CHEM 7 TITRATIONS AND REACTION STOICHIOMETRY

Volumetric Analysis - when the analysis is performed by ***measuring volumes of solutions*** –using a **burette** and **pipette.**

The material in solution is called the **analyte**; the volume of analyte taken is called the **aliquot,** it is delivered by a ***pipette*** of fixed volume into a conical flask**.**

A ***burette*** is a graduated tube with a tap that is used to deliver a controlled volume of **titrant** to the solution being analysed in the conical flask – the titrant is added to the solution until the reaction is complete, called the 'end-point' (stoichiometric point) and the volume measured is called the **titre.** The completion of the reaction (when it reaches the stoichiometric point) is determined by an **indicator,** which is usually a coloured dye that changes colour –when this occurs, it is called the **'end point'** of the titration.

The overall process, as one liquid is added to the other, is called a **titration.**

Eg. Consider the **Acid / Base** titration (A neutralisation reaction)

$$1\ Na_2CO_3 + 2\ HC\ell \rightarrow 2\ NaC\ell + H_2CO_3$$

Stoichiometry :

$$\frac{\text{mol } Na_2CO_3}{1} = \frac{\text{mol } HC\ell}{2}$$

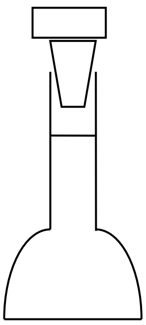
So, $1 \text{ mol } Na_2CO_3 = \text{mol } HC\ell / 2$

Ie., $\text{mol } HC\ell = 2 \times \text{mol } Na_2CO_3$

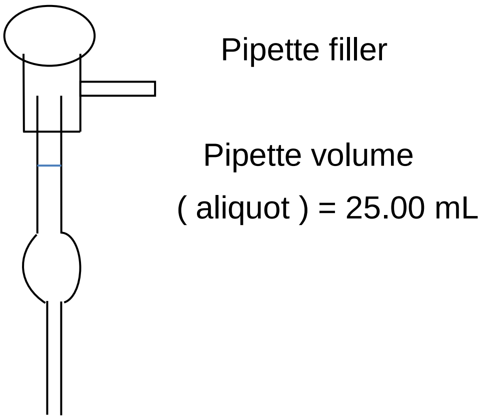
(See example calculations on next page of this Tip Sheet).

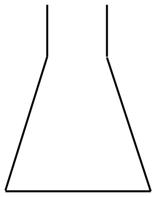
TASK :To determine the exact concentration of a HCl solution by titration of an aliquot of a standard Na_2CO_3 solution ($[Na_2CO_3] = 0.04761$ mol/L).

A. Place an exact volume of standard Na_2CO_3 solution (25.00 mL) in a conical titration flask :



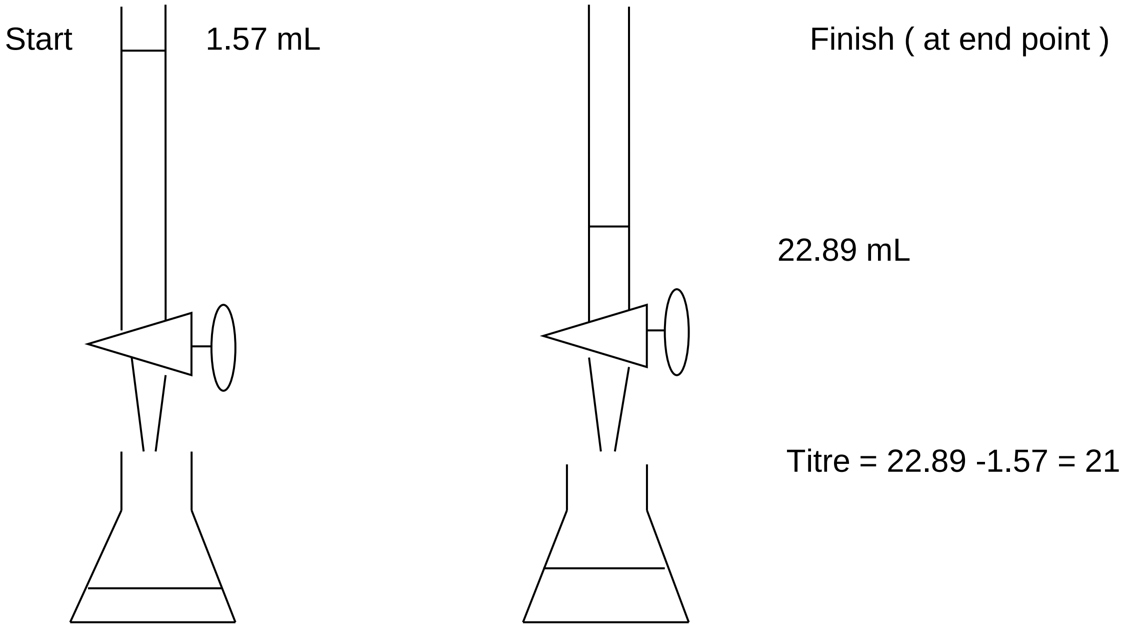
$C_{Na2CO3} = 0.04761$ M





B. Using a burette, add an exact volume of HCl(21.32 mL) to neutralise the Na_2CO_3 using an appropriate indicator for the following overall chemical reaction :

$Na_2CO_3 + 2HCl \rightarrow 2\ NaCl + H_2CO_3$



Titre = 22.89 -1.57 = 21.32 mL

C. Calculate the exact concentration of the HCl solution:

From balanced equation

$\text{mol HCl} = 2 \times \text{mol } Na_2CO_3$

$C_{HCl} \times V_{HCl} = 2 \times C_{Na2CO3} \times V_{Na2CO3}$

$C_{HCl} \times 21.32 / 1000 = 2 \times 0.04761 \times 25.00/1000$ so $C_{HCl} = 0.1117$ mol/L

As another example, consider the **Acid / Base** titration (a neutralisation reaction)

Note that **H_2SO_4 is termed a di-protic acid, because it can provide 2 H^+ ions per molecule -likewise, phosphoric acid, H_3PO_4 , is termed a tri-protic acid, because it can release 3 H^+ ios per molecule.**

$$1.H_2SO_4 = 2.H^+ + SO_4^{2-} + 2.\,Na^+OH^- \longrightarrow 2.Na^+ + SO_4^{2-} + 2.H_2O$$

Removing "Spectator" ions gives :

$$2.H^+ + 2.\,OH^- \longrightarrow 2.H_2O$$

When a 25.00 mL aliquot of a solution of sodium hydroxide (NaOH) was titrated to the stoichiometric point with a 0.0987 molar solution of sulphuric acid (H_2SO_4), an average titre of 15.48 mL was obtained. What is the molar concentration of the NaOH solution, and what mass of NaOH ($M_r = 40.0$ g mol^{-1}) does it contain per litre ?

From the stoichiometric equation ;

$$\frac{\text{mol } H_2SO_4}{1} = \frac{\text{mol NaOH}}{2}$$

Now, number of mol = concentration x volume (n = C x V)

ie. n = C (mol L^{-1}) x V (L) = C (mol L^{-1}) x V (mL)/1000

$$\frac{\textbf{mol } \mathbf{H_2SO_4}}{1} = \frac{0.0987 \text{ mol L}^{-1} \text{ x } 15.48 \text{ mL}}{\cancel{1000 \text{ mL L}^{-1}}} = \frac{\textbf{mol NaOH}}{2} = \frac{[\text{NaOH}] \text{ mol L}^{-1} \text{ x } 25.00 \text{ mL}}{2 \quad \text{x} \quad \cancel{1000 \text{ mL L}^{-1}}}$$

$$\text{So, } [\text{NaOH}] = \frac{2 \text{ x } 0.0987 \text{ mol L}^{-1} \text{ x } 15.48 \cancel{\text{ mL}}}{25.00 \cancel{\text{ mL}}} = \mathbf{0.1222 \text{ mol L}^{-1}}$$

Now **mass NaOH per Litre** = Conc mol L^{-1} x M_r g mol^{-1}

$$= 0.1222 \cancel{\text{ mol}} \text{ L}^{-1} \text{ x } 40.0 \text{ g} \cancel{\text{ mol}^{-1}} = 4.888 \text{ g L}^{-1}$$

Back Titrations are performed when it is not practical to titrate by direct reaction. In this case an amount of reagent is added in excess, then after reaction with the analyte is complete, the excess reagent remaining is determined by direct titration.

Eg : $CaCO_3$ in limestone, coral or sea shells ; or **ammonia** (NH_3) in an ammonium (NH_4^+) salt

Halides (Cl^{-1}, Br^{-1}, I^{-1}) by Volhard method (in seawater or waste water) eg **$CaCO_3$ (limestone, coral, sea shells)**

Total mol HCl added

$=C_{HCl} x V_{HCl}$

(added)

Mol HCl reacted with $CaCO_3$ mol HCl reacted / **2** = Mol $CaCO_3$	$\mathbf{2}.HCl + CaCO_3 \xrightarrow{boil} Ca^{2+} + 2.C\ell^- + H_2O + CO_2$

Mol HCl in excess (titrated with NaOH) $= C_{NaOH} x V_{NaOH}$	$HCl + NaOH \rightarrow H_2O + Na^+ + Cl^-$

Now, Total mol HCl added = mol HCl in excess + mol HCl reacted with $CaCO_3$

So, $C_{HCl} x V_{HCl}$ (added) = $C_{NaOH} x V_{NaOH}$ (back titration of excess) + mol HCl reacted with $CaCO_3$

mol HCl reacted with $CaCO_3$ = $C_{HCl} x V_{HCl}$ (added) - $C_{NaOH} x V_{NaOH}$ (back titration of excess)

Mol $CaCO_3$ = ½ [$C_{HCl} x V_{HCl}$ (added) - $C_{NaOH} x V_{NaOH}$ (back titration of excess)]

Halides (Cl^{-1}, Br^{-1}, I^{-1})

Total mol $AgNO_3$ added

$=C_{AgNO3} x V_{AgNO3}$

(added)

Mol $AgNO_3$ reacted with chloride Mol Cl^- = mol $AgNO_3$	$\mathbf{Ag^+ + Cl^-} \rightarrow AgCl(s)$

Mol $AgNO_3$ in excess (titrated with CNS^-) $= C_{CNS-} x V_{CNS-}$	$\mathbf{Ag^+ + CNS^-} \rightarrow AgCNS(s)$

Now, Total mol $AgNO_3$ added = mol $AgNO_3$ in excess + mol $AgNO_3$ reacted with Cl^-

So, $C_{AgNO3} x V_{AgNO3}$ = $C_{CNS-} x V_{CNS-}$ (back titration of excess) + mol $AgNO_3$ reacted with Cl^-

mol $AgNO_3$ reacted with Cl^- = $C_{AgNO3} x V_{AgNO3}$ - $C_{CNS-} x V_{CNS-}$ (back titration of excess)