STOICHIOMETRY II

- Stoichiometry in chemical equations means the quantitative relation between the amounts of reactants consumed and product formed in chemical reactions as expressed by the balanced chemical equation for the reaction.
- It is the relationship between the amount of reactants and products in chemical reactions.

	$CaCO_{3(s)}$	+	$2HCl_{(aq)}$	$\longrightarrow$	$CaCl_{2(aq)}$	+	$H_2O_{(l)}$	+	$CO_{2(g)}$
mole	1		2		1		1		1
mass	100g		2(36.5g)		111g		18g		44g

- Stoichiometric Coefficient is the number multiplying the entire chemical formulas in chemical equations. It is 2 for HCl, and 1 for $CaCO_3$, $CaCl_2$, H_2O and CO_2 but stoichiometry coefficient of 1 is not written explicitly.
- Stoichiometric Coefficient gives the relative number of each substance that reacted or produced in the reaction that is well balanced.

CHEMICAL ANALYSIS

QUALITATIVE

Answer question what is present?

QUANTITATIVE

Answer question how much is present?

Gravimetry

(mass measurement)

Volumetry

(volume measurement)

- Acid – base Reaction
- Redox Reaction
- Precipitation Reaction
- Complexation Reaction

VOLUMETRIC/ TITRIMETRIC ANALYSIS

- This is a quantitative analysis which is based on volume measurement of solutions that react together during a chemical reaction
- The process by which a solution is gradually added to a sample (solution) is known as TITRATION
- The solution that is being gradually added which is usually contained in the burette is called TITRANT. In most cases its concentration is always known.
- The second solution which is often pipetted into a conical or Erelemeyer flask in which titrant is always being added is called ANALYTE or TITRAND. Its concentration is not always known hence it is to be sought for
- The volume of titrant which is required to react completely with the analysed substance in the titrand is called TITRE VALUE of the titration
- EQUIVALENT POINT OR STOICHIOMETRIC POINT of the titration is defined as the stage at which the volume of titrant added is exactly that required by the stoichiometric relation between titrant and titrand (analyte)
- This is often determined with an indicator or instrument and it is estimated as the end point of the reaction.

Class Discussion: Distinguish between equivalence point and end point of a reaction.

BASIC HINTS IN TITRIMETRY

- The data involved in a typical titration entail the followings:
  - Volume of analyte/titrand (usually pipetted)
  - Molarity/concentration of analyte/titrand (to be determined or sought for)
  - Volume of titrant solution needed to reach the stoichiometric point (titre value)
  - Molarity/concentration of titrant
- Use the following three steps:
  - Step1: Use the volume of titrant and its concentration/molarity to calculate the number of moles of titrant species added from the burette i.e.

    Number of moles of titrant = volume of titrant used (litre) × molarity of titrant (mole/litre)
  - Step2: Write the stoichiometric relation between the analyte and titrant to generate mole ratio or conversion factor and then multiply the moles of titrant by the ratio. i.e.

Substance required/ substance given = Analyte/ Titrant = conversion factor

Number of mole of analyte present = number of moles of titrant used × conversion factor

  - Step3: Calculate the concentration/molarity of the analyte by dividing the number of mole of analyte by the initial volume of the solution i.e.

    Molarity of analyte = number of moles of analyte/ volume of solution(litre)

- **CLASSWORK**

25.00mL of a solution of oxalic acid, $H_2C_2O_4$ was titrated with 0.500M $NaOH_{(aq)}$ and that the stoichiometric point was reached after 38.00mL of the solution of base had been added. What is the molarity of the oxalic acid?

Solution:

Step1: The moles of NaoH added = volume of NaoH × Molarity of NaoH

= $(38.00 \times 10^{-3}$ L) × 0.500 mol/L

= 1.90×10^{-2} mol

Step2 : The neutralization reaction is

$$H_2C_2O_{4(aq)} + 2NaOH_{(aq)} \longrightarrow Na_2C_2O_{4(aq)} + 2H_2O_{(l)}$$

The stoichiometric relation required is 1mole $H_2C_2O_4$ ≡ 2moles NaOH

Mole ratio or Conversion factor = Sub. required/Sub. given= Analyte/Titrant

= 1mole $H_2C_2O_4$ /2moles NaOH

Number of moles of $H_2C_2O_4$= Number of mole of titrant used × conversion factor

= 1.90×10^{-2} mol×1mole $H_2C_2O_4$ /2moles NaOH

= 9.50×10^{-3} mol $H_2C_2O_4$

Step3: The molarity of oxalic acid = Number of moles of $H_2C_2O_4$/Volume of $H_2C_2O_4$

= 9.50×10^{-3} mol $H_2C_2O_4$/ 38.00×10^{-3} L $H_2C_2O_4$

= 0.380M $H_2C_2O_4$

STANDARD SOLUTION: PREPARATION & PROPERTIES

- Solutions are homogeneous mixtures of both solvent and solute
- A standard solution is one which contains a known amount of solute in a known amount of solution or a solution of known concentration
- Standard solutions could be classified as (i) Primary Standards and (ii) Secondary Standards
- Primary standards are reference materials or chemicals which are highly purified chemical compounds that are used to determine concentration of any solution by titration
- Examples of primary standards are (a) Anhydrous Na_2CO_3 (b) potassium hydrogen phthalate

(c) $K_2Cr_2O_7$ for reducing agent (d) NaCl for $AgNO_3$ (e) Ammonium ethanedioate (f) Sodium ethanedioate (g) Ethanedioic acid

PROPERTIES OF PRIMARY STANDARDS

- Highly pure with impurity less than 0.01%
- Definite composition
- Readily soluble in solvent
- Readily available at moderate cost
- Reasonable high molecular weight
- Unreactive to normal constitute of air
- Not hydrated, hygroscopic or efflorescence
- Stable at room temperature and to normal drying temperature (about 110 ^{O}C) of the oven

SECONDARY STANDARDS

- These are solutions whose concentrations has been accurately determined by titration of a primary standard and they are used to standardize other solutions.
- The process by which the concentration of standard solution is determined by titration with primary standard is called STANDARDIZATION
- They do not possess the properties of primary standards stated above but usually used for titration
- They are solutions prepared by diluting concentrates stock solution to approximately desire concentration and this concentration is determined by standardizing them with primary standards
- Examples of secondary standards are NaOH, HCl, Hydrated Na_2CO_3, H_2SO_4 etc

PREPARATION OF STANDARD SOLUTIONS

- Primary or secondary standard solutions are prepared in the same way
- The only difference is in the physical state of the chemical either solid or liquid
- Solid chemicals (such as NaOH, $KMnO_4$, $AgNO_3$,Na_2CO_3) need to be weighed while liquid chemicals (concentrate e.g. HCl, H_2SO_4, NH_4OH, HNO_3) need to be measured in volume using burette, automatic pipette, cylinder

PREPARATION OF STANDARD SOLUTIONS FROM SOLID CHEMICALS

- The following process should be taken in preparing standard solution:
  - Step1: Ascertain the volume V of the solution
  - Step2: Ascertain the concentration C of the solution
  - Step3: Find out the number of mole of solute needed to prepare volume V of concentration C of the solution
  - Step4: Convert the number of mole to its equivalent mass

EXAMPLE

Preparation of 250 cm^3 of 0.20M NaOH solution

- Step1: Volume V of NaOH solution is 250cm^3
- Step2: Concentration C of NaOH solution is 0.20M
- Step3: No of mole = $\frac{\text{Concentration C} \times \text{Volume V } (cm^3)}{1000} = \frac{0.2 \times 250}{1000} = 0.05\text{mole}$
- Step4: Mass of NaOH needed = No of mole × Molar mass = 0.05 × 40g = 2g
- Weigh 2g of NaOH and dissolve in little quantity of distilled water and make up the solution to 250cm^3 with distilled water in 250 cm^3 standard flask

PREPARATION OF STANDARD SOLUTION FROM LIQUID CHEMICAL (CONCENTRATE)

- Concentrated acids such as HNO_3, HCl, H_2SO_4 etc are usually in liquid form
- To prepare their standard solution, it is necessary to know the assay, density (specific gravity), the molar mass in order to find the concentration (molarity) of the acid
- Assay is the percentage by mass of the actual acid contained in the concentrated acid
- Let:
  - The assay of the concentrated acid be W%
  - The density (specific gravity) of the acid be d(g/cm^3)
  - The molar mass be M
- The concentration (molarity) of the acid in mol/dm^3 be Y, $Y = \frac{W\% \times d(g/cm^3) \times 1000}{M}$
- Then the volume of the concentrated acid that will be needed to prepare a known volume of the required concentration of acid solution will be calculated using dilution law $C_1V_1 = C_2V_2$

EXAMPLE: The assay of HCl is 36% and its density is $1.18g/cm^3$. Calculate the concentration (mol/dm^3) of HCl and the volume required to prepare $250cm^3$ of 0.50M HCl solution.

- Answer: The concentration (mol/dm^3) of HCl $Y = \frac{W\% \times d(g/cm^3) \times 1000}{M} = \frac{36/100 \times 1.18 \times 1000}{36.5} = 11.64$

$C_1V_1 = C_2V_2$, $V_1 = ?$, $C_1 = 11.64mol/dm^3$, $C_2 = 0.5mol/dm^3$, $V_2 = 250cm^3$

$V_1 = C_1/C_2V_2 = 11.64/0.5 \times 250 = 10.74cm^3$

The volume of HCl required to prepare $250cm^3$ of 0.5M HCl solution is $10.74cm^3$

CONCENTRATIONS: MOLARITY AND VOLUMETRIC CALCULATIONS

- Concentration of a solution is the amount of solute in a given volume of the solution
- Various concentration units are:
  - Molarity (M or mol/dm^3), Normality (N), Formality (F), Molality (m), %weight per volume (%w/v) , %volume per volume (%v/v), %weight per weight (%w/w), part per hundred (pph), part per million (ppm), part per billion (ppb)
  - The focus here is Molarity
- Molarity of a solution is the number of moles of a solute in one dm^3 (one litre) solution.
  - $$\text{Molarity} = \frac{\text{Number of mole}}{\text{Volume } (dm^3)} \quad \text{or} \quad \frac{\text{Number of moles}}{\text{Volume } (cm^3)} \times 1000$$
  - A molar solution of a compound is the one which contains one mole or molar mass of the compound in one dm^3 (one litre) of the solution e.g. one molar solution of sodium hydroxide is the one that contains one mole or 40g of sodium hydroxide in one dm^3 (one litre) of the solution.
  - Note:
    - Molarity = mole/ dm^3 (litre)
    - Number of specified entities per dm^3 (litre) = molarity $\times 6.02 \times 10^{23}$
    - Concentration in g/dm^3 = molarity × molar mass

VOLUMETRIC CALCULATIONS BASED ON STOICHIOMETRIC COEFFICIENTS IN NEUTRALIZATION, REDOX, PRECIPITATION AND COMPLEXATION REACTION

- Basically volumetric calculations are used in
  - Standardization of unknown solution
  - Calculating molar mass of compounds, percentage purity, water of crystallization and solubility as applied to neutralization, redox, precipitation and complexation reactions.
- The calculations involve
  - Well balance equation of the reaction
  - Volumes of solution used
  - Concentration of the standard solution

CALCULATION (NEUTRALIZATION REACTION)

- A solution of nitric acid contains 0.67g in 100mL. 31.0mL of this solution neutralized 25.0mL of a sodium carbonate solution. Calculate the concentration of carbonate solution (HNO_3=63, Na_2CO_3= 106)

Answer

$$2HNO_{3(aq)} + Na_2CO_{3(aq)} \longrightarrow 2NaNO_{3(aq)} + H_2O_{(l)} + CO_{2(g)}$$

2moles of HNO_3 reacted with 1mole of Na_2CO_3

Concentration of HNO_3 = $0.67g/100cm^3 = 6.7g/1000cm^3 = 6.7g/dm^3$

Molarity of HNO_3 = $\frac{\text{conc. In g/dm}^3}{\text{molar mass}} = \frac{6.7}{63}\ \text{mol/dm}^3 = 0.106\ \text{mol/dm}^3$

Number of mole of HNO_3 that reacted = $\frac{\text{volume of } HNO_3 \times \text{molarity of } HNO_3}{1000}$

$$= \frac{31.0cm^3 \times 0.106mol/dm^3}{1000} = 3.3 \times 10^{-3} \text{ mole}$$

Since 2mole of HNO_3 reacted with 1 mole of Na_2CO_3

D/4 3.3×10^{-3} mole HNO_3 will react with $\frac{3.3 \times 10^{-3}}{2}$ mole of Na_2CO_3 = 1.65×10^{-3} mole Na_2CO_3

It means that $25cm^3$ Na_2CO_3 solution contains 1.65×10^{-3} mole Na_2CO_3

$1000cm^3$ Na_2CO_3 solution will contain $\frac{1000cm^3 \times 1.65 \times 10^{-3} \text{ mole } Na_2CO_3}{25cm^3}$ = 0.066M = 0.07M

The concentration of the carbonate solution is $0.07mol/dm^3$ (0.07M)

CLASSWORK

- **REDOX REACTION:** A 25mL acidic sample of iron (II) chloride was titrated to the end point with 15.32mL of 0.009158M potassium permanganate. Calculate the concentration and mass of the iron (II) chloride in the titrand.
- **PRECIPITATION REACTION:** A saturated solution of $Pb(NO_3)_2$ was prepared at 22°C. 27mL of this solution required 46mL of NaCl solution containing 96g/L for complete precipitation at 22°C in (a) mol/L (b) g/L (Na = 23, Cl = 35.5, Pb = 207, N = 14, O = 16)
- **COMPLEXATION REACTION:** A 50mL solution of calcium (II) ion was titrated with 32.76mL of 0.1000M EDTA (Ethylenedinitrilotetraacetic acid or Ethylenediaminotetraacetic acid) to Eriochrome Black T end point. Calculate the concentration of the calcium solution
- FOR FUTHER PRACTICE, CHECK THE NOTE FOR MORE QUESTIONS TO PRACTISE