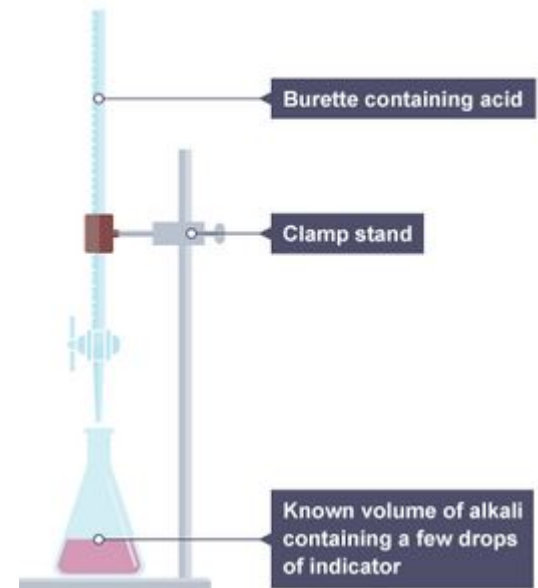# F Y B Tech Chemistry

Practical Sessions

- **Analytical chemistry** studies and uses instruments and methods used to separate, identify, and quantify matter.
- There are two branches in **analytical chemistry**:
- 1) Qualitative **analysis**: A qualitative analysis determines the presence or absence of a particular compound, but not the mass or concentration.
- 2) Quantitative **analysis**: Quantitative analysis is the measurement of the quantities of particular chemical constituents present in a substance.
- **Gravimetric analysis:** Gravimetric analysis involves determining the amount of material present by weighing the sample before and/or after some transformation.
- **Volumetric analysis:** Titration involves the addition of a reactant to a solution being analyzed until some equivalence point is reached.

Volumetric Titrations

- Measuring the volume of a unknown substance that combines with volume of a known substance in definite proportions is called as Volumetric analysis or titration. Adding increments of a reagent to a solution of an analyte until the reaction is complete.

- It is this method of quantitative analysis that allows us to determine the concentration of the

- analyte.

- Four types of volumetric titrations are:

- 1) Acid-base

- 2) Complexometric

- 3) Redox

- 4) Precipitation

Burette containing acid

Clamp stand

Known volume of alkali containing a few drops of indicator

- **Basic principles of volumetric analysis**
- The solution to be analysed contains an unknown amount of a compound.

- The reagent of unknown concentration reacts
- with another chemical in
- the presence of an indicator to show
- the end-point.
- It's the point indicating the completion
- of the reaction.

TITRANT

The solution of known concentration used in titration (added from burette) are known as titrant

Titrant

- The indicator is chosen such that the point of the colour change (the end point) nearly coincides with the equivalence point.
- The volumes are measured by titration which completes the reaction between the solution and reagent.

- The volume and concentration of reagent which are used in the titration give the amount of reagent and solution.

- The amount of unknown chemical in the specific volume of solution is calculated.
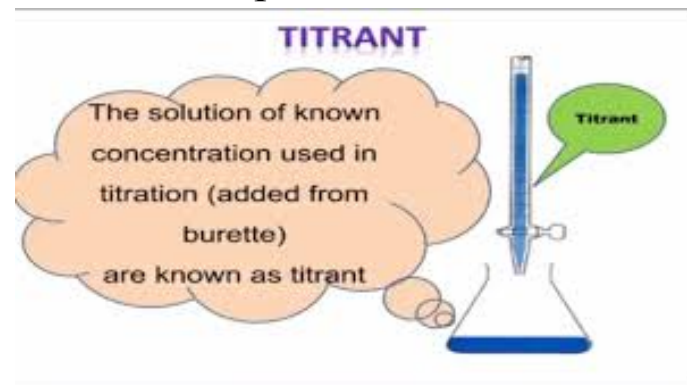
Mole Concept

- A mole is defined as the amount of a substance that contains exactly $6.02214076 \times 10^{23}$ 'elementary entities' of the given substance.

- The number $6.02214076 \times 10^{23}$ is popularly known as the Avogadro constant and is often denoted by the symbol 'N_A'. The elementary entities that can be represented in moles can be atoms, molecules, monoatomic/polyatomic ions, and other particles (such as electrons).

- For example, one mole of a pure carbon-12 (^{12}C) sample will have a mass of exactly 12 grams and will contain $6.02214076 \times 10^{23}$ (N_A) number of ^{12}C atoms. The number of moles of a substance in a given pure sample can be represented by the following formula:

Molarity

- **Molarity** (M) is the amount of a substance in a certain volume of solution. **Molarity** is defined as the no. of moles of a solute per liter of a solution. **Molarity** is also known as the molar concentration of a solution.

- **Molarity formula and units**
- The units of molarity are M or mol/L. A 1 M solution is said to be "one molar."
- **M = no. of moles solute / volume of the solution (L)**
- **No. of moles = Given weight of the solute/ Mol. wt. of the solute**

- **Problems**

  Q. Determine the molarity of 3.72 moles of NaCl in 575 ml of solution.

- Q What is the molarity of 650 ml of solution containing 63 grams of Na_2CO_3?

- Q How many moles of H_2SO_4 are present in 1.63 liters of a 0.954 M solution?

- Q What is the concentration of the NaCl solution that results when 0.150 L of a 0.556-M solution is allowed to evaporate until the volume is reduced to 0.105 L?
- $(0.15 \times 0.556)/0.105 = 0.79$

Normality

- Normality is one of the terms used to measure the concentration of a solution.

- It is abbreviated as 'N' and is sometimes referred to as the equivalent concentration of a solution.

- It is mainly used as a measure of reactive species in a solution and during titration reactions or particularly in situations involving acid-base chemistry.

- Normality is described as the number of equivalents of solute present in one litre of a solution.

- Normality = Number of equivalents
-                         volume of solution in liters

Problems

- Q1. What is the normality of the following?
- a) 0.1381 M NaOH
- b) 0.0521 M H_3PO_4
- c) 0.321 g sodium carbonate in 250.0 mL of solution

Q2. If 25.00 mL of citric acid solution is titrated with 28.12 mL of 0.1718 N KOH, what is the concentration of citric acid?

Q3. What is the normality of an acid if 21.18 mL were needed to titrate 0.1369 g Na_2CO_3?

No. of equivalents of Na_2CO_3 = 0.00258

Normality of acid = 0.00258/ 0.02118 = 0.12

Experiment No. 1
Estimation of total hardness of a given sample of water by EDTA

- **Objective**
- To determine the total hardness of a water sample by complexometric titration method.
- Ethylene di amine tetra acetic acid (EDTA) is used as chelating agent. It forms complex with divalent cations such as Ca^{2+} and Mg^{2+} ions in stoichiometric amount and thus hardness can be determined as ppm of $CaCO_3$.
- **Hardness** in **water** is due to the presence of dissolved salts of calcium and magnesium.
- **Hardness of water** is determined by titrating with a standard solution of ethylene diamine tetra acetic acid (EDTA) which is a complexing agent. Since EDTA is poorly soluble in **water**, the disodium salt of EDTA is taken for this **experiment**.

Complexation Reactions

- **Coordination compounds** contain coordinate covalent bonds formed between metal ions with groups of anions or polar molecules.
  - Metal ion – Lewis acid
  - Bonded groups or chelating agent – Lewis base

- **Complex ion** – ion in which a metal cation is covalently bound to one or more molecules or ions

- Components of a coordination compound
 - Complex ion (enclosed in square brackets)

$$K_2[PtCl_6]$$

  - Counter ions
- Some coordination compounds do not contain a complex ion

$$Fe(CO)_5$$

  - Most of the metals in complexes are transition metals

- Properties of transition metals
  - Have incompletely filled d subshells
  - Or react to form ions with incompletely filled d subshells
    - Distinctive colors
    - Catalytic activity
    - Tendency to form complex ions
  - Exhibit variable oxidation state

- *Ligands* - the molecules or ions that surround the metal in a complex ion
  - Must contain at least one unshared pair of valence electrons
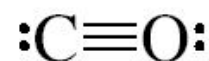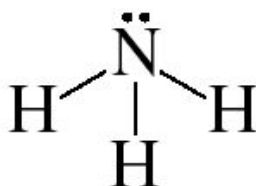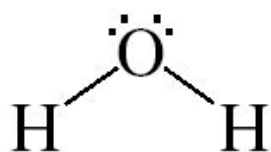
  - *Donor atom* – atom in the ligand directly bonded to the metal atom
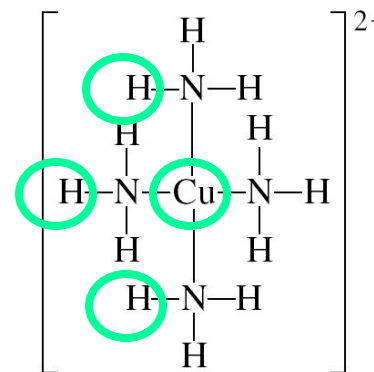
- Coordination number – number of donor atoms surrounding the central atom
  - Common coordination numbers: 4 and 6
- Classifications of ligands
  - Monodentate – 1 donor atom
  - Bidentate – 2 donor atoms
  - Polydentate - > 2 donor atoms
  - ***Chelating agents*** – another name for bidentate or polydentate ligands
- Overall charge on the complex ion is determined by
  - Oxidation state of the metal
 - Charges on the ligands

TABLE 22.3 — Common Ligands

Name	Structure
Monodentate	
Ammonia	$H-\ddot{N}-H$ with H below
Carbon monoxide	$:C\equiv O:$
Chloride ion	$:\ddot{\underset{..}{Cl}}:^{-}$
Cyanide ion	$[:C\equiv N:]^{-}$
Thiocyanate ion	$[:\ddot{\underset{..}{S}}-C\equiv N:]^{-}$
Water	$H-\ddot{\underset{..}{O}}-H$
Bidentate	
Ethylenediamine (en)	$H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2$
Oxalate ion	$\left[\begin{array}{cc} :\ddot{O} & \ddot{O}: \\ \parallel & \parallel \\ C & -C \\ :\ddot{O}. & .\ddot{O}: \end{array} \right]^{2-}$
Polydentate	
Ethylenediaminetetraacetate ion (EDTA)	(structure as shown) $^{4-}$

Determination of Hardness by EDTA Method

- **EDTA**

  -EthyleneDiamineTetraAcetic

  Acid

- **Chelating agent**

- **Hexadentate ligand**

- **Na_2EDTA is preferred as it ıs**

  more soluble in water
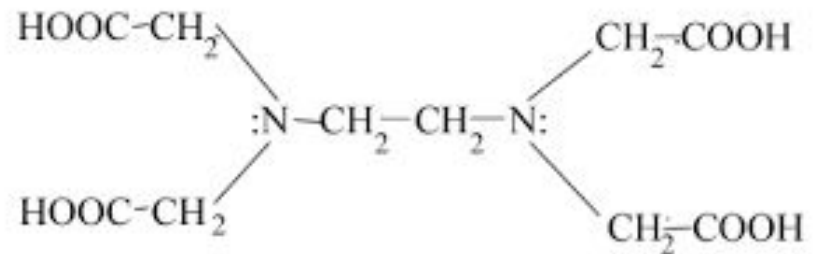
structure of EDTA

Structure of Ca-EDTA complex and EBT
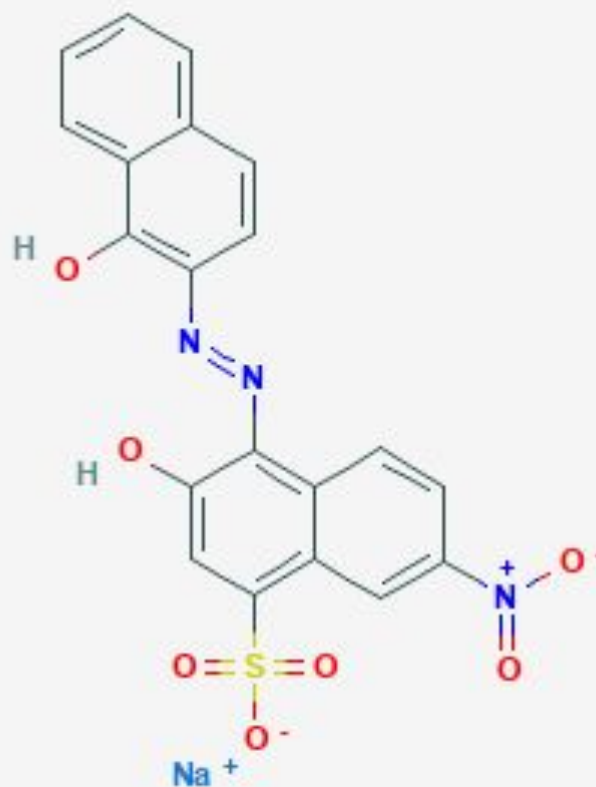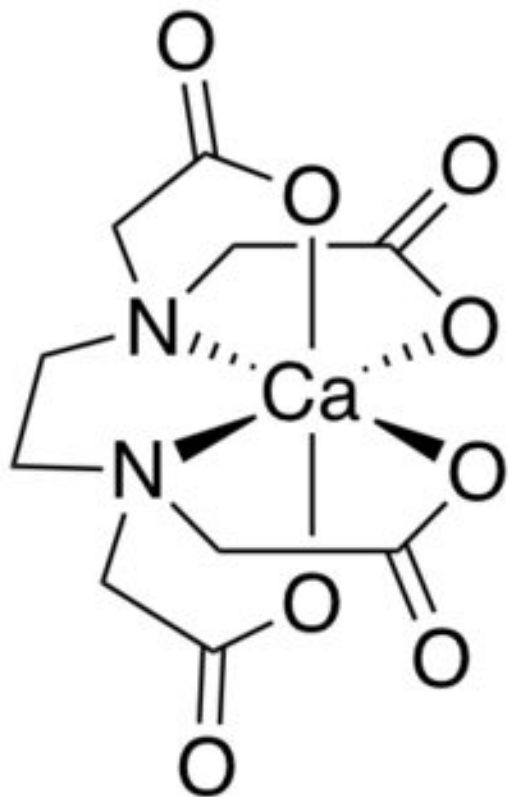
Determination of Hardness by EDTA Method

• Complexometric titration

• Eriochrome Black T is used as indicator

• pH 10 is maintained by Buffer ($NH_4Cl + NH_4OH$)

• **Hardness = (B.R x Molarity of EDTA x100 x 1000) / V**

• V is volume of water sample used for titration

• B. R. = volume of EDTA solution (burette reading)

Procedure

Part-A: **Preparation of standard 0.01 M $ZnSO_4.7 H_2O$**

Part-B: **Standardization of Na_2EDTA by $ZnSO_4. 7H_2O$ solution**

Part-C: **Determination of total hardness using Std. Na_2EDTA**

- **Procedure**

- **Part – A:- Preparation of standard 0.01 M $ZnSO_4.7 H_2O$**
- Weigh accurately 0.29 g of pure zinc sulphate on a watch glass.

- Transfer it to 250 ml beaker.

- Dissolve it in distilled water. Take washings of watch glass.

- Transfer the solution to 100 ml volumetric flask. Take washings of beaker also.

- Dilute the solution up to the mark with distilled water and shake it to make it homogeneous.

- **Part – B: -Standardization of Na_2EDTA solution by double burette method**
- Fill the **burette one** with **given Na_2EDTA (approx.0.01M) solution**. Fill **burette two** with above **standard $ZnSO_4$ solution (0.01M)**. Take by burette two, 5ml of 0.01M standard solution of zinc sulphate in conical flask.

-

- Add 3ml of buffer of pH 10 and 3 drops of Eriochrome black– T indicator. Titrate it against Na_2EDTA till color changes from wine red to blue. Let this burette reading be X_1 ml corresponds to volume of EDTA.

- To the same flask add one ml (6ml) of zinc sulphate from burette two. The colour changes to wine red. Add Na_2EDTA solution by burette one till blue colour appears. Let this reading be X_2 ml.

- To the same solution add one ml (7ml) of zinc sulphate solution by burette two. Colour changes to wine red again. Add Na_2EDTA solution from burette one till blue colour appears. Let this reading be X_3 ml. From this three readings calculate exact molarity of Na_2EDTA solution

- **Part – B :-Observation**
- Burette1   - Na_2EDTA solution (0.01 M) approx Burette2
    -    $ZnSO_4$ solution (0.01 M)
- Indicator   -   Eriochrome   Black-T End point-
  Wine red to blue
- **Reaction**   -
- Zn^{2+} + EBT $\longrightarrow$ Zn-EBT + $2H^+$
-                                 wine-red
- Zn-EBT + EDTA $\longrightarrow$ Zn-EDTA + EBT
-   Blue

- **Part – B: -Standardization of Na_2EDTA solution by double burette method**

- Fill the burette one with given Na_2EDTA (approx.0.01M) solution.

- Fill burette two with above standard $ZnSO_4$ solution. Take by burette two, 5ml of 0.01M standard solution of zinc sulphate in conical flask.

- Add 3 ml of buffer of pH-10 and 3 drops of Eriochrome black– T indicator.

- Titrate it against Na_2EDTA till color changes from wine red to blue.

- Let this reading be X_1ml.

Reactions involved in Hardness

$$M^{2+} + EBT \rightarrow \underset{\text{Wine red}}{M\text{-}EBT} + 2H^+$$

$$M\text{-}EBT + EDTA \rightarrow M\text{-}EDTA + \underset{\text{(Blue)}}{EBT}$$

- **Calculation** To calculate exact molarity of EDTA (0.01M approx.)
- $M_1 V_1 = M_2 V_2$
- Separately calculate the molarities and take the average of the three values

    Molarity of EDTA=M' =   Molar

- **Part – C:-To find out total hardness of given water sample**
- Fill the **burette one** with given Na_2 EDTA solution.
- Fill **burette two** with given **hard water sample**.
- Take from burette two, 5ml of hard water in a conical flask.
- Add 3ml of buffer of pH10 and 3 drops of Eriochrome black–T indicator. Titrate it against Na_2EDTA till colour changes from wine red to blue.
- Let this reading be Y_1ml.
- To the same flask add one ml (6ml) of hard water by burette two. Color changes to wine-red.
- Add Na_2EDTA solution by burette one till blue color appears.
- Let this reading be Y_2ml.
- To the same solution add 1ml (7ml) of hard water by burette two.
- Add Na_2EDTA solution from burette one till blue color appears.
- Let this reading be Y_3ml.

- **Burette1**
- Na_2EDTA
- $Y_1=$ $Y_2=$ $Y_3=$
- **Burette2**
- Hard water sample
- 5 ml   6 ml   7 ml

Experiment No. 2

- **Aim: Determination of alkalinity of given sample of water**

- **Objective**
- To determine the alkalinity i.e. the ability of water to resist changes in its pH due to carbonate, bicarbonate and hydroxide ions present in water.

- The alkalinity of water is determined by titrating a water sample against standard solution of acid in an acid-base titration.
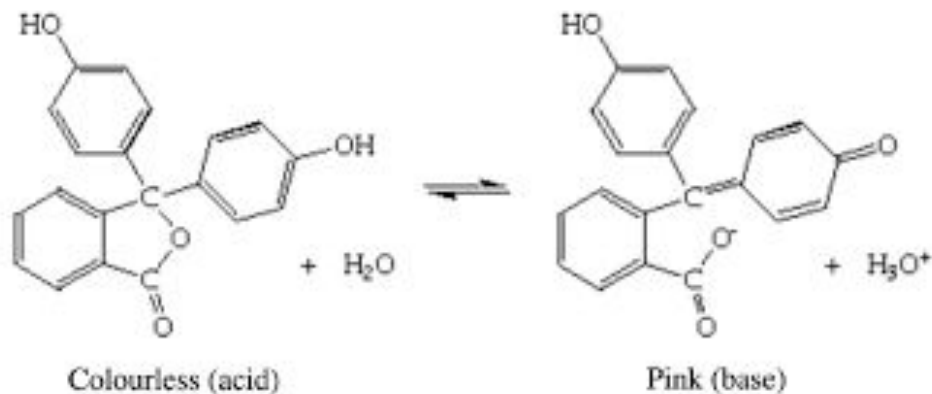
- **Apparatus**
- Burette, Conical flask (250 ml), Volumetric Flask, Burette Stand etc.

- **Chemicals**
  - 0.02 N HCl, Phenolphthalein indicator, Methyl Orange indicator, water Samples etc.

Alkalinity

- **Acid Neutralizing Capacity of Water**

- **Range of Alkalinity**: River Water is between 100 and 250 mg/l. Fresh water amounts range from 20-200 mg/l.

- It is measured by titrating the solution with a monoprotic acid such as HCl until its pH changes abruptly, or it reaches a known endpoint where that happens.

- **Phenolphthalein And Methyl Orange** Are Used As **Indicators**

- **Alkalinity is expressed in units of ppm or mg/L in terms of $CaCO_3$**, which corresponds to the amount of monoprotic acid added as a titrant.

Alkalinity Types

- **Only HO$^-$**

- **Only CO$_3^{2-}$**

- **Only HCO$_3^-$**

- **OH$^-$ & CO$_3^{2-}$ together**

- **CO$_3^{2-}$ & HCO$_3^-$ together**

- **OH$^-$ + HCO$_3^-$ ---▢ CO$_3^{2-}$ + H$_2$O**

Colourless (acid)   + H$_2$O   Pink (base)   + H$_3$O$^+$

Reactions Involved

P

$$OH^- \; + \; H^+ \; \rightarrow \; H_2O$$

$$CO_3^{2-} \; + \; H^+ \; \rightarrow \; HCO_3^-$$

M

$$HCO_3^- \; + \; H^+ \; \rightarrow \; H_2O + CO_2\uparrow$$
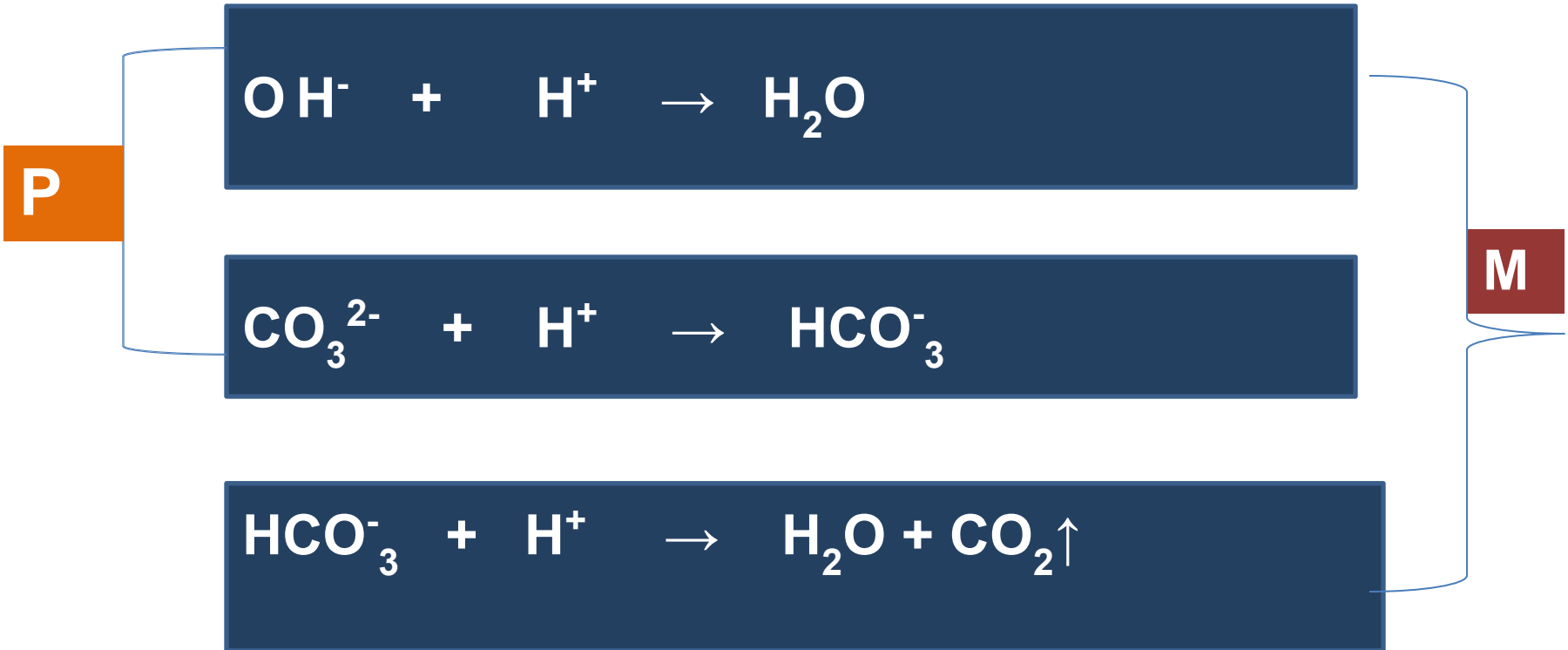
P= Phenolphthalein Alkalinity; M =Total alkalinity

-         0.0   volume of acid = V_1 = 10 ml
- P   V1
- V2   M V_2 = 16.0 ml $V_1 > V_2/2$
-        10.0
-        16.0 $M-P=V_2-V_1=16.0-10.0 = 6.0$ ml
-       $2(V_2-V_1)$ is the total volume consumed for complete neutralization of carbonates, hence the Carbonate Alk = 2(M-P)
- Hence OH^- = M- 2(M-P)=total - carbonates
-       = M-2M + 2P = 2P - M

-           0.0 volume of acid = 10 ml = V_1

- P V_1

- V_2 M $V_2 = 22.0$ ml $V_1 < V_2/2$

-          10.0 $CO_3^{2-} = 2P = 2V_1$

-                   $HCO_3 = M - 2P = V_2 - 2V_1$

-          22.0

Computing Alkalinity

- **Phenolphthalein alkalinity (P)**

  P $= (V_{1HCl} \times N_{HCl} \times 50 \times 1000) / V_{H2O}$ ppm of $CaCO_3$ equivalents.

- **Methyl orange alkalinity (M) OR Total alkalinity**

  M $= (V_{2HCl} \times N_{HCl} \times 50 \times 1000) / V_{H2O}$ ppm of $CaCO_3$ equivalents

- 1 g equivalent of the acid = 1 g equivalent of $CaCO_3$
- 1000 ml of 1N HCl = 50 g of $CaCO_3$
- 1ml of 1N HCl = 50 mg of $CaCO_3$
- V_1 ml of 'Y' N HCl = V_1 x Y x 50 mg of $CaCO_3$

- Let the volume of water = V ml
- Therefore 1000 ml of water will contain $\dfrac{V_1 \times Y \times 50 \times 1000}{V}$ mg of $CaCO_3$

- V_1 ml = volume of acid consumed till phenolphthalein end point
- V_2 ml = volume of acid consumed for the complete titration (Phph + MO)

Individual Alkalinity

Relation between P & M	OH^-	CO_3^{2-}	HCO_3^-
P = 0	-	-	M
P = M	P(M)	-	-
P=1/2 M	-	2P	-
P>1/2M	2P-M	2(M-P)	0
P<1/2M	-	2P	M-2P

Experiment No. 4

Estimation of moisture and ash content in the given coal sample

Coal

Coal is a hard rock which is burnt as a solid fossil fuel to obtain huge amount of thermal energy. It is mostly carbon but also contains hydrogen, sulfur, oxygen and nitrogen. It is a black or brown colored sedimentary rock formed from peat, by the pressure of rocks laid down later on top.

Time

Pressure

Heat

Peat

Lignite

Coal

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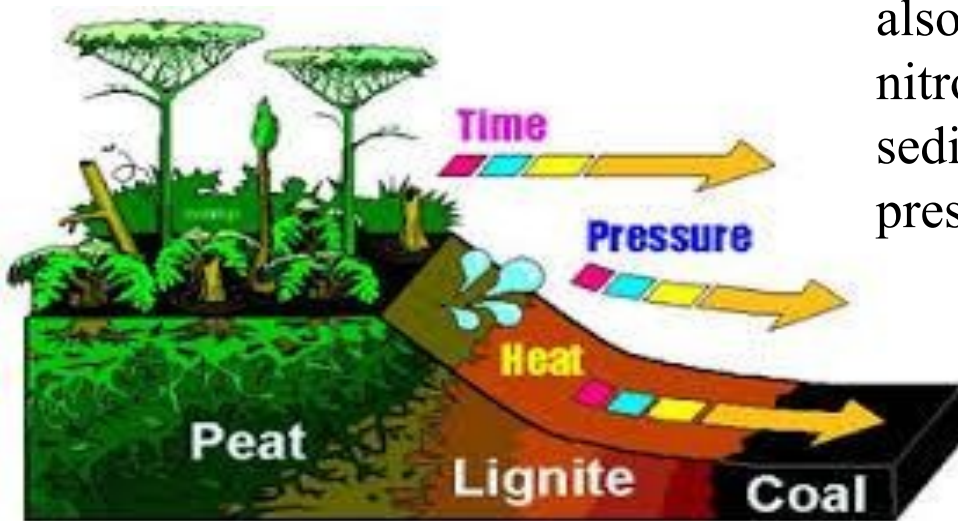
Some facts about coal

- The largest consumer and importer of coal is China. China mines almost half the world's coal, followed by India with about a tenth. Australia accounts for about a third of world coal exports followed by Indonesia and Russia.

- **Types of coal**

- Peat is a precursor of coal; has around 45% moisture.

- Lignite, or brown coal, the lowest rank of coal, most harmful to health, used almost exclusively as fuel for electric power generation.

- Sub-bituminous coal, whose properties range between those of lignite and those of bituminous coal, is used primarily as fuel for steam-electric power generation.

- Bituminous coal, a dense sedimentary rock, usually black, but sometimes dark brown, often with well-defined bands of bright and dull material. It is used primarily as fuel in steam-electric power generation and to make coke.

- Anthracite, the highest rank of coal is a harder, glossy black coal used primarily for residential and commercial space heating.

Table: Types of coal

Coal	Dry, Carbon content (%)	Moisture content before drying (%)	Dry, volatile content (%)	Heat Content (MJ/kg)
Anthracite	86-92	7-10	3-14	32-33
Bituminous coal	76-86	8-18	14-46	23-33
Sub-Bituminous coal	70-76	18-38	42-53	18-23
Lignite	65-70	35-55	53-63	17-18
Peat	<60	75	63-69	15

- **Analysis of Coal**

- The composition of coal is reported as a **proximate analysis (moisture, volatile matter, ash and fixed carbon,) and an ultimate analysis (ash, carbon, hydrogen, nitrogen, oxygen, and sulfur).**

- The most common **volatile matter in coal** is water, carbon dioxide, and sulfur dioxide, methane. High-**volatile matter** may also be associated with spontaneous combustion, especially in low-rank **coals**. Hence, knowledge of **volatile matter** is important for safety, handling, and transporting **coal**.

- Ash is the non-combustible residue formed from the inorganic or mineral components of the coal. Coals of worst quality that are burned commercially in the United States produce about 28% ash, but elsewhere in the world coals of **up to 40%** ash are in use.

- Coal is an abundant natural resource that can be used as a source of energy, as a chemical source from which numerous synthetic compounds (e.g., dyes, oils, waxes, pharmaceuticals, and pesticides) can be derived, and in the production of coke for metallurgical processes.

- Coal is a major source of energy in the production of electrical power using steam generation.

- In addition, gasification and liquefaction of coal produce gaseous and liquid fuels that can be easily transported (e.g., by pipeline) and conveniently stored in tanks.

- Coal mines and coal-preparation plants have caused much environmental damage.

- Surface areas exposed during mining, as well as coal and rock waste (which were often dumped indiscriminately), weather rapidly, producing abundant sediment and soluble chemical products such as sulfuric acid and iron sulfates.

- Potentially toxic elements, leached from the exposed coal and adjacent rocks, were released into the environment.

- Since the 1970s, stricter laws have significantly reduced the environmental damage caused by coal mining in developed countries, though more-severe damage continues to occur in many developing countries.

Coal Analysis

Proximate Analysis

- Moisture
- Volatile matter
- Ash
- Fixed Carbon

Ultimate analysis

- Carbon
- Hydrogen
- Nitrogen
- Sulfur
- Oxygen

Proximate Analysis

Sr.No	Parameter	Apparatus used	Temperature	Exposure time
1)	Moisture	Hot air Oven	110 ^{0}C	1 hr
2)	Volatile Matter	Muffle Furnace	925 ^{0}C	7 minutes
3)	Ash	Muffle Furnace	750 ^{0}C	30 minutes

- **Apparatus+ Equipments**
- Crucible, Desiccator, Pair of tongs, Electric Oven, Muffle furnace, weighing balance etc.

-

- **Chemicals**
- Coal sample, anhydrous calcium chloride
-

Principle

- Proximate analysis is an **thermogravimetric analysis** which is essential to assess suitability of coal for a particular application.
- Proximate analysis is determination of moisture content, volatile matter, ash content and fixed carbon content.
-
- This gives information about the practical utility of coal.

- **Moisture content** is the loss in weight of coal when heated in crucible at 110°C for one hour.

- The amount of **volatile matter** evolved and its composition depend on quality of the coal and also on temperature, rate of heating and time of heating.

- **Ash content** of coal is the weight of residue left after complete combustion of the Coal sample at 750°C. Ash also reduces the quality of the coal.

- The percentage of fixed Carbon is then calculated by summing up of %moisture, %volatile matter and %ash
-

Procedure

- **Part -A: Moisture Content**
- Take 0.8 g of powdered coal sample in pre-weighed silica crucible. Heat the sample in an electric oven at 110℃ for one hour. Take out the crucible and keep in desiccator, when cool then weigh it. Note the weight of the crucible+coal after you get constant weight.

- **Part -B: Volatile Matter**
- **Keep the coal sample in muffle furnace at 950** ℃ for 7 minutes. Take out the crucible and keep it in the desiccator to cool it down to room temp. Weigh the crucible+coal.

- **Part-C: Ash Content**
- Heat the remaining coal without the lid in a muffle furnace at 750℃ for 30 minutes. Take out the crucible and cool in the desiccator and weigh it. The residue remaining in the crucible is the ash.

-

Proximate Analysis Calculation

$$Moisture(M) = \frac{m - m1}{m} \times 100$$

$$Volatile\ Matter\ (VM) = \frac{m1 - m2}{m} \times 100$$

$$Ash = \frac{weight\ of\ ash}{weight\ of\ coal} \times 100$$

Ash = (m_3/m) x 100

$$fixed\ Carbon\ (\%) = 100 - (\ M\% + VM\% + ash\%)$$

Significance of proximate analysis

- **Low moisture content indicates better quality of coal**

- **Low VM   indicates better quality of coal**

- **Low ash content implies good quality coal**

- **Higher the carbon content indicate better the quality of coal.**

Numericals

1) **1.508 g of coal sample was heated at 110 ºC for 1h. On cooling the weight of the sample was found as 1.478 g. Strong heating of the sample at 950 ºC for 7 min. carried out in a closed crucible. The sample on cooling weighed 1.058g. Calculate % moisture and % volatile matter present in the sample.**

2) **1.2 g of coal sample heated at 105-110 ºC for 1 h, after heating the sample weighed 1.16 g. This remaining sample of coal ignited at constant weight of 0.09 g. In another experiment, 1.2 g of sample was heated in a crucible at 950 ºC for 7 min. After cooling the residue weighed 0.8 g. Calculate % of fixed carbon**

- % Moisture = (1.2-1.16)/1.2 * 100
- = 3.33%
- % Ash = 0.09/1.2 * 100
- = 7.5
- %moisture + % VM = (1.2-0.8)/1.2 * 100
- = 33.33
- %VM = 33.33-3.33 = 30 = (1.16-0.8)/1.2 *100
- Fixed carbon = 100 – (7.5 +33.33)
- = 59.17