO_3$

2.00×10^{-2} mol $\longrightarrow$ z

Cross multiply and solve for z.

$$x_{\,CaCO_3} = 2.00 \times 10^{-2}\, mol\ (HCl\ reacted) \times \frac{1\ molCaCO_3}{2\ mol\ HCl} = 1.00 \times 10^{-2}\, mol$$

$$mass_{\,CaCO_3} = 1.00 \times 10^{-2}\, mol \times 100.09\ \frac{g}{mol} = 1.009\ g$$

$$Percent\ CaCO_3 = \frac{1.009\ g}{1.25\ g} \times 100\% = 80.07\%$$