RGPVBTECH.COM

ENGINEERING CHEMISTRY

UNIT-I: WATER-ANALYSIS, TREATMENTS AND INDUSTRIAL APPLICATIONS:
Sources, Impurities, Hardness & its units Determination of hardness by EDTA method, Alkalinity & it's determination and related numerical problems

UNIT-II: BOILER PROBLEM & SOFTENING METHODS:
Boiler troubles (Sludge & Scale, Priming & Foaming, Boiler Corrosion, Caustic Embrittlement) Softening methods (Lime-Soda, Zeolite and Ion Exchange Methods) and related numerical problems

UNIT-III: LUBRICANTS AND LUBRICATION:
Introduction, Mechanism of lubrication, Classification of lubricants, significance & determination of Viscosity and Viscosity Index, Flash & Fire Points, Cloud & Pour Points, Aniline Point, Acid Number, Saponification Number, Steam Emulsification Number and related numerical problems

Unit-IV: POLYMER & POLYMERIZATION:
Introduction, types of polymerization, Classification, mechanism of polymerization (Free radical & Ionic polymerization), Thermoplastic & Thermosetting polymers, Elementary idea of Biodegradable polymers Preparation, properties & uses of the following polymers - PVC, PMMA, Teflon, Nylon 6, Nylon 6:6, Polyester, phenol formaldehyde, Urea- Formaldehyde, Buna N, Buna S, Vulcanization of Rubber

UNIT-V: PHASE EQUILIBRIUM AND CORROSION:
Phase diagram of single component system (Water), Phase diagram of binary Eutectic System (Cu-Ag.), Corrosion - Types, Mechanisms & prevention.

UNIT-VI: SPECTROSCOPIC TECHNIQUES AND APPLICATION:
Principle, Instrumentation & Applications of electronics spectroscopy, Vibrational & Rotational Spectroscopy of diatomic molecules

UNIT-VII: PERIODIC PROPERTIES:
Effective Nuclear Charge, Variations.-'s, p d & f Orbital energies of atoms in periodic table, Electronics Configuration, atomic & Ionic sizes, electron affinity & electronegativity, polarizability & Oxidation

UNIT 1

WATER-ANALYSIS, TREATMENTS AND INDUSTRIAL APPLICATIONS SOURCES, IMPURITIES, HARDNESS & ITS UNITS

Q.1. Describe in brief the different sources of water.

Ans. We know that water is a essential compound for living organism. The water which is used by living beings occurs from different sources of water, basically there are two main sources of water which are as follows -

(i) Surface water

(ii) Underground water.

(i) Surface Water - Water which is available from the earth surface is called surface water. It is generally clear and colourless and acidic in nature due to dissolved CO_2 and organic matter. Rain water is a purest form of water because it is obtained by the process of distillation.

(ii) Underground Water - Some part of rain water which is reaches the inner surface of earth, is called underground water mainly spring water and well water.

Generally spring and well water is clear in appearance due to the filtering action of the soil, but this type of water contain moreover dissolved salts. Thus, water available from these sources contains more hardness and high organic impurities.

Q.2. What are the types of surface water?

Ans. Surface water includes following types of water

(i) Rain Water-Rain water is obtained from evaporation of surface water. It is the purest form of natural water, during its downward journey through the atmosphere it dissolved a considerable amount of industrial gases (like CO2, SO2, NO_2 etc.). Rain water is expensive to collect and irregular in supply.

(ii) River Water - River water contain dissolved minerals like chlorides, sulphates, bicarbonates of sodium, magnesium, calcium and iron. Water from sources, rain and spring, flow over the surface of land. The composition of river water is not constant. In river water the greater is the amount of dissolved impurities. The amount of dissolved impurities depends on its contact of the soil.

(iii) Lake Water Lake water has more constant chemical composition. It has high quantity of organic matter but lesser amount of dissolved minerals. The chemical composition of lake water is constant. -

(iv) Sea Water - It is the most impure form of the natural water, because sea water contains various types of impurities. We know that all rivers join sea and throw in the impurities carried by them. There are many salts present in sea water. Bicarbonates of potassium magnesium and calcium and other harmful compounds present in sea water.

Q.3. Write different type of sources of impurities in water.

Ans. Some important sources of impurities in water are as follows -

(i) Water takes up impurities from the ground, or soil with which it comes into contact.

(ii) Gases (e.g., O2, CO_2 etc.) are picked up from the atmosphere by rain water.

(iii) Impurities are also introduced in water when it comes into contact with sewage or industrial waste.

(iv) When some organic impurities are introduced in water by decomposition of plants and animals remains.

Q.4. How many types of impurities are present in water?

Ans. Following types of impurities are present in water -

(i) Suspended Impurities - These impurities impart turbidity, colour and odour to water. It may be organic (oil globules, vegetable and animal matter) or inorganic (clay and sand) in nature.

(ii) Dissolved Impurities - These impurities are owing to the presence of dissolved salts like carbonates, bicarbonates, chlorides and sulphates of calcium, magnesium, iron and sodium. Hardness in water is due to the presence of these salts. Dissolved gases like O2, CO_2 etc., also come under this category.

(iii) Colloidal Impurities - Products from organic waste, finely divided silica and clay etc., are agents come under colloidal impurities.

(iv) Microorganisms - They include bacterias, fungi and algae.

Q.5. Define hardness. What are its units and it conversion ? (R.G.P.V., June 2013)

Ans. The soap consuming power of water is known as hardness of water. It is characteristic of water which prevent the lathering of soap. The hardness of water is presence due to several salts (like Ca, Mg) and other heavy metal ions like, Fe^{+2}, Al^{+3} and Mn^{+2} etc. When a sample of hard water is treated with soap then it does not produce lather.

We know that,

We know that,

$$1 \text{ ppm or mg} = 1 \text{ part per } 10,00,000 \text{ parts of water}$$
$$1°Cl = 1 \text{ part per } 70,000 \text{ parts of water}$$
$$1°Fr = 1 \text{ part per } 1,00,000 \text{ parts of water}$$
$$\therefore \quad 10,00,000 \text{ ppm or mg} = 70,000°Cl = 1,00,000°Fr$$
$$100 \text{ ppm} = 7°Cl = 10°Fr$$
$$1 \text{ ppm} = 0.07°Cl = 0.1°Fr$$
$$1°Cl = 14.3 \text{ ppm (app.)} = 1.43°Fr \text{ (app.)}$$
$$1°Fr = 10 \text{ ppm} = 0.7°Cl$$

Q.6. What are the types of hardness ?

Or

Define temporary and permanent hardness of water.

Ans. The hardness of water is of two types -

(i) Temporary Hardness - This type of hardness is due to the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals (like Fe +2, A1+3, Mn+2 etc.). Hence, the temporary hardness is also known as carbonates hardness. Temporary hardness is destroyed on boiling with water. The salts which are responsible for temporary hardness are Ca(HCO3)2 and Mg(HCO3)2. The degradation reaction of bicarbonates are below -

$$Ca(HCO_3)_2 \xrightarrow{\text{Boil}} CaCO_3\downarrow + H_2O + CO_2\uparrow$$
$$\text{(Soluble)} \qquad \qquad \text{(Insoluble)}$$

$$Mg(HCO_3)_2 \xrightarrow{\text{Boil}} MgCO_3\downarrow + H_2O + CO_2\uparrow$$
$$\text{(Soluble)} \qquad \qquad \text{(Insoluble)}$$

(ii) Permanent Hardness - This type of hardness of water is due to the presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other heavy metals. Permanent hardness is not destroyed on boiling. Hence the salts responsible for permanent hardness are given below -

CaCl2, MgCl2, CaSO4, FeSO4, Al2(SO4)3 etc.

In permanent hardness carbonates is not present so permanent hardness is also known as non-carbonate or non alkaline hardness.

Q.7. Define hardness. Explain the cause of hardness in water.

Ans. The soap consuming power of water is known as hardness of water. It is characteristic of water which prevent the lathering of soap. The hardness of water is presence due to several salts (like Ca, Mg) and other heavy metal ions like, Fe+2, A1+3 and Mn+2 etc. When a sample of hard water is treated with soap then it does not produce lather.

We know that,

We know that,

$$1 \text{ ppm or mg} = 1 \text{ part per } 10,00,000 \text{ parts of water}$$
$$1°Cl = 1 \text{ part per } 70,000 \text{ parts of water}$$
$$1°Fr = 1 \text{ part per } 1,00,000 \text{ parts of water}$$
$$\therefore \quad 10,00,000 \text{ ppm or mg} = 70,000°Cl = 1,00,000°Fr$$
$$100 \text{ ppm} = 7°Cl = 10°Fr$$
$$1 \text{ ppm} = 0.07°Cl = 0.1°Fr$$
$$1°Cl = 14.3 \text{ ppm (app.)} = 1.43°Fr \text{ (app.)}$$
$$1°Fr = 10 \text{ ppm} = 0.7°Cl$$

The hardness of water is of two types -

(i) Temporary Hardness - This type of hardness is due to the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals (like Fe +2, A1+3, Mn+2 etc.). Hence, the temporary hardness is also known as carbonates hardness. Temporary hardness is destroyed on boiling with water. The salts which are responsible for temporary hardness are Ca(HCO3)2 and Mg(HCO3)2. The degradation reaction of bicarbonates are below -

$$\underset{\text{(Soluble)}}{Ca(HCO_3)_2} \xrightarrow{\text{Boil}} \underset{\text{(Insoluble)}}{CaCO_3\downarrow} + H_2O + CO_2\uparrow$$

$$\underset{\text{(Soluble)}}{Mg(HCO_3)_2} \xrightarrow{\text{Boil}} \underset{\text{(Insoluble)}}{MgCO_3\downarrow} + H_2O + CO_2\uparrow$$

(ii) Permanent Hardness - This type of hardness of water is due to the presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other heavy metals. Permanent hardness is not destroyed on boiling. Hence the salts responsible for permanent hardness are given below -

CaCl2, MgCl2, CaSO4, FeSO4, Al2(SO4)3 etc.

In permanent hardness carbonates is not present so permanent hardness is also known as non-carbonate or non alkaline hardness.

Q.8. What is degree of hardness? Give relationship between the various units of hardness. (R.G.P.V., Jan./Feb. 2008)

Or

Explain why hardness of water is expressed in terms of CaCO3 equivalent. (R.G.P.V., June 2011)

Or

Why hardness of water estimated equivalent of CaCO3? What are the different units of hardness? (R.G.P.V., Dec. 2012)

Ans. Degree of Hardness - Although the hardness of water is never present in the form of calcium carbonate because it is insoluble in water, it is always calculated in terms of CaCO3. Therefore "degree of hardness of water is conveniently expressed in terms of equivalent amount of CaCO3. The reason for choosing CaCO3 as the standard for calculating hardness of water is the ease in calculation as its molecular weight is exactly 100.

Thus the amount of various hardness causing substances in terms of CaCO3 can be calculated on the basis of the following relations -

(i) 1 g mole or 162 g of $Ca(HCO_3)_2$ = 1 g mole or 100 g of CaCO3

(ii) 1 g mole or 111 g of $CaCl_2$ = 1 g mole or 100 g of CaCO3

(iii) 1 g mole or 136 g of $CaSO_4$ = 1 g mole or 100 g of CaCO3

(iv) 1 g mole or 146 g of $Mg(HCO_3)_2$ = 1 g mole or 100 g of CaCO3

(v) 1 g mole or 95 g of $MgCl_2$ = 1 g mole or 100 g of CaCO3

(vi) 1 g mole or 120 g of $MgSO_4$ = 1 g mole or 100 g of CaCO3. Thus, the various types of hardness in a water sample may be calculated as below -

Temporary hardness = Hardness due to $Ca(HCO_3)_2$ + Hardness due to $Mg(HCO_3)_2$.

Permanent hardness = Hardness due to $CaCl_2$ + Hardness due to $CaSO_4$ + Hardness due to $MgCl_2$ + Hardness due to $MgSO_4$.

Total hardness Temporary hardness + Permanent hardness

The soap consuming power of water is known as hardness of water. It is characteristic of water which prevent the lathering of soap. The hardness of water is presence due to several salts (like Ca, Mg) and other heavy metal ions like, Fe^{+2}, Al^{+3} and Mn^{+2} etc. When a sample of hard water is treated with soap then it does not produce lather.

We know that,

We know that,

$$1 \text{ ppm or mg} = 1 \text{ part per } 10,00,000 \text{ parts of water}$$
$$1°Cl = 1 \text{ part per } 70,000 \text{ parts of water}$$
$$1°Fr = 1 \text{ part per } 1,00,000 \text{ parts of water}$$
$$\therefore \quad 10,00,000 \text{ ppm or mg} = 70,000°Cl = 1,00,000°Fr$$
$$100 \text{ ppm} = 7°Cl = 10°Fr$$
$$1 \text{ ppm} = 0.07°Cl = 0.1°Fr$$
$$1°Cl = 14.3 \text{ ppm (app.)} = 1.43°Fr \text{ (app.)}$$
$$1°Fr = 10 \text{ ppm} = 0.7°Cl$$

Q.9. Define alkaline and non-alkaline hardness of water. Mention various units use for its expression and show their relation also. (R.G.P.V., June 2014)

Ans. Alkaline and Non-alkaline Hardness of Water-"Alkaline hardness" is defined as the hardness due to the bicarbonates, carbonates and hydroxides of the hardness-producing metals. It is also called "carbonate hardness". The "nonalkaline hardness" is obtained by subtracting the "alkaline hardness" from the "total hardness". This is also known as "non-carbonate hardness".

Units of Hardness - The units of hardness are as follows -

(i) Parts per Million (ppm) - This is the most common unit for expressing the hardness of water. It is defined as the number of parts by weight of calcium carbonate present per million (10^6) parts by weight of water i.e.,

1ppm = 1 part of $CaCO_3$ in 10^6 parts of water.

(ii) Milligrams per Litre (mg/L) - It is defined as the number of milligrams of $CaCO_3$ present in one litre of water i.e.,

1 mg/litre = 1 mg of $CaCO_3$ equivalent hardness in 1 litre of water Since, weight of 1 litre of water = 1 kg = 1000 g = 1000 x 1000 mg = 10^6 mg .

1 mg/litre = 1 mg of $CaCO_3$ per 10^6 of water mg 1 part of $CaCO_3$ per 10^6 parts of water = 1 ppm.

Thus, mathematically both the units are equal.

(iii) Degree Clarke (°Cl) – It is the number of grains (1/7000 lb) of $CaCO_3$ present per gallon (10 lbs or 70,000 grains) of water i.e., it is the parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.

Mathematically, 1°Cl = 1 grain of $CaCO_3$ per gallon of water

1 part of $CaCO_3$ per 70,000 parts of water.

(iv) Degree French (Fr) - It is the parts of CaCO3 equivalent hardness per lakh (105) parts of water i.e.,

1°Fr = 1 part of CaCO3 equivalent per 105 parts of water.

Relationship -

The soap consuming power of water is known as hardness of water. It is characteristic of water which prevent the lathering of soap. The hardness of water is presence due to several salts (like Ca, Mg) and other heavy metal ions like, Fe^{+2}, $A1^{+3}$ and Mn^{+2} etc. When a sample of hard water is treated with soap then it does not produce lather.

We know that,

We know that,

$$1 \text{ ppm or mg} = 1 \text{ part per } 10,00,000 \text{ parts of water}$$
$$1°Cl = 1 \text{ part per } 70,000 \text{ parts of water}$$
$$1°Fr = 1 \text{ part per } 1,00,000 \text{ parts of water}$$
$$\therefore \quad 10,00,000 \text{ ppm or mg} = 70,000°Cl = 1,00,000°Fr$$
$$100 \text{ ppm} = 7°Cl = 10°Fr$$
$$1 \text{ ppm} = 0.07°Cl = 0.1°Fr$$
$$1°Cl = 14.3 \text{ ppm (app.)} = 1.43°Fr \text{ (app.)}$$
$$1°Fr = 10 \text{ ppm} = 0.7°Cl$$

Q.10. How is hardness of water expressed in various units ? Write relationship between these. Prove that 1 ppm = 1 mg/L. (R.G.P.V., May 2018)

Ans.

Relationship -

The soap consuming power of water is known as hardness of water. It is characteristic of water which prevent the lathering of soap. The hardness of water is presence due to several salts (like Ca, Mg) and other heavy metal ions like, Fe^{+2}, $A1^{+3}$ and Mn^{+2} etc. When a sample of hard water is treated with soap then it does not produce lather.

We know that,

We know that,

$$1 \text{ ppm or mg} = 1 \text{ part per } 10,00,000 \text{ parts of water}$$
$$1°Cl = 1 \text{ part per } 70,000 \text{ parts of water}$$
$$1°Fr = 1 \text{ part per } 1,00,000 \text{ parts of water}$$
$$\therefore \quad 10,00,000 \text{ ppm or mg} = 70,000°Cl = 1,00,000°Fr$$
$$100 \text{ ppm} = 7°Cl = 10°Fr$$
$$1 \text{ ppm} = 0.07°Cl = 0.1°Fr$$
$$1°Cl = 14.3 \text{ ppm (app.)} = 1.43°Fr \text{ (app.)}$$
$$1°Fr = 10 \text{ ppm} = 0.7°Cl$$

Units of Hardness - The units of hardness are as follows -

(i) Parts per Million (ppm) - This is the most common unit for expressing the hardness of water. It is defined as the number of parts by weight of calcium carbonate present per million (106) parts by weight of water i.e.,

1ppm = 1 part of $CaCO_3$ in 106 parts of water.

(ii) Milligrams per Litre (mg/L) - It is defined as the number of milligrams of $CaCO_3$ present in one litre of water i.e.,

1 mg/litre = 1 mg of $CaCO_3$ equivalent hardness in 1 litre of water Since, weight of 1 litre of water = 1 kg = 1000 g = 1000 x 1000 mg = 106 mg .

1 mg/litre = 1 mg of $CaCO_3$ per 106 of water mg 1 part of $CaCO_3$ per 106 parts of water = 1 ppm.

Thus, mathematically both the units are equal.

(iii) Degree Clarke (°Cl) – It is the number of grains (1/7000 lb) of $CaCO_3$ present per gallon (10 lbs or 70,000 grains) of water i.e., it is the parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.

Mathematically, 1°Cl = 1 grain of $CaCO_3$ per gallon of water

1 part of $CaCO_3$ per 70,000 parts of water.

(iv) Degree French (Fr) - It is the parts of $CaCO_3$ equivalent hardness per lakh (105) parts of water i.e.,

1°Fr = 1 part of $CaCO_3$ equivalent per 105 parts of water.

Q.11. Why does hard water consume a lot of soap?

Ans. Hard water contains soluble salts of calcium (Ca) and magnesium (Mg). When hard water is used for washing and bathing purposes, it does not lather freely with soap, but produces sticky precipitates of calcium and magnesium soaps. The formation of such insoluble precipitates consume soap till hardness is completely precipitated. Hence causes wastage of a lot of soap being used

Q.12. Write short note on CaCO3 equivalent. (R.G.P.V., Dec. 2013)

Ans. The concentration of hardness as well as non-hardness constituting ions are, usually, expressed in terms of equivalent amount of CaCO3, since this mode permits the multiplication and division of concentration, when required. The equivalent of CaCO3

$$\text{The equivalent of CaCO}_3$$

$$= \frac{\left[\begin{array}{c}\text{Mass of hardness -}\\\text{producing substance}\end{array}\right] \times \left[\begin{array}{c}\text{Chemical equivalent}\\\text{of CaCO}_3\end{array}\right]}{\text{Chemical equivalent of hardness - producing substance}}$$

$$= \frac{\text{Mass of hardness - producing substance} \times 50}{\text{Chemical equivalent of hardness - producing substance}}$$

Q.13. What are the disadvantages of hard water?

Ans. Following are disadvantages of hard water as given below -

(i) In Domestic Use -

(a) Washing - Hard water, when used for washing purposes, does not lather freely with soap.

(b) Bathing-Hard water does not lather freely with soap solution, but produces sticky scum on the bath-tub and body. Hence, the cleaning quality of soap is depressed and a lot of it is wasted.

(c) Drinking-Hard water causes bad effect on our digestive system. (d) Cooking - Due to the presence of dissolved hardnessproducing salts, the boiling point of water is elevated. Consequently, more fuel and time are needed for cooking.

(ii) In Industrial Use -

(a) Sugar Industry - Water containing sulphates, nitrates, alkali carbonates etc., when used in sugar refining, causes difficulties in the crystallization of sugar. Moreover, the sugar so-produced may be deliquescent.

(b) Paper Industry - Calcium and magnesium salts tends to react with chemical and other materials employed to provide a smooth and glossy (i.e., shining) finish to paper. Moreover, iron salts may even affect the colour of the paper being produced.

(c) Textile Industry - Hard water causes much of the soap to go as waste, because hard water cannot produce good quality of lather Moreover, precipitates of calcium and magnesium soaps adhere to the fabrics. (d) Laundry - Hard water, if used in laundry, causes much of the soap used in washing to go as waste. Iron salts may even cause coloration of the clothes.

(e) Concrete Making - Water containing chlorides and sulphates, if used for concrete making, affects the hydration of cement and the final strength of the hardened concrete.

(iii) In Steam Generation in Boilers - For steam generation, boilers are almost invariably employed. If the hardwater is fed directly to the boilers, there arise many troubles such as -

(a) Scale and sludge formation

(b) Corrosion

(c) Priming and foaming

(d) Caustic embrittlement.

Q.14. Explain hardness of water. How it is expressed in various units ? Discuss harmful effects of hardwater in boilers. (R.G.P.V., Nov. 2018)

Ans. Alkaline and Non-alkaline Hardness of Water-"Alkaline hardness" is defined as the hardness due to the bicarbonates, carbonates and hydroxides of the hardness-producing metals. It is also called "carbonate hardness". The "nonalkaline hardness" is obtained by subtracting the "alkaline hardness" from the "total hardness". This is also known as "non-carbonate hardness".

Units of Hardness - The units of hardness are as follows -

(i) Parts per Million (ppm) - This is the most common unit for expressing the hardness of water. It is defined as the number of parts by weight of calcium carbonate present per million (10^6) parts by weight of water i.e.,

1ppm = 1 part of $CaCO_3$ in 10^6 parts of water.

(ii) Milligrams per Litre (mg/L) - It is defined as the number of milligrams of $CaCO_3$ present in one litre of water i.e.,

1 mg/litre = 1 mg of $CaCO_3$ equivalent hardness in 1 litre of water Since, weight of 1 litre of water = 1 kg = 1000 g = 1000 x 1000 mg = 10^6 mg .

1 mg/litre = 1 mg of $CaCO_3$ per 10^6 of water mg 1 part of $CaCO_3$ per 10^6 parts of water = 1 ppm.

Thus, mathematically both the units are equal.

(iii) Degree Clarke (°Cl) – It is the number of grains (1/7000 lb) of CaCO3 present per gallon (10 lbs or 70,000 grains) of water i.e., it is the parts of CaCO3 equivalent hardness per 70,000 parts of water.

Mathematically, 1°Cl = 1 grain of CaCO3 per gallon of water

1 part of CaCO3 per 70,000 parts of water.

(iv) Degree French (Fr) - It is the parts of CaCO3 equivalent hardness per lakh (105) parts of water i.e.,

1°Fr = 1 part of CaCO3 equivalent per 105 parts of water.

Relationship -

The soap consuming power of water is known as hardness of water. It is characteristic of water which prevent the lathering of soap. The hardness of water is presence due to several salts (like Ca, Mg) and other heavy metal ions like, Fe^{+2}, Al^{+3} and Mn^{+2} etc. When a sample of hard water is treated with soap then it does not produce lather.

We know that,

We know that,

$$1 \text{ ppm or mg} = 1 \text{ part per } 10,00,000 \text{ parts of water}$$
$$1°Cl = 1 \text{ part per } 70,000 \text{ parts of water}$$
$$1°Fr = 1 \text{ part per } 1,00,000 \text{ parts of water}$$
$$\therefore \quad 10,00,000 \text{ ppm or mg} = 70,000°Cl = 1,00,000°Fr$$
$$100 \text{ ppm} = 7°Cl = 10°Fr$$
$$1 \text{ ppm} = 0.07°Cl = 0.1°Fr$$
$$1°Cl = 14.3 \text{ ppm (app.)} = 1.43°Fr \text{ (app.)}$$
$$1°Fr = 10 \text{ ppm} = 0.7°Cl$$

Following are disadvantages of hard water as given below -

(i) In Domestic Use -

(a) Washing - Hard water, when used for washing purposes, does not lather freely with soap.

(b) Bathing-Hard water does not lather freely with soap solution, but produces sticky scum on the bath-tub and body. Hence, the cleaning quality of soap is depressed and a lot of it is wasted.

(c) Drinking-Hard water causes bad effect on our digestive system. (d) Cooking - Due to the presence of dissolved hardnessproducing salts, the boiling point of water is elevated. Consequently, more fuel and time are needed for cooking.

(ii) In Industrial Use -

(a) Sugar Industry - Water containing sulphates, nitrates, alkali carbonates etc., when used in sugar refining, causes difficulties in the crystallization of sugar. Moreover, the sugar so-produced may be deliquescent.

(b) Paper Industry - Calcium and magnesium salts tends to react with chemical and other materials employed to provide a smooth and glossy (i.e., shining) finish to paper. Moreover, iron salts may even affect the colour of the paper being produced.

(c) Textile Industry - Hard water causes much of the soap to go as waste, because hard water cannot produce good quality of lather Moreover, precipitates of calcium and magnesium soaps adhere to the fabrics. (d) Laundry - Hard water, if used in laundry, causes much of the soap used in washing to go as waste. Iron salts may even cause coloration of the clothes.

(e) Concrete Making - Water containing chlorides and sulphates, if used for concrete making, affects the hydration of cement and the final strength of the hardened concrete.

(iii) In Steam Generation

Q.15. If silica is present in water, what harmful effects it can cause ?(R.G.P.V., Dec. 2014)

Ans. Silica (SiO_2), even present in small quantities, deposits as calcium silicate or magnesium silicate ($MgSiO_3$). These deposits are very difficult to remove.

Q.16. What is the principle of EDTA titration ? Describe briefly the method used for determining hardness by EDTA method. (R.G.P.V., Dec. 2008)

Or

How is hardness of water determined by EDTA method ? Describe. (R.G.P.V., Dec. 2017)

Or

Write short note on EDTA method(R.G.P.V., May 2019)

Or

Discuss chemistry involved in complex metric method of determining hardness of water. (R.G.P.V., June 2013)

Ans. EDTA method is more accurate than the other method. Ethylene diamine tetra-acetic acid (EDTA) has the following structure forms

$$HOOCH_2C \diagdown \atop HOOCH_2C \diagup N-CH_2-CH_2-N \diagup ^{CH_2COOH} \diagdown _{CH_2COOH}$$

Principle - EDTA method is based on the following principle -

(i) Eriochrome black-T (a blue coloured dye) forms wine red coloured unstable complex with calcium and magnesium ions (present in water)

$Ca^{2}+$ + Eriochrome black-T → $Ca^{2}+$ chrome black-T complex

(ii) EDTA (ethylene diamine tetra-acetic acid) takes calcium and magnesium ions from the above unstable complex and forms a colourless stable complex with the regeneration of blue coloured dye (eriochrome black-T).

$Ca^{2}+$ chrome black-T complex + EDTA → $Ca^{2}+$ EDTA + Eriochrome black 1

Hence the amount of used EDTA corresponds the hardness of water, the end point of the titration will be change of colour from wine red to blue. Method - The important steps of the method are as given below -

(i) Preparation of Standard Water - Dissolve 1.0 of pure, dry CaCO3 in minimum quantity of dilute HCl and then evaporate the solution to dryness on a water bath. Dissolve the residue in distilled water to make 1 litre solution. Each ml of this solution thus contains 1 mg of CaCO3 eq. hardness. (ii) Preparation of EDTA Solution - Dissolve 4 g of crystals + 0.1 g $MgCl_2$ in 1 litre of distilled water. pure EDTA

(iii) Preparation of Indicator - Dissolve 0.5 g of Eriochrome blackT in 100 ml of alcohol.

(iv) Preparation of Buffer Solution - Add 67.5 g of NH4Cl to 570 ml of concentrated ammonia solution and then dilute with distilled water to 1 litre. (v) Standardization of EDTA Solution - Rinse and fill the burette with EDTA solution. Pipette out 50 ml of standard hard water in a conical flask. Add 10 to 15 ml of buffer solution and 4 to 5 drops indicator. Titrate with EDTA solution, till wine-red colour changes to clear blue. Let the volume be used V_1 ml.

(vi) Titration of Unknown Hard Water - Titrate 50 ml of water sample just in step (v). Let the volume be used V_2 ml.

(vii) Titration of Permanent Hardness - Take 250 ml of the water sample in a large beaker. Boil it, till the volume is reduced to about 50 ml [when all the bicarbonates are decomposed to insoluble CaCO3 + $Mg(OH)_2$]. Filter, wash the precipitate with distilled water, collecting filtrate and washing in a 250 ml measuring flask. Finally make up the volume to 250 ml with distilled water. Then, titrate 50 ml of boiled water sample just as in step (v). Let the volume be used V3 ml. Titrate 50 ml of boiled water sample just as in step (v). Let the volume be used V3 ml.

Calculations – 50 ml of standard hard water = V_1 ml of EDTA

∴ 50×1 mg of $CaCO_3 = V_1$ ml of EDTA

∴   1 ml of EDTA = $50/V_1$ mg of $CaCO_3$ eq.

Now, 50 ml of given hard water = V_2 ml of EDTA

$$= \frac{V_2 \times 50}{V_1} \text{ mg of } CaCO_3 \text{ eq.}$$

∴   1L (1,000 ml) of given hard water = $1{,}000\ V_2/V_1$ mg of $CaCO_3$ eq.

∴   Total hardness of water = $1{,}000\ V_2/V_1$ mg/L = $1{,}000\ V_2/V_1$ ppm   ...(i)

Now, 50 ml of boiled water = V_3 ml of EDTA

$$= \frac{V_3 \times 50}{V_1} \text{ mg of } CaCO_3 \text{ eq.}$$

∴   1,000 ml (= 1L) of boiled water

$$= 1{,}000\ V_3/V_1 \text{ mg of } CaCO_3 \text{ eq.}$$

∴   Permanent hardness = $1{,}000\ V_3/V_1$ ppm   ...(ii)

and temporary hardness = Total hardness – Permanent hardness

$$= 1{,}000 \left[\frac{V_2}{V_1} - \frac{V_3}{V_1} \right] \text{ppm}$$

$$= \frac{1{,}000\ (V_2 - V_3)}{V_1} \text{ppm} \qquad\qquad\text{...(iii)}$$

Advantages – This method is better than other methods, because of the (i) Greater accuracy (ii) Convenience and (iii) More rapid procedure.

Q.17. Explain the method of determination of mixed alkalinity in water. (R.G.P.V., Dec. 2010)

Ans. The alkalinity of treated water or natural water is normally due to the c presence of bicarbonate, carbonate and hydroxide compounds of calcium, magnesium, sodium and potassium. Borates, phosphates and silicates etc., 1 compounds also contribute to alkalinity. It is customary to calculate the hydroxide, (carbonate and bicarbonate alkalinities from the titre values with a standard acid.

In alkalinity titrations of water phenolphthalein and methyl orange indicators are commonly used.

In process of titration take 100 ml of water sample into a clean conical v flask, and add two drops of phenolphthalein indicator. After this process titrate S the sample with standard HCl solution until the pink colour just disappears. Note the titre value as the phenolphthalein end point. After this process add 2-3 drops of methyl orange indicator to the same solution and continue the titration until a sharp colour change from yellow to red. Note the total titre value from the beginning of the experiment which is taken as methyl orange end point. Standard HCl for phenolphthalein end point.

$$\therefore \quad [P] \text{ mg/L} = \frac{\text{Standard HCl for phenolphthalein end point in ml} \times 1 \times 1000}{\text{ml of sample taken for titration}}$$

$$\text{Total alkalinity mg/L} = \frac{\text{Standard HCl used for methyl orange end point in ml} \times 1 \times 1000}{\text{ml of sample taken for titration}}$$

Q.21. Explain various units of hardness of water giving their relationship. Discuss method for determination of alkalinity in given water sample.

Q.18. Give reason -

(i) Alkalinity due to OH and HCO3 ions cannot be present simultaneously in water.

(ii) If Na₂SO4 dissolve in water. It will create the alkalinity in water.(R.G.P.V., Dec. 2012)

Ans.

(i) The possibility of OH and HCO3 together is rules out because of the fact that they combine instantaneously to form CO ions.

OH + HCO3 → CO² + H₂O

i.e., NaOH + NaHCO3 → Na₂CO3 + H₂O

So, OH and HCO3- ions cannot exist together in water.

Thus alkalinity due to OH and HCO3- ions cannot be presen simultaneously in water.

(ii) By alkalinity of water, mean the total content of those substance in it which causes an increased (OH-) upon dissociation or due to hydrolysis So, Na₂SO4 dissolve in water it will create OH- and produce alkalinity in water

UNIT 2

BOILER PROBLEM & SOFTENING METHODS

Q.1. Why is water soften before using in boiler? (R.G.P.V., Dec. 2012)

Ans. Water used for steam generation should be sufficiently pure particularly with respect to hardness), otherwise it would cause boiler problems such as scale and sludge formation, priming and foaming, boiler corrosion, etc. Hence water is properly softened before feeding it to boiler.

Q.2. Discuss scale and sludge formation.

Or

Write a note on scales and sludges.(R.G.P.V., May 2019)

Ans. In a boiler, water is continuously evaporated to form steam. This ncreases the concentration of dissolved salts. Finally a stage is reached when the ionic product of these salts exceeds their solubility product and hence they are thrown out as precipitates.

If the precipitates formed are soft loose and slimy, these are known as sludges; while if the precipitate is hard and adhering on the inner walls, it is called as scale.

Fig. 2.1 Sludge and Scale Formation in Boilers

Sludge - Sludge is a soft, loose and slimy precipitate formed within the boiler. Sludges are formed by substances which have greater solubilities in hot water than in cold water, e.g., $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ etc. If sludges are formed along with scales, then former gets entrapped in the latter and both get deposited as scales.

at Scales - Scales are hard deposits firmly sticking to the inner surfaces the boiler. They are difficult to remove, even with the help of hammer chisel, and are the main source of boiler troubles. Scales may be formed ins the boiler due to decomposition of calcium bicarbonate.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2 \uparrow \downarrow$$

Scale -

This is the main cause of scale formation in low-pressure boilers becau in high-pressure boilers calcium carbonate reacts with water to form solut calcium hydroxide

$$CaCO_3 + H_2O \rightarrow Ca(OH)_2 + CO_2 \uparrow$$

Q.3. What is boiler trouble ? Explain the causes of scale formation,(R.G.P.V., Dec. 2021)

Ans.

Water used for steam generation should be sufficiently pure particularly with respect to hardness), otherwise it would cause boiler problems such as scale and sludge formation, priming and foaming, boiler corrosion, etc. Hence water is properly softened before feeding it to boiler.

In a boiler, water is continuously evaporated to form steam. This ncreases the concentration of dissolved salts. Finally a stage is reached when the ionic product of these salts exceeds their solubility product and hence they are thrown out as precipitates.

If the precipitates formed are soft loose and slimy, these are known as sludges; while if the precipitate is hard and adhering on the inner walls, it is called as scale.
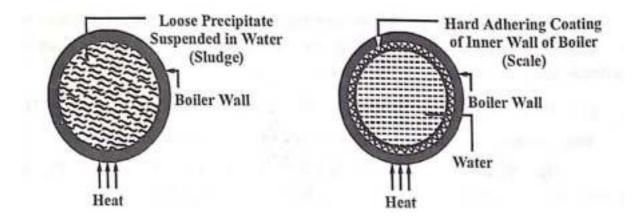

Fig. 3.1 Sludge and Scale Formation in Boilers

Sludge - Sludge is a soft, loose and slimy precipitate formed within the boiler. Sludges are formed by substances which have greater solubilities in hot water than in cold water, e.g., $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ etc. If sludges are formed along with scales, then former gets entrapped in the latter and both get deposited as scales.

at Scales - Scales are hard deposits firmly sticking to the inner surfaces the boiler. They are difficult to remove, even with the help of hammer chisel, and are the main source of boiler troubles. Scales may be formed ins the boiler due to decomposition of calcium bicarbonate.

$$Ca(HCO3)2 \rightarrow CaCO_3 + H_2O + CO_2 \uparrow \downarrow$$

Scale -

This is the main cause of scale formation in low-pressure boilers becau in high-pressure boilers calcium carbonate reacts with water to form solut calcium hydroxide

$$CaCO_3 + H_2O \rightarrow Ca(OH)_2 + CO_2 \uparrow$$

Q.4. What are disadvantages of sludge formation in boiler ?

Ans. Sludge formation has following disadvantages -

(i) They are poor conductors, so wastage of heat generated occu

(ii) If sludges are formed alongwith scales they get entrapped scales and deposits on inner walls of boiler as scale.

(iii) If sludge formation in excess, then it is interferes with t working of boiler.

(iv) Due to choking in pipe excess pressure is generated, whi may cause burst of boiler.

Q.5. How can sludge formation be prevented in boiler?

Ans. Sludge formation can be prevented by applying following methods

(i) By using well softened water in boiler.

(ii) By frequently 'blow-down operation', (i.e., partial removal concentrated water through a tap at the bottom of boiler, when extent hardness in the boiler becomes alarmingly high).

Q.6. Write disadvantages of scale formation. (R.G.P.V., June 201

Ans. Disadvantages of scale formation are as follows -

(i) Wastage of Fuel - Scales have a poor thermal conductivity, the rate of heat transfer from boiler to inside water is greatly reduced.

(ii) Decrease in Efficiency - Deposition of scales in the valves a condensers of the boiler, choke them partially. This results in decrease efficiency of the boiler.

(iii) Lowering of Boiler Safety - Over heating of boiler is to be do in order to maintain a steady supply due to scale formation. This causes distorti of boiler tube and also makes the boiler unsafe to bear the pressure of the steam

(iv) Danger of Explosion - If suddenly high pressure is developed, which may even cause explosion of the boiler.

Q.7. Differentiate between scale and sludge. How are scales formed? What are disadvantages of scales ? (R.G.P.V., June 2010)

Ans. Difference between Scale and Sludge -

S.No.	Scales	Sludges
(i)	Scales are hard deposits.	Sludges are soft loose and slimy precipitate.
(ii)	They stick very firmly to the inner surface of boiler and are very difficult to remove.	They are non-adherent deposits and can be easily removed.
(iii)	Formed by substance like $CaSO_4$, $Mg(OH)_2$ etc.	Formed by substances like $CaCl_2$, $MgCl_2$, $MgSO_4$, $MgCO_3$ etc.
(iv)	Formed generally at heated portions of the boiler.	Formed at comparatively colder portions of the boiler.
(v)	Decrease the efficiency of boiler and chances of explosions are also there.	They decrease the efficiency of boiler but are less dangerous.
(vi)	It cannot be removed by blow-down operations.	It can be removed by blowdown operation.

Q.9. Give the prevention methods of scale formation. Ans. Scales are removed by mechanical methods

(i) If the scales are loosely adhering, it can be removed with the help of scraper or piece of wood or wire brush.

(ii) If the scales are brittle it can be removed by giving therma| shocks. (i.e., heating the boiler and then suddenly cooling with cold water).

(iii) If the scales are loosely adhering, they can also be removed by frequent blow-down operation. Blow-down operation is partial removal of hard water through a 'tap' at the bottom of the boiler, when extent of hardness in the boiler becomes alarmingly high. 'Make-up' water is addition of fresh softened water to boiler after blow-down operation.

(iv) If the scales are adherent and hard, they can be removed by dissolving them by adding chemicals e.g., CaCO3, scales can be dissolved by using 5-10% HCl. Calcium sulphate scales can be removed by adding EDTA, since the Ca-EDTA complex is highly soluble in water.

Q.11. Write notes on the priming and foaming (R.G.P.V., March/April 2010)

Ans. Priming or wet steam is the passage of water particles mixed with steam from the boiler. This generally happens when steam is formed at a great speed in the boiler. Priming is caused by -

(i) The presence of dissolved impurities particularly the suspended ones. The high steam velocities

(iii) Sudden ebullition.

Foaming is the persistent formation of foam or bubbles in the boiler, that can be break easily. Foaming cause the following harmful effects -

(i) Wet steam carries dissolved salts of water with it to the super heater where these are deposited after the evaporation of water. The deposited salts hinder the flow of steam and hence reduce the efficiency.

(ii) A small amount of wet steam may also be carried from the superheater to the turbine blades. Thus, dissolved salts are deposited on the blades which consequently reduce the efficiency of turbine.

(iii) A small portion of wet steam may also enter the steam engine cylinder. Since water is incompressible and unable to escape the cylinder quickly it I may cause serious problems.

Q.12. Discuss the following terms

(i) Blowdown operation

(ii) Carry over. [R.G.P.V., Jan./Feb. 2008, Nov. 2018]

Ans. (i) Blowdown Operation – Blowdown operation is partial removed of hard water through top at the bottom of boiler, when extent of hardness in the boiler becomes alarmingly high. An internal treatment is accomplished by adding a proper chemical to the boiler water either to precipitate the scale forming impurities in the form of sludges, which can be removed by blowdown operation, or to convert them into compounds, which will stay in dissolved form in water and thus do not cause any harm.

(ii) Carry Over - As steam rises from the surface of the boiling water in the boiler, it may be associated with small droplets of water. Such steam, containing liquid water, is called wet steam. These droplets of water naturally carry with them some suspended and dissolved impurities present in the boiler water. This phenomenon of carrying of water by steam along with impurities is called "carry over". This is mainly due to priming and foaming.

Q.13. What is boiler corrosion ? Discuss its causes. (R.G.P.V., Dec. 2013)

Or

Write short note on boiler corrosion. (R.G.P.V., Dec. 2017)

Ans. The process in which decay of boiler material by a chemical or electro-chemical attack by its environment is called boiler corrosion. Main causes for boiler corrosion are as follows -

(i) Dissolved Oxygen - This is the most usual corrosion causing | factor. Water usually contains about 8 ppm of dissolved oxygen at room temperature. Dissolved oxygen reacts with the iron material of boiler in presence of water and under prevailing high temperature to form ferric oxide (rust).

$2 Fe + 2H_2O + O_2 \rightarrow 2 Fe(OH)_2 \downarrow 2 Fe(OH)2 + O_2 \rightarrow Fe_2O3$

(ii) Carbon Dioxide-There are two sources of CO2 in boiler water, viz. dissolved CO_2 in raw water and CO_2 formed by decomposition of bicarbonates in H_2O according to the equation. $CO_2 + H_2O \rightarrow H_2CO3$ CO_2 is also released inside the boiler.

$Mg(HCO3)2 \rightarrow Mg CO3 + H_2O,+ CO_2$

(iii) Acid from Dissolved Salts – Water containing dissolved Mg salt liberates acids on hydrolysis.

$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$

When liberated acid reacts with iron in chain like reaction to produce HO again thus

$Fe + 2HCl \rightarrow FeCl_2 + H_2 \uparrow FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$ Consequently pressure of even a small amount of $MgCl_2$ will caus corrosion of iron to a large extent.

Q.14. Explain boiler corrosion and its prevention. (R.G.P.V., Dec. 2010)

Ans.

1 Prevention of Boiler Corrosion - The corrosion of boiler is preventer by adding a calculated amount of an alkali substance in water for releas; acidity. The concentration of alkali (NaOH) in boiler is maintained by keeping the pH between 8.0 and 9.0. In boiler water also added excess amount o phosphate. Dissolved oxygen eliminate from boiler by adding calculated amoun of Na_2SO4, hydrazine or sodium sulphate. Reactions can be represent as – 1 1

$2Na_2SO3 + O_2 \rightarrow 2Na_2SO4$

$H_2N-NH_2 + O_2 \rightarrow\rightarrow N_2 + 2H_2O$ $Na_2S + 2O_2 \rightarrow Na_2SO4$

The carbondioxide can be removed from the boiler by adding calculated amount of ammonium hydroxide or by mechanical deaeration process along with oxygen. Reaction can be represent as -

$2NH4OH + CO_2 \rightarrow (NH4)2CO3 + H_2O$

Q.15. Write short note on caustic embrittlement (R.G.P.V., June 2007, Dec. 2008, 2013)

Ans. "Caustic embrittlement is the phenomenon during which boile material becomes brittle due to the accumulation of caustic substances." It is well known fact that slight excess of sodium carbonate is used during the softening of water (lime-soda process) for the complete removal of calcium and magnesium salts in the form of carbonates. Due to evaporation of water in boilers, the concentration of sodium carbonate increases and thus it undergoes hydrolysis to form sodium hydroxide in the boiler.

$Na_2CO3 + H_2O \rightarrow 2NaOH + CO_2$

Q.16. How can caustic embrittlement prevented in boiler?

Ans. The caustic embrittlement can be prevented by the following ways - (i) Sodium phosphate is used in place of sodium carbonate during softening process.

(ii) Sodium sulphate should be used in boiler water. This blocks the hair cracks in the boiler.

(iii) Lignin or Tannin should be added in boiler water which blocks the hair cracks.

Boiler Problem & Softening Methods 37

SOFTENING METHODS (LIME-SODA, ZEOLITE AND IONEXCHANGE METHODS) AND RELATED NUMERICAL PROBLEMS

Q.17. What is softening of water? Why it is essential?

Ans. The water which is used for domestic and industrial purpose is sufficiently pure. It should, therefore, be freed from hardness producing salts before put to use. The process of removing hardness-producing salts from water, is known as softening of water.

Softening of water is a very essential process for hard water, when it is not suitable for domestic as well as industrial use. The hardness of water is responsible for scale formation, sludge formation and also for corrosion of boiler. Thus treated water is softened and then it made suitable for industrial as well as domestic or municipal purpose.

Q.18. How many methods are used for softening of hard water?

Ans. The hardness causing salts can be removed from water by following two methods - external treatment, and internal treatment.

. (i) External Treatment - The external treatment of water is carried out before its entry into the boiler. This treatment prevents boiler problems. It can be done by

(a) Lime soda process

(b) Zeolite process

(c) Ion-exchange process.

All are preventive methods.

(ii) Internal Treatment - The internal treatment of boiler feed water is done by conditioning of water in the boiler itself by the addition of chemicals. This is essentially a corrective method to remove those salts which are not completely removed by external treatment of water softening. The following conditioning methods are used in the internal treatment -

(a) Colloidal conditioning

(b) Phosphate conditioning

(c) Carbonate conditioning

(d) Calgon conditioning.

Q.19. Describe lime-soda process of softening of water giving diagram and reactions involved (R.G.P.V., Sep. 2009)

Ans. Lime-soda Process 8 In this process the soluble calcium and magnesium salts in water are chemically converted into insoluble compounds, by adding calculated amounts of lime [$Ca(OH)_2$] and soda [Na_2CO_3]. In this process, calcium carbonate [$CaCO_3$] and magnesium hydroxide [$Mg(OH)_2$], so precipitated are filtered off.

Chemical Reaction Involved in Lime-soda Process In lime-sodą process various soluble impurities, which are causing hardness, are chemically converted into insoluble precipitate. In this process a suspension of calcium hydroxide and Na_2CO_3 is added to water in calculated quantities, which is based on the concentration of impurities in nature. The various chemical reactions involved in this process, based on above principle are given below. -

(i) Removal of dissolved CO_2 and H_2S

$Ca(OH)2 + CO2 \rightarrow CaCO3 + H_2O$ $Ca(OH)2 + H_2S \rightarrow CaS + 2H_2O$

(ii) Neutralization of free mineral acids $Ca(OH)2 + 2HCl \rightarrow CaCl_2 + 2H_2O$ $Ca(OH)2 + H_2SO4 \rightarrow CaSO4 + 2H_2O$

(iii) Removal of temporary hardness

$Ca(OH)2 + Ca(HCO3)2 \rightarrow 2CaCO3 + 2H_2O$

$2Ca(OH)_2 + Mg(HCO3)2 \rightarrow Mg(OH)2 + 2CaCO3 + 2H_2O$

(iv) Removal of permanent magnesium hardness

$Ca(OH)2 + MgCl_2 \rightarrow Mg(OH)_2 + CaCl_2$ $Ca(OH)2 + MgSO4 \rightarrow Mg(OH)2 + CaSO4$

(v) Removal of dissolved iron and aluminium salts

$Ca(OH)2 + FeSO4 \rightarrow Fe(OH)2 + CaSO4$

$2Fe(OH)2 + H_2O + 0$ $3Ca(OH)2 + Al2(SO4)3 \rightarrow 2Al(OH)3 + 3CaSO4$

Reaction of soda, it removes all the calcium permanent hardness thus,

$Na_2CO3 + CaCl_2 \rightarrow CaCO3 + 2NaCl \rightarrow 2Fe(OH)3$

$Na_2CO3 + CaSO4 \rightarrow CaCO3 + Na2SO4$

Water softened by this process contains considerable quantities of soluble salts like NaCl and Na2SO4 and hence cannot be used in high pressure boiler. Types of Lime-soda Process - The lime-soda process may be broadly classified into two categories.

(i) Cold Lime-soda Process In this type of lime-soda process, mixed calculated quantity of chemicals with water at room temperature (25. 30°C), then precipitate formed is finally divided and which is not settle down and filtered easily.

In this solution we add a small amount of coagulants, which hydrolysed into a gelatinous precipitate of aluminium hydroxide, and the fine precipitate of entraps. In cold lime-soda process sodium aluminate ($NaAlO_2$) used as a coagulants which helps the removal of silica as well as oils if present in water.

The reactions which includes in this process are as follows -

$NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)3$

$Al2(SO4)3 + 3Ca(HCO3)2 \rightarrow 2Al(OH)3 + 3CaSO4 + 6CO_2$

In this process, mostly two types of water softeners used for softening of water which are -

(a) Intermittent type softener

(b) Continuous type softener.

The continuous type softener is given in fig. 2.2.

Method - In this process, raw water and requisite amount of lime, soda and coagulants are feed at room temperature from the top into an inner chamber of vertical circular chamber fitted with a paddle stirrer (see fig. 2.2). Vigorous stirring ensures continuous mixing and thus as the raw water and chemicals flow down, softening of water takes place. The softened water is allowed to come into the outer co-axial chamber. The softened Feed Inlet water rising up passes through a wood-fiber filter whereby traces of sludges are removed. The sludge settles down in the bottom of outer chamber by the time the softened water reaches

up from it is periodically through the sludge outlet. Filtered soft water comes out continuously through the filtered softened water outlet at the top.
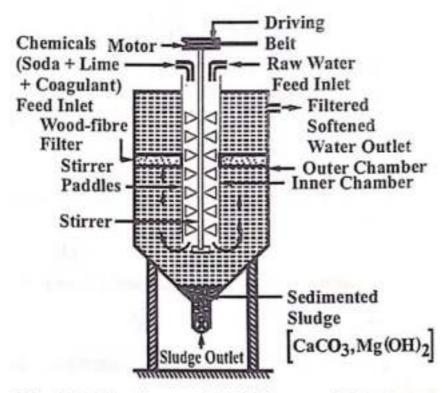

Fig. 2.2 Continuous Cold Lime-soda Softener

Fig. 2.2 Continuous Cold Lime-soda

(ii) Hot Lime-soda Process In this process water is treated with softening chemicals (only Na_2CO_3 is used for softening) at a temperature of 80°C to 150°C. In this process take sodium carbonate in excess into boiler then sodium carbonate is decompose into sodium hydroxide at high pressure and temperature reaction is as follows -

Heat $Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2\uparrow$

The reaction proceeds faster and the softening capacity of hot lime-soda process is increased to many fold.

Sodium carbonate so produced goes into the softener and reacts with non-alkaline hardness of sodium and calcium carbonate.

$Ca(HCO_3)_2 + 2NaOH \rightarrow CaCO_3 + Na_2CO_3 + 2H_2O$

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$

$Mg(HCO_3)_2 + 4NaOH \rightarrow Mg(OH)_2 + 2Na_2CO_3 + 2H_2O$

$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl$

This process is also used for removing silica from water.

Two types of softener used in this process which are intermittent continuous type. Continuous type hot lime-soda softener is shown in fig.
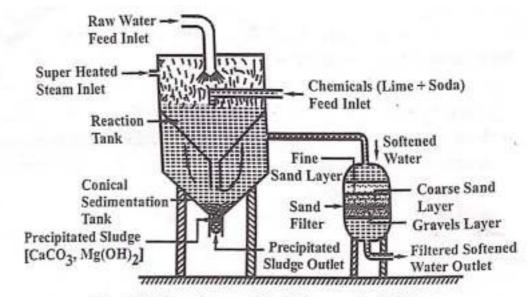

Fig. 2.3 Continuous Hot Lime-soda Softener

Fig. 2.3 Continuous Hot Lime-soda Softener

Q.20. Write short note on lime-soda process.

Or

Write brief note on lime-soda process (R.G.P.V., May 2019)

Ans. Refer to Q.19.

Q.21. Give the chemical reactions involved in lime-soda process of softening of water. (R.G.P.V., Dec. 2008, 2012)

Ans. Refer to Q.19.

Q.22. What are the advantages and disadvantages of lime-soda process?

Ans. The advantages of lime-soda process are as follows -

(i) It is very economical process.

(ii) In this process iron and magnese are also removed from the water.

(iii) In this process, amount of pathogenic bacterias in water is considerably reduced, due to alkaline nature of treated-water.

(iv) It removes not only hardness causing salts but also minerals.

(v) If this process is combined with coagulation, lesser amounts of coagulants that will be needed.

The disadvantages of lime-soda process are as follows -

(i) Careful operation and skilled supervision is required for efficient and economical softening.

(ii) Water which is softened by lime-soda process, contains appreciable concentration of soluble salts, such as sodium sulphate and cannot be used in high pressure of boilers.

(iii) This can remove hardness only upto 15 ppm, which is not good for boilers.

(iv) Disposal of large amounts of sludge posts a problem.

Q.23. Write the equations involved in the lime-soda process. Give the advantages of hot lime-soda process over cold lime-soda process. (R.G.P.V., June 2014)

Ans. Equations Involved in Lime-soda Process - Refer to Q.19.

Advantages of Hot Lime-soda Process Over Cold Lime-soda Process -

(i) Hot lime-soda process is very economical.

(ii) This process is very fast.

(iii) Hot lime-soda process requires no coagulant.

(iv) Hot lime-soda process produces water of comparatively lower residual hardness

Q.24. What are the advantages of hot lime-soda process?

Ans. The hot lime-soda process has following advantages -

(i) In this process the reaction proceeds fast.

(ii) The softening capacity of hot process increased to many fold.

(iii) The precipitate and sludge formed settle down rapidly and hence, no coagulants are needed.

(iv) Hot lime-soda process produces water of comparatively lower residual hardness at 15 to 30 ppm.

Q.25. Explain why presence of silica is not desirable in high pressure boilers. (R.G.P.V., June 2011)

Ans. Because silicates forms the hardest scale. Presence of silica, causes the formation of very firmly sticking deposits of calcium silicate and magnesium silicate scale in the boiler. These scales are very difficult to remove.

Q.26. Distinguish between hard water and soft water.

Ans. Hard water is one which does not produce lather with soap solution readily, but forms a white insoluble scum; while soft water gives lather easily on shaking it with soap solution. Alternatively, hard water contains dissolved f calcium and magnesium salts, while soft water does not contain dissolved calcium and magnesium salts in it.

Q.27. What are zeolites? How softening of hard water is carried out by zeolite process ? Also write advantages and disadvantages of the process.(R.G.P.V., Feb. 2010)

Or

Discuss chemistry involved in zeolite process of softening hard water. (R.G.P.V., Nov/Dec. 2007, Dec. 2011)

Or

Explain the principle and process of zeolite process of softening har (R.G.P.V., June 2013)

Or

Discuss zeolite method of water softening with its limitation.(R.G.P.V., Dec. 2014
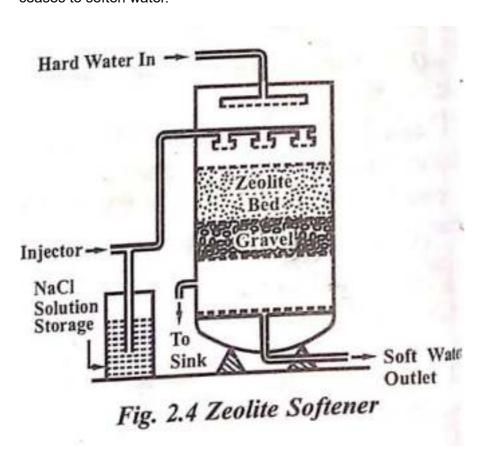
Or

What are zeolites? How do they function in removing the hardness water ?(R.G.P.V., Dec. 2011)

Ans. **Zeolite Process** - In this process the zeolite or permutit is used fo softening of water. In Greek permutit means boiling stone. The permutiti sodium aluminium orthosilicate ($Na_2Al2Si_2O8.xH_2O$ or Na_2Ze) where Ze: $Al_2Si_2O8.xH_2O$. Zeolite have the property of exchanging their sodium ion easily with calcium or magnesium ions when they come in contact with har water. Mostly zeolite are of two types -

(i) Natural Zeolites - This types of zeolites are non-porous amorphous and durable for examples, natrolite $Na_2O.Al_2O3.4SiO2.2H_2O$. (ii) Synthetic Zeolite – This type of zeolites are porous and posses: a gel structure. These zeolite are also possess higher exchange capacity pe unit weight compared to natural zeolites. They are prepared by heating together sodium carbonate (Na_2CO3), alumina (Al_2O3) and $SiO2$.

Method - The zeolite softener consists of a steel tank packed with a thick layer of permutit. The water enters at the top and passes through the bed of zeolite, housed in a cylindrical tank shown in fig. 2.4.

The both process removes temporary as well as permanent hardness. When the permutit is completely converted into calcium or magnesium zeolites then it gets exhausted and it ceases to soften water.

Fig. 2.4 Zeolite Softener

Chemical Reactions Involved in this Process - The water enters at the top and passes through the bed of zeolite where the chemical reactions occur as follows -

$Ca(HCO3)2 + Na_2Ze \rightarrow CaZe + 2NaHCO3$

$Mg(HCO3)2 + Na_2Ze \rightarrow Mg\ Ze + 2NaHCO3$

$CaCl_2 + Na_2Ze \rightarrow CaZe + 2NaCl$

$CaSO4 + Na_2Ze \rightarrow CaZe + Na_2SO4$

$MgSO4 + Na_2Ze \rightarrow MgZe + Na_2SO4$

$MgCl_2 + Na_2Ze \rightarrow MgZe + 2NaCl$

The permutit can be made active by passing 10% solution of sodium chloride or brine solution.

$CaZe + 2NaCl \rightarrow Na_2Ze + CaCl_2$

$MgZe + 2NaCl \rightarrow MgCl_2 + Na_2Ze$

By this process the soluble salts of calcium and magnesium can thus easily be removed. After sometime, the zeolite is completely converted into magnesium and calcium zeolites and it ceases to soften water, i.e., it gets exhausted. At this stage, the supply of hard water is stopped.

Advantages - It has following advantages

(i) This method can produce zero hardness

UNIT 3

LUBRICANTS AND LUBRICATION

Q.1. Define lubricant.

Or

Write short note on lubricants. (R.G.P.V., June 2010)

Ans. Lubricants is defined as "any substance introduced between two moving/sliding surfaces with a view to reduce the frictional resistance between these two is called a lubricant".

In other words "A substance which is capable of reducing the friction between two surfaces which are sliding over each other is known as lubricant".

Q.2. Write the functions of a lubricant. (R.G.P.V., Dec. 2011)(R.G.P.V., Nov./Dec. 2007)

Or

What are the functions of a lubricating oil? (R.G.P.V., June 2010)

Ans. Functions of lubricant are given as follows -

(i) Lubricants avoid direct contact between the rubbing surfaces, reduces surface deformation, wear and tear.

(ii) It acts as a coolant as it reduces loss of energy in the form of heat. (iii) It reduces waste of energy and increases the efficiency of machines. (iv) It reduces maintenance and running cost of the machine. (v) It avoids unsmooth relative motion of the moving or sliding parts. (vi) Sometimes it also act as a seal in internal combustion engines. (vii) It reduces expansion of metal by local frictional heat.

Q.3. Why antioxidants are added to lubricants ? Give examples of also. (R.G.P.V., Dec. 2010)

Ans. Lubricating oils usually contain a small percentage of unsaturat hydrocarbons, which get easily oxidized under operating conditions to fors gummy products of high viscosities. Consequently, antioxidants are added hydrocarbon oils to avoid oxidation of lubricating oils.

Q.4. Define lubrication.

Ans. Lubrication may be defined "any substance introduced between t moving/sliding surfaces with a view to reduce the frictional resistance betwe these two is called a lubricant. When a surface slides over another surface, the (are three basic physical factors which can affect the over all wear between the 1

(i) Distance between the surfaces 1

(ii) Force acting on the surfaces

(iii) Surface texture.

Q.5. What are the different mechanisms of lubrication ? Discu hydrodynamic film lubrication. (R.G.P.V., June 2006, 2007, 2010, 2016)
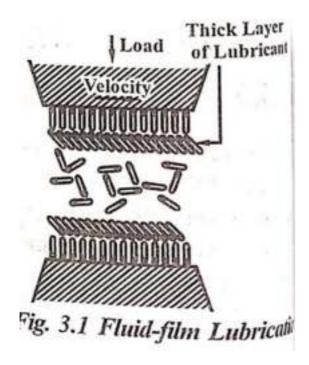
Ans. There are two basic mechanism by which the reduction of friction achieved - 1

(i) Solid Lubrication - In this type of lubrication, the two surfac are coated with a substance (solid). Graphite lowers the coefficient of fricti between the two surfaces as they slide over each other.

(ii) Fluid Lubrication - In this type of lubrication, a fluid film maintained between the two surfaces which keeps them from contact wi each other so that only resistance to motion is due to the stickiness or viscosi of the fluid. This method is widely used.

There are mainly three type of mechanisms by which lubrication is done

(i) Boundary lubrication or thin film lubrication

(ii) Extreme pressure lubrication

(iii) Fluid film or thick film or hydrodynamic lubrication.

Fluid Film or Thick Film or Load Velocity Thick Layer of Lubricant Hydrodynamic Lubrication In this lubrication the moving/sliding surfaces are separated from each other by a thick film of fluid so that direct surface to surface contact and welding of junctions rarely occurs. The resistance to movement of sliding or moving parts is only due to the internal resistance between the particles of the lubricant moving over each other. Therefore, the lubricant chosen should have minimum viscosity under Fig. 3.1 Fluid-film Lubrication working conditions and at the same time, it should remain in place and separate the surfaces (see fig. 3.1).

Fig. 3.1 Fluid-film Lubrication

Hydrodynamic friction occurs in the case of a shaft running at a fair speed as well as in well lubricated bearing with not too high load (see fig. 3.2).

Hydrocarbon oils are considered to be satisfactory lubricants for fluid film lubrication. In order to maintain viscosity of the oil in all seasons of year, ordinary hydrocarbon lubricants are blended with selected long chain polymers. Fig. 3.2 Hydrodynamic Lubrication Bearing Lining Rotating Shaft in Floating Lubricant Thick Film of Lubricant
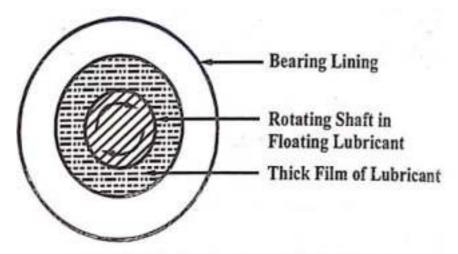
Fig. 3.2 Hydrodynamic Lubrication

Q.6. Define lubrication. Describe hydrodynamic mechanism of lubrication. (R.G.P.V., Dec. 2013)

Or

Define the term lubrication. Explain hydrodynamic lubrication. (R.G.P.V., Dec. 2011)

Ans. Refer to Q.4 and Q.5.

Q.7. Define the terms lubrication and lubricant. Write the functions of lubricant. Discuss the basic principle of lubrication. (R.G.P.V., June 2012)

Ans. Lubrication - Refer to Q.4.

Lubricant-Refer to Q.1.

St Functions of Lubricant - Refer to Q.2.

Basic Principle of Lubrication Principle of Lubrication - There are two basic mechanism by which the reduction of friction is achieved.

(i) Solid Lubrication - Refer to Q.5 (i).

(ii) Fluid Lubrication - Refer to Q.5 (ii).

(iii) Hydrodynamic Lubrication - Refer to Q.5.

Q.8. Discuss the mechanism of boundary lubrication.

Or

Explain the mechanism of thin layer lubrication. (R.G.P.V., Dec. 2010)

Ans. When an oil film is subjected to a high load or viscosity of the oil is too low or speed of the moving parts is very low, the film decreases in thickness to a point where fluid lubricant film breaks down. At this stage, the lubrication is maintained by a boundary film, whose thickness may be as small as two molecules i.e., a monomolecular layer adhering to each moving surface. af Boundary lubrication or thin layer lubrication is shown in fig. 3.3.

The friction force, in presence of boundary film is usually 30-40 times move than under hydrodynamic lubrication. It is independent of the viscosity of the lubricant, and sliding velocity of the contacting surfaces but it directly proportional to the load. The friction force is considerably influenced by the oiliness of the lubricant. For boundary lubrication, the lubricant molecules should have -
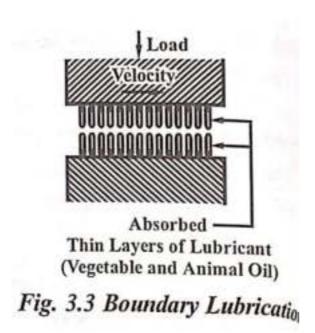
Fig. 3.3 Boundary Lubrication

Fig. 3.3 Boundary Lubrication

(i) Active groups or atoms, which can form chemical linkages wit the metal or other surfaces.

(ii) Good oiliness and low pour point.

(iii) High viscosity index.

(iv) Long hydrocarbon chains.

(v) Lateral attraction between the chains.

(vi) Polar groups to promote spreading and orientation over the metallic surfaces at high pressure.

(vii) Resistance to heat and oxidation.

Q.9. Write a short note on boundary lubrications.[R.G.P.V., Nov. 2018]

Ans. Refer to Q.8.

Q.10. Write a note on extreme pressure lubrication. (R.G.P.V., June 2004, Dec. 2006, 2008, June 2011)

Ans. High local temperature is attained when the moving or siliding surface are under very high speed and pressure, under such conditions, liquid lubricant may vaporize, fail to stick and even decompose. To solve these extreme pressur conditions, some special types of additives are added into mineral oils. Thes are known as extreme pressure additives. These additives are capable to with stand with very high temperatures and loads, and also form on metal surface more durable films. Organic compounds are the important additives which have active radicals or groups like sulphur, phosphorus and chlorine. Thes compounds react with metallic surfaces, at predominent high temperatures to form metallic sulphide,

phosphides and chlorides. These metallic compound possess high melting points and serve as good lubricant under extrem temperature and pressure conditions.

Q.11. Write brief note on mechanism of lubrication.

Ans. Refer to Q.5, Q.8 and Q.10.

Q.12. What are lubricants ? Discuss various theories to explain working of lubricants. (R.G.P.V., May 2018)

Ans. Refer to Q.1, Q.5, Q.8 and Q.10.

Q.13. What are greases ? Discuss various types of greases with uses. (R.G.P.V., June 2010)

Or

What are greases ? Mention their some specific uses.

Or

Write a brief note on greases.

Or

Write note on lubricating greases.(R.G.P.V., Jan./Feb. 2007)

or

What are greases ? Discuss important types of greases. (R.G.P.V., June 2007)

Ans. Semi-solid lubricants or greases are neither bound in the solid state nor in the liquid state at ordinary temperature. The liquid lubricant used may be a petroleum oil or a synthetic oil. However, the nature of soap decides, the temperature upto which the grease can be used, its consistency and its wear and oxidation resistance. Grease have higher shear or frictional resistance than oils and, therefore can support much heavier loads at lower speeds. They also don't require as much attention unlike the lubricating liquids, but grease have a tendency to separate into oils and soaps. For example, greases, vaselins, waxes etc. as follows

Important types of greases can be classified

(i) Cup Grease - They are emulsions of petroleum lubricating oils with water containing calcium oliate or stereate as stabilizer. They are used for general purposes at a temperature below 80°C.

(ii) Soda-base Grease - These are prepared by mixing sodium soaps with petroleum oils and are suitable for use near heat and in differential gears.

(iii) Lithium Soap Greases - They are prepared by mixing lithium soaps with petroleum oils and are suitable for use at low temperature.

(iv) Axle Greases - These are prepared from slaked lime and resin oil with addition of petroleum oil after sometime grease separates out. This grease is water resistant and employed as axle grease.

Uses of Greases - Some specific uses of grease are as follows -

(i) In situations where oil cannot remain in place, due to of high load, low speed, intermittent operation, sudden jerks etc. For example-Rail axle boxes.

(ii) In gears and bearings, that work at high temperatures.

(iii) In sealing of bearings against entry of dirt, dust, grit or moisture.

(iv) In situations where spurting or dripping of oil is undesirable. For example - In machines preparing paper, textile, edible, articles etc.

Q.14. Write a short note on solid lubricants. (R.G.P.V., Dec. 2003, June 2005, Jan./Feb. 2008, March/April 2010)

Ans. Solid lubricant is a material which separate two moving surfaces under boundary conditions and decreases the amount of wear. Solid lubricants are used where -

(i) Operating conditions are such that a lubricating film cannot be secured by use of lubricating oils or greases.

(ii) Contamination of lubricating oil or grease is unacceptable, for example, in commutator bushes of electrical generator and motors.

(iii) The operating temperatures or load is too high, even for a semisolid lubricants to remain in the position.

(iv) Combustible lubricants must be avoided.

Many solid lubricants contain grains of particles which may damage the delicate parts of the machinery. Hence they are used only in special cases like where oil and greases cannot be used in high temperature and high load conditions, aerospace devices and certain other environments under such conditions the solid film lubricants comes handy.

An ideal solid lubricant should have low shear strength, good thermal conductivity, chemical inertness and stability at the operating conditions.

The commonly used solid lubricants are graphite, molybdenum disulphide, talc, mica, french chalk, boron nitride etc. Molybdenum disulphide and graphite are the most widely used solid lubricants as both are having laminar layer lattice structure.

Q.15. Explain with informative note on graphite. (R.G.P.V., June 2013)

Or

Write a note on structure of graphite and its use as a solid lubricant.(R.G.P.V., June 2009)

Ans. Graphite is the most widely used of all solid lubricants. It is very soapy to touch, non-inflammable and resistant to oxidation by air below 375°C. the absence of air, it can be used upto very much higher temperatures. Graphite is used either in powder form or as suspension. Suspension of graphite in oil or water is brought about with the help of an emulsifying agent like tannin. When graphite is dispersed in oil, it is called 'oildag' and when it is dispersed in water, it is called 'aquadag'. 'Aquadag is used where a lubricant free from oil is needed e.g., in food stuff industry.

Graphite consists of a multitude of flat plates, one atom thick, which are held together by only weak bonds, so that the force to shear the crystals parallel to the layers is low. Carbon atom in graphite are arranged in regular hexagons and each atom is linked by covalent bonds to three other atoms but its distance from the forth one is more than double hence this fourth valency bond is not fixed but moves about and hence there is no strong bonding between different layers (see fig. 3.4).
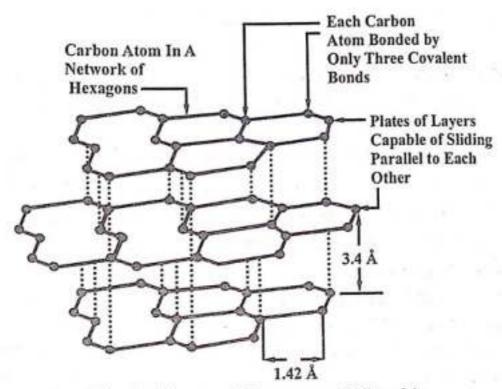

Fig. 3.4 Layered Structure of Graphite

Fig. 3.4 Layered Structure of Graphite

Uses of Graphite - There are many uses of graphite. Some important uses of graphite are as follows -

As a lubricant in air-compressors, lathes, general machine-shop-works, foodstuffs industry, railway track-joints, open gears, chains, cast iron bearings, internal combustion engine etc.

Q.16. Discuss in brief synthetic lubricants. (R.G.P.V., Jan./Feb. 2006)

Ans. Petroleum based lubricants can be used under abnormal conditions like extremely high temperature chemically reactive atmosphere etc., by employing certain specific additives. However synthetic lubricants have been developed which alone can meet the most drastic and sever conditions such as those existing in the aircraft engine, in which the same lubricant may have to be used in the temperature range of 50°C to 250°C. Such a lubricant should possess low freezing point, high viscosity-index and also should be noninflammable. Modern synthetic lubricants possess in general, the following distinguishing characteristics -

(i) They are non-inflammable in nature.

(ii) They have high flash and fire point,

(iii) They have high thermal stability at high operating temperatures.

(iv) They have high viscosity index.

(v) They are chemically stable.

Important synthetic lubricating agents are given as -

(i) Polymerized hydrocarbons.

(ii) Poly-glycol and related compounds.

(iii) Organic amines, imines and amides.

(iv) Silicones.

(v) Fluoro carbons.

Q.17. Define lubricant. Discuss the classification of lubricants. (R.G.P.V., Dec. 2013)

Ans. Lubricant - Refer to Q.1. Classification - Lubricants are classified on the basis of their physical state, main classes are -

(i) Liquid lubricants or lubricating oils

(ii) Semi-solid lubricants or greases

(iii) Solid lubricants.

(i) Liquid Lubricants or Lubricating Oils-Lubricating oils reduces friction between two moving or sliding metallic surfaces by providing a continuous fluid film in between them. Lubricating oils are further classified into animal or vegetable oil and mineral or petroleum oil. Sometimes blended oils are also used.

Besides reducing the friction between two moving surfaces they serve the following purposes also -

(a) Cooling

(b) Sealing agent

(c) Corrosion preventers.

A good lubricating oil must possess following characteristics -

(a) Low vapour pressure

(b) Adequate viscosity for specific operating condition

(c) A low freezing point

(d) Heat stability

(e) High oxidation resistance

(f) Non-ferrous corrosive properties.

They can be further classified into following classes

(a) Vegetable Oils - Vegetables oils are obtained from plants and are used to lubricate delicate apparatus scientific equipments, watches etc. Examples are olive oil, palm oil, castor oil, rapeseed oil etc.

(b) Animal Oils - They are obtained from animal bodies and are used to lubricate sewing machines, gums, and other light machinery. Examples are neat food oil, whale oil, lard oil, tallow oil, hazelnut oil etc.

(c) Mineral Oils - These oils are obtained from residual mass left during crude petroleum distillation and are obtained by further distillation of residue under certain conditions. They are used in lubricating cutting tools, textile machines and with additives in internal combustion engines.

(d) Blended Oils - Mineral oils are mixed with animal or vegetable oils to reduce pour point, improve viscosity, increase oiliness, resist oxidation and reduce corrosion. This mixture of oil is known as blended oils.

(e) Synthetic Oils - They are chemically prepared compounds and are very effective under various conditions.

They are of following types -

(1) Polyethers-Polyethers have good lubricating properties and can withstand high temperature. They are used as lubricant in steel rolling mills, ceramic kiln, vacuum pumps etc.

(2) Diesters - They have good lubricating properties and are stable at high temperature. They are used as lubricant in jet engines.

(3) Silicones - They have remarkable resistance to heat and cold and are used as hydrolic fluids to lubricate furnace doors and electroplating equipment. They can be used under highly corrosive conditions.

(4) Fluorocarbons - They are resistant to heat or chemical attack. They are used in oxygen generating equipment as they do not get corroded with oxygen or with H_2O2 in rocket motors and in atomic energy plants.

(ii) Semi-solid Lubricants or Greases - Refer to Q.13.

(iii) Solid Lubricants - Refer to Q.14.

Q.18. Define the term lubricant. Give classification of lubricants with examples. Write important functions of lubricant.(R.G.P.V., June 2003, Jan./Feb. 2007, Feb. 2010, June 2011)

Ans. Definition of Lubricants and its Functions - Refer to Q.1 and Q.2. Classification - Refer to Q.17.

Q.19. Give two examples of each lubricating oils, greases and solid lubricants. (R.G.P.V., Dec. 2014)

Ans. Lubricating Oils - Vegetables oils, petroleum oils.

Greases - Vaselines, waxes.

Solid Lubricants - Graphite, molybdenum disulphide.

the factors to be considered for selecting a lubricant. (R.G.P.V., Jan./Feb. 2008) Ans. Selection of Lubricants for Some Specific Use - In selecting a lubricant for a particular job, the service conditions and requirement are to be related with the properties of the lubricant. For example, if a lubricant used at a high temperature, undergoes volatilisation of a portion of it, leaving a residual oil, such a mistake should be avoided. Therefore a careful study of various

Q.20. Write properties and their correct interpretation is necessary for the selection of lubricants for a particular job. Selection of a lubricant for a few typical job; are as follows -

(i) Lubricants for Refrigerator System - Oil with low pour-point low viscosity and low cloud-point is needed. So, naphthalene base-oils are preferred

(ii) Lubricants for High Pressure and Low Speed - Like rail axle boxes wire ropes tractor rollers etc., are greases and blended thick oil.

(iii) Lubricants for Gears - Lubricants for gears are subjected to extreme-pressures. So, they should - (a) Possess high resistance to oxidation. (b) To have a high load-carrying capacity.

(c) Possess good oiliness i.e., stick well to the gear teeth. (d) Not to be removed by centrifugal force from the place of application. Consequently, thick mineral lubricating oils containing extreme. pressure additives (like metallic soaps and chlorine sulphur or phosphorus compounds) are employed.

(iv) Lubricants for I.C. Engines - In an I.C. engine, the lubricant is to be exposed to high temperatures. Therefore, the lubricant should possess high viscosity index i.e., low variation of viscosity with temperature) and high thermal stability i.e., it should neither evaporate easily nor decompose at the operating high temperatures.

(v) Lubricant for Very High Pressure and Low-speeds - Such as for tractor, rollers, concrete mixtures, lathes, railway track joints, etc. Under these conditions, solid lubricants like graphite, mica, soapstone etc., are employed either in dry powder form or as emulsion in oil or water.

(vi) Lubricants for Spindle in Textile Industry-For spindle moving at very high speeds thin oils are used. For better results oxidation and rust inhibitors are added to the oils.

(vii) Lubricants for Cutting Tools - Cutting fluids are lubricants used in machining, cutting and grinding of metals. In these operations a metal is continuously removed from the surface and a fresh metal surface, free from any oxide is continuously exposed to the tool used. It is used for two types of cuttings.

(a) For Heavy Cutting - The most effective lubricants are cutting oils. The cutting oils are essentially mineral oils of low viscosities containing additives like fatty oils and chlorinated compounds.

(b) In Light Cuttings - The most effective are oil-emulsions. Oil-emulsions have some what smaller lubricating effects than cutting oils, but they are more efficient as cooling media due to high heat capacity of water, which is present in them as an external phase.

(viii) Lubricants for Transformers - The functions of the lubricating oil in an electrical transformer are to insulate the windings and to carry away the heat generated, when the transformer is on-load. The oil must possess good dielectric properties and because efficient heat transfer depends on ready circulation, it must be of low viscosity. Moreover, transformer oil to some extent is exposed to air. Consequently when the transformer is on-load, such exposure coupled with elevated temperature, electrical stress and catalytic influence of copper, tend to produce chemical changes in the oil, leading to the formation of acids and sludge.

Q.21. What is viscosity?

Ans. Viscosity is the most important property of any lubricating oil, because it determines the main operating characteristics of the lubricants, for example, it is not possible to maintain a liquid oil film between two moving or sliding surfaces if the viscosity of the lubricant is too low and hence excessive wear will occur. Excessive friction will take place, if the viscosity of the lubricant is too high.

Viscosity is the force in dynes required to move one square cm of the liquid over another surface with a velocity of one cm per sec. Its unit is poise.

Q.22. How can you determine viscosity and viscosity index of a thin lubricating oil? (R.G.P.V., June 2007)

Or

Explain with informative note on viscosity and viscosity index.(R.G.P.V., June 2013)

Ans. Viscosity - Refer to Q.21.

Consider two layers of a liquid which are separated by a distance, d and moving with a relative velocity force difference, v then force per unit area. F = nv/d

where, n(eta) = Viscosity coefficient.

= = If v 1 unit (e.g., cm/sec), d 1 unit (e.g., cm) then, F = n, hence viscosity coefficient may be defined as "the force per unit area required to maintain a unit velocity gradient between two parallel layers".

• Viscosity Index - The rate at which the viscosity of an oil changes with temperature is measured by an arbitrary scale known as the viscosity index (V.I.). If the viscosity of lubricating oil falls rapidly as the temperature is raised, it has a low viscosity index.

On the other hand, if viscosity of lubricating oil is only slightly affected on raising the temperature, its viscosity index is high.

Determination of Viscosity Index of Lubricating Oil - For viscosity index determination, we use a series of two types of standards oils. Paraffinic base Pennsylvanian oils (V.I. = 100) and naphthanic-base Gulf oils (V.I. = 0) Against each of these viscosities is marked at 100°F and 210°F. The former: are known as 'H' oils and the latter as 'L' oils.

Step I The viscosities of the oil under test at 100°F and also at 210° are first found out, let these values be 'U' and 'V' respectively. The difference between the two values should be high if the oil is poor and low if the oil is good.

Step II - Now from the list of H-oils (with V.I. = 100), the oil which has the same viscosity at 210°F as the oil under test is selected and its corresponding viscosity at 100°F is read off. Let it be H.

Step III – Then from the list of L-oils (with V.I. = 0), the oil which has same viscosity at 210°F as the oil under test is selected, and its corresponding viscosity at 100°F is read off. Let it be L. Then

L-U V.I. = L-H x 100

where, L= Viscosity at 100°F of the low viscosity standard oil (i.e., Gulf oil) having a V.I. of 0 and also having the same viscosity, at 210°F at the oil under test. U = Viscosity at 100°F of

the oil under test. H = Viscosity at 100°F of the high viscosity standard oil (i.e., Pennsylvanian oil) having a V.I. of 100 and also having the

same viscosity at 210°F as the oil under test.

Q.23. What do you mean by viscosity index? Or Write brief note on viscosity index.(R.G.P.V., Dec. 2012) (R.G.P.V., Dec. 2017)

Or

Write short note on viscosity index.(R.G.P.V., May 2018)

Ans. Refer to Q.22.

Q.24. How would you determine the viscosity of a lubricating oil using Redwood viscometer? (R.G.P.V., Jan./Feb. 2008)

Ans. **Measurement of Viscosity** - The apparatus which is used to measure viscosity of an oil is called viscometer. Mostly viscosity of lubricating oil can be measured by two types of viscometer-Redwood viscometer and Engler's viscometer. Redwood Viscometer - It is of two types - (i) Redwood viscometer No. "1" (ii) Redwood viscometer No. "2". Redwood viscometer No. "1" is commonly used for determining viscositie of thin lubricating oils and is shown in fig. 3.5. Redwood viscometer No. "2"} used for measuring viscosities of highly viscous oils like fuel oil.

In a viscometer, a fixed volume of the liquid is allowed to flow, from a given height, through a standard capillary tube under its own weight and the time of flow in second is noted. The time in seconds is proportional to true viscosity.

The Redwood viscometers consists of a cylinder made of copper or brass. The walls of this oil cylinder are 2-3 mm in thickness. Its diameter is about 5 cm and depth is about 9 cm. At the lower end it is provided with a tapering central hole into which a jet is fixed. The other cylinder or both having a side tube for heating the liquid surrounds it. Oil Heating Tube
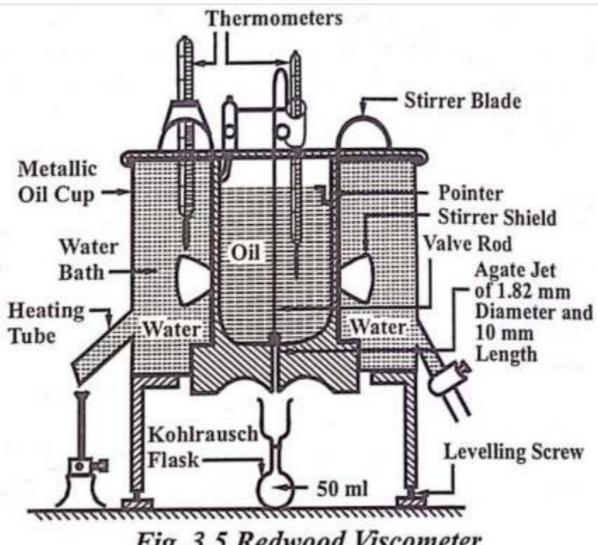
Fig. 3.5 Redwood Viscometer

Fig. 3.5 Redwood Viscometer

The revolving stirrer distributes the heat produced. Thermometer measures the temperature of the bath and the oil. The water contained in the bath can be heated either by heating the side tube by a burner or lamp. A ball present on the jet serves as a valve. A special kind of flask called Kohlrausch flask having a capacity of 50 c.c. is used for receiving the oil from the jet. The oil whose viscosity is desired is filled in the internal cylinder and is heated by heating the water bath when the temperatures become stationary the ball is lifted and 50 ml of the oil is allowed to pass through the jet the time taken is recorded. The viscosity is calculated by the relation

$$V = N \, S_2 D1 \, S_1 D_2$$

D_1 and D_2 are densities (specific gravity) of the standard oil (rapeseed oil) and the experimental oil. S_1 and S_2 are the number of seconds taken by standard oil and the experimental oil.

N = Constant, its value is 1 for water and 100 for rapeseed oil.

Q.25. How would you determine the viscosity of a lubricating oil using Engler's viscometer?

Ans. In this method we measure viscosity of oil at 20°C by measuring the ratio of flow of oil and water from the same aperture. The volume of both the liquids is taken as 200 ml.

Apparatus consists of a vessel of 250 ml volume, in which the oil under test is filled. This vessel is surrounded by a water bath. At the bottom of the vessel there is a agate jet, which is closed with a pin. The whole apparatus is balanced on three screws and can be levelled by adjusting them. Two thermometers, one in oil vessel and other in water bath are fitted. Water bath is also fitted with a stirrer. A specifically designed flask of 250 ml volume is kept below agate jet.
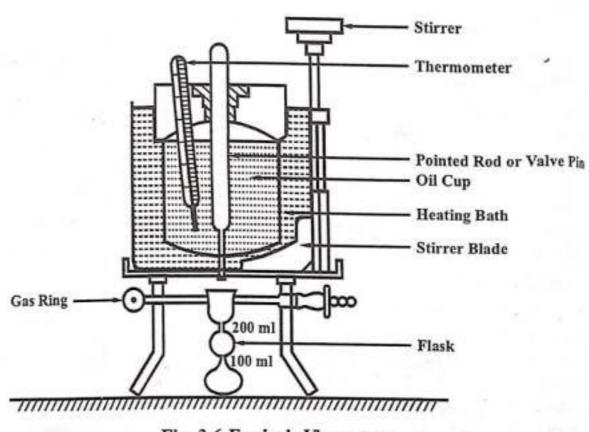

Fig. 3.6 Engler's Viscometer

Fig. 3.6 Engler's Viscometer

Before starting the experiment, level the instrument. Now 250 ml oil, whose viscosity is to be measured is filled in the oil vessel. Temperature is kept at 20°C. At this temperature, we open the agate jet and note down the time of flowing 200 ml of oil. Now, we calculate the flowing time of 200 ml water at 20°C. Viscosity is calculated by calculating the ratio of both the readings. The Engler's viscometer is shown in fig. 3.6.

Q.26. How will you determine the viscosity of lubricating oil by Redwood viscometer? Also differentiate between Redwood viscometer No. 1 and R.W.V. No.2. (R.G.P.V., March/April 2010)

Ans. Determination of Viscosity of Lubricating Oil by Redwood Viscometer - Refer to Q.24.

Differences between Redwood viscometer No.1 and R.W.V. No. 2 are given as follows -

S.No.	R.W.V. No.1	R.W.V. No.2
(i)	It is commonly used for determining viscosities of thin lubricating oil.	It is used for measuring viscosities of highly viscous oils like fuel oil.
(ii)	It has a jet of bore diameter 1.62 mm and length 10 mm.	It has a jet of bore diameter 3.8 mm and length 15 mm.

Q.27. Define flash point and fire point.(R.G.P.V., Jan./Feb. 2007, Dec. 2012)

Ans. "Flash point is the lowest temperature at which the oil lubricant gives off enough vapours that ignite for a moment, when a tiny flame is brought near it", while fire point is the lowest temperature at which the vapours of the oil burns continuously for at least five seconds, when a tiny flame is brought near it.

Q.28. Discuss the method of flash point determination by Abel's apparatus. (R.G.P.V., June 2008)

Ans. Flash point of an oil can be determined by making use of Abel's apparatus as shown in fig. 3.7. The oil to be tested is placed in a small metal cup surrounded by a water bath and then heated slowly on the water bath. The cover of the metal cup is opened from time to time and vapour of oil ignited by a tiny flame introduced momentarily by means of an automobile device. The temperature at which the oil vapours burns with a slight explosion is noted as the flash point.
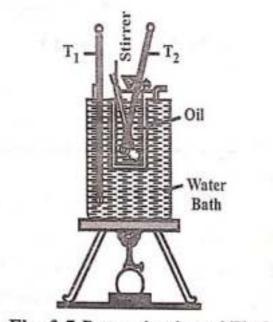
Fig. 3.7 Determination of Flash Point

Fig. 3.7 Determination of Flash Point

Q.29. Define flash point and fire point. Describe the determination of flash point by Pensky-Marten's apparatus. (R.G.P.V., June 2010, 2014)

Or

Discuss flash point determination by Pensky-Marten's apparatus. What is the significance of the test ? (R.G.P.V., Sept. 2009, Feb. 2010)

Or

Discuss the method of determination of flash and fire point of a lubricating oil by Pensky-Martin's apparatus. (R.G.P.V., June 2017)

Ans. For definition of flash point and fire point, refer Q.27.

Flah and fire points of an lubricant is a very important property of a lubricating oil. The oil with low flash and fire points is not safe as it can catch fire. In most cases, the fire points are 5 to 40° higher than the flash points. The

flash and fire points do not have any bearing with the lubricating BurnerOpening properties of the oil, but these Test Oil Flame are important when oil is exposed to high temperature service. A good lubricant should have flash point at least above the temperature at which it is to be used. Air Bath Pilot Burner Oil which is shown in fig. 3.8.
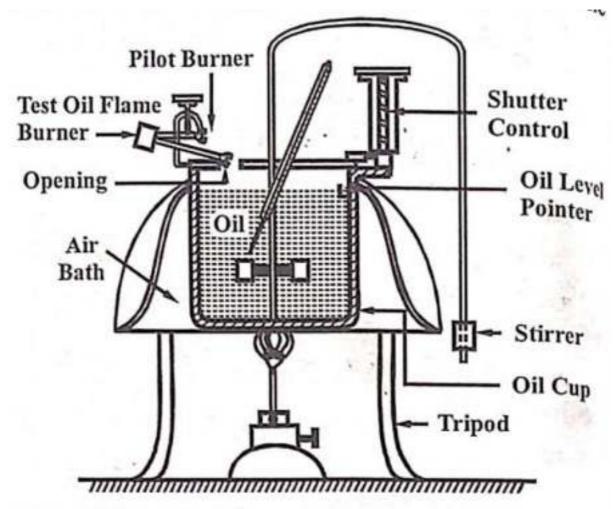
Fig. 3.8 Pensky-Marten's Flash-point Apparatus

Fig. 3.8 Pensky-Marten's Flash-point Apparatus

The Pensky-Marten's apparatus consists of following parts -

(i) Oil Cup - It is about 5 cm in diameter and 5.5 cm deep. The level to which oil is to be filled is marked inside the cup. The cup lid is provided with four openings of standard size through one of these passes a thermometer, while the second opening is used for introducing test flame. Through third opening passes stirrer carrying two brass blades while the fourth is meant for admission of air.

(ii) Shutter - It is a lever mechanism, provided at the top of the cup. By moving the shutter, opening in the lid opens and flame is dipped into this opening, thereby bringing the flame over the oil surface.

(iii) Flame Exposure Device - It is a tiny flame, which is connected to the shutter by a lever mechanism.

(iv) Air Bath - An oil cup is supported by its flange over an air-bath, which is heated by a gas burner.

(v) Pilot Burner – As the test-flame is introduced in the opening, it gets extinguished, but when the test flame is returned to its original position, it is automatically lighted by the pilot burner.

Working - Oil under examination is filled upto the mark in the oil cup and then heated by heating the air bath by a burner. Stirrer is worked between tests at a rate of about 1 to 2 revolutions per second. Heat is used so as to raise the oil temperature by about 5°C per minute. At every 1°C rise of temperature, test flame is introduced for a moment, by working the shutter. The temperature at which a distinct flash appears inside the cup, is recorded as the flash point.

The heating is continued thereafter and the test flame is used as before. When the oil ignites and continues to burn for at least 5 seconds, the temperature reading is recorded as the fire point of the oil.

Q.30. Write short note on flash point.(R.G.P.V., May 2018)

Ans. Refer to Q.29.

Q.31. Write short notes on - -

(i) Flash and fire point

(ii) Viscosity index.

Ans. (i) Flash and Fire Point - Refer to Q.29.

(ii) Viscosity Index - Refer to Q.22.

Q.32. What is lubricant? Discuss following properties of lubricant giving their significance -

(i) Viscosity index(R.G.P.V., Dec. 2015)

(ii) Flash point.(R.G.P.V., May 2019)

Ans. Lubricant - Refer to Q.1. (i) Viscosity Index - Refer to Q.22. (ii) Flash Point - Refer to Q.29.

Q.33. Define lubricant and mention the chief function of a lubricant. Explain flash fire point. (R.G.P.V., June 2013)

Ans. Lubricant and their Chief Function - Refer to Q.1 and Q.2. Flash Fire Point - Refer to Q.29.

Q.34. Define cloud and pour points. (R.G.P.V., June 2010)

Ans. Cloud and pour points indicate the suitability of lubricants in cold conditions. In cold countries this property is very important because if cloud point is high the lubricating oil can freeze inside the machines.

The cloud point is defined as, the temperature at which the oil becomes cloudy or hazy in appearance.

Pour point of a liquid is the temperature at which the liquid ceases to flow on cooling.

A good lubricant must have low pour point, at least lower than the atmospheric or operating temperature.

Q.35. Write the significance of cloud and pour points.(R.G.P.V., June 2010)

Ans. Cloud point is useful for estimating the temperature at which filter screens in the fuel intake system of diesel engines might become clogged because of wax separation. Filterability depends on type of wax, micro crystalline or amorphous. The amorphous wax is sticky in nature and would more easily clog filter screens.

Pour-points indicate the suitability of lubricants in cold conditions. Lubricant used in machine working at low temperature should possess low pour-point, otherwise solidification of lubricant will cause jamming of the machine. Pourpoint values of petroleum and non-petroleum lubricants are significant as many operations must function is sub-freezing conditions.

Q.36. How can you determine cloud and pour point of a lubricating oil?

Ans. When an oil is cooled slowly, the temperature at which it becomes cloudly or hazy in appearance, is called its "cloud point", while the temperature at which the oil ceases to flow or pour, is called its pour point". Cloud and pour points show the suitability of lubricants in cold conditions. Lubricant used in a machine working at a low temperatures should possess low pour point otherwise solidification of lubricant will cause jamming of the machine.

Pour point is determined with the help of pour point apparatus. The apparatus consists of a jar in which oil sample under test is filled. It is closed from the top by a cork, fitted with a thermometer. The jar is surrounded by other jacketed cylinder. At the bottom of the jacket, their fitted a disk of cork. This apparatus is shown in fig. 3.9.
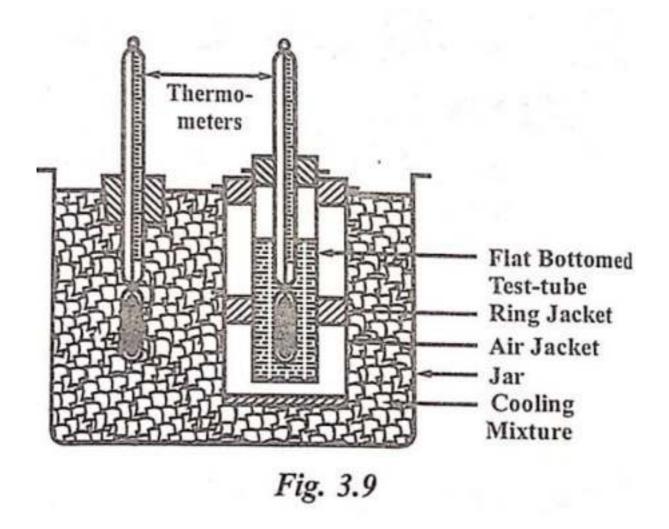
Fig. 3.9

The whole apparatus is surrounded by freezing mixture (ice + $CaCl_2$), contained in a jar. The oil sample present in the cooling bath is cooled till it does not flow on tilting the jar. After every 2° fall in temperature the jar is carefully removed from the cooling bath and tilted gently to see the movement of the oil. The process is continued, till the oil does not show any flow on tilting the jar horizontally for 5 seconds. If the oil shows any movement, the jar is replaced in the jacket again and the process is continued. Till a point is reached when oil shows no movement for 5 seconds. The temperature corresponding to this point is recorded as pour point.

Q.37. What is carbon residue ?

Ans. Lubricating oils contain high percentage of carbon in combined form. On heating, they decompose depositing a certain amount of carbon. The carbon depositing in machine is introlerable, particularly in internal combustion engines and air-compressors. A good lubricant should deposit least amount of carbon in use.

Q.38. How can you determine carbon residue in any lubricating oil? (R.G.P.V., June 2007, March/April 2010, Dec. 2010)

Ans. Carbon residue in lubricating oils is estimated by Conradson's methodIn this method, a weighted quantity of oil is taken in silica crucible. This crucible is covered with skidmore crucible provided with a opening to escape out volatile This matter. combination is placed in a iron crucible covered with chimney shaped iron hood. Heat Iron crucible is heated slowly Insulator for 10 minutes till flame appears and then it is heated strongly for about 15 minutes till the burning of vapours of volatile matter. This apparatus is shown in fig. 3.10. - Bridge (Flame Height Guide) Chimney Lid Hood Skidmore Silica Crucible Asbestos Insulation Meker Burner Fig. 3.10 Conradson's Apparatus

After cooling weight of residue left is determined. Percentage of carbon residue can be calculated by the following formula -

$$\text{Carbon residue} = \frac{\text{Weight of residue left}}{\text{Weight of oil sample taken}} \times 100$$

Q.39. Describe with their significance of the aniline point.

Or

Explain why "A lubricant should have high aniline point". (R.G.P.V., April 2009)

Ans. Aniline point of an oil is defined as "the minimum equilibrium solution temperature for equal volumes of aniline and oil sample". Aniline point of an oil gives an indication of the possible tendency of deterioration of an oil when it comes in contact with packing, rubber sealings etc. Aromatic hydrocarbons have a tendency to dissolve natural rubber and certain types of synthetic rubbers. Consequently, low aromatic content in the lubricants is desirable. A higher aniline point means a higher percentage of paraffinic hydrocarbons and hence, a lower percentage of aromatic hydrocarbons.

Aniline point is determined by mixing equal volume of oil sample and aniline in test tube. Mixture is heated till solution becomes homogeneous, the test tube is allowed to cool. The temperature at which two faces, oil and aniline separate out is recorded as aniline point. A good lubricant should have high aniline point, because low aniline point represent high aromatic content in oil, which can cause deterioration of rubber articles if present in machine. So lubricant with high aniline point is preferred.

Q.40. Discuss following regarding lubricants giving significance -(R.G.P.V., Dec. 2017)

(i) Aniline point (ii) Flash point.

Ans. (i) Aniline Point - Refer to Q.39.

(ii) Flash Point - Refer to Q.29.

Q.41. What is lubrication? Give classification of lubricants with examples. Explain following giving the significance (R.G.P.V., Nov. 2018)

(i) Viscosity index

(ii) Flash point

(iii) Aniline point.

Ans. Lubrication - Refer to Q.4.

Classification of Lubricants - Refer to Q.17.

(i) Viscosity Index - Refer to Q.22.

(ii) Flash Point - Refer to Q.29.

(iii) Aniline Point - Refer to Q.39.

Q.42. Comment on the following -(R.G.P.V., June 2008)

(i) Oils having high viscosity need not necessarily have high viscosity index.

(ii) An ideal lubricant should have low aniline point.

(iii) Closed cup apparatus gives a more reliable flash point than that given by the open cup apparatus.

Ans. (i) Oils having High Viscosity Need not Necessarily have High Viscosity Index - Because if the viscosity of an oil falls rapidly as the temperature is raised, it has a low viscosity index. On the other hand, if viscosity of an oil is only slightly affected on raising temperature its viscosity index is high.

(ii) An Ideal Lubricant Should have Low Aniline Point - No, ideal lubricant should not have low aniline point. Low aniline point represent high aeromatic content in oil, which can cause deterioration of rubber articles if present in machine. So lubricant with high aniline point is preferred.

(iii) Closed Cup Apparatus Gives a More Reliable Flash Point than that Given by the Open Cup Apparatus - Because in open cup apparatus some vapours of oil escapes out so higher temperature is required to form more vapours in open cup apparatus.

But in closed cup apparatus vapours are collected inside the apparatus so flash point appears at a lower temperature. It is more reliable than open cup apparatus.

Q.43. Explain why?

(i) Graphite act as a good lubricant on the surface of moon (R.G.P.V., April 2009)

(ii) Aniline point of a lubricant should be high. (R.G.P.V., April 2009, June 2011)

Ans.

(i) Graphite act as a good Lubricant on the Surface of Moon - Temperature on moon is 110ºC during day time and - 150°C during night. So oil or grease cannot act as a lubricant under these conditions. On the otherhand, a solid lubricant like graphite is very little effected by temperature changes. Hence, graphite acts as a good lubricant on the surface of the moon.

(ii) Aniline point of a Lubricant should be high - Aniline point of an oil is defined as "the minimum equilibrium solution temperature for equal volumes of aniline and oil sample". Aniline point of an oil given an indication of the possible tendency of deterioration of an oil when it comes in contact with packing, rubber scaling etc. A higher aniline point means a higher percentage of paraffinic hydrocarbons and hence, a lower percentage of aromatic hydrocarbons. A good lubricant should have high aniline point. Because low aniline point represent high aromatic content in oil, which can cause deterioration of rubber articles if present in machine. So lubricant with high aniline point is preferred.

Q.44. What do you mean by neutralization number?

Ans. Neutralization number refers to the determination of acidic and basic constituents of an oil. Determination of acidic constituents is referred to as "Acid number or value needed to neutralize the free acids in 1 gm of oil".) Generally free acid are not present in the lubricants, unless refined in faulty manner. A lubricating oil should possess acid value less than 0.1. Value greater than 0.1 shows that oil has been oxidized. This will, consequently, lead to corrosion, besides gum and sludge formation.

Q.45. Explain the determination and significance numbers. of saponification (R.G.P.V., June 2016)

Ans. **Determination of Saponification Number of an Oil** - It is the number of milligrams of KOH needed to saponify 1 gm of oil. By saponification number we can find out the presence and percentage of animal, vegetable oil in the lubricant.

Vegetable or animal oils when treated with KOH hydrolysis takes place and soap and glycerol are formed.

$$
\begin{array}{ll}
CH_2O.CO.C_{17}H_{35} & CH_2OH \\
| & | \\
CHO.CO.C_{17}H_{35} + 3KOH \longrightarrow CHOH + 3C_{17}H_{35}COOK \\
| & | \\
CH_2O.CO.C_{17}H_{35} & CH_2OH \quad\quad Soap \\
\quad\quad Oil & Glycerol
\end{array}
$$

- Take a clean and dry 100 ml conical flask. Using a 2, pipette, transfer 1.5 ml of the oil sample provided in the conical flask. Add 15 m Procedure well of 0.5 N ethanolic KOH into the flask containing the oil. Mix the contents Place a funnel at the neck of the conical flask

and place it in the boiling water bath for half an hour till all the oil globules disappear and a yellow cake formed by potassium salts of fatty acids. After half an hour, take out the conical flask, cool it to room temperature. Add 20 ml of distilled water in the flask, and shake till a clear solution is formed. Now add 1-2 drops of phenolphthalein as an indicator. Titrate with 0.5 NHCl till the colour is changed from red to colourless. Note the titre value. -

Also run a blank titration, without using oil under similar conditions note the titre value. and

Observation – Volume of HCl needed for saponified solution = T ml
Volume of HCl needed for blank titration = B ml
Volume of HCl utilized = (B – T) = Blank test reading value.
According to normality equation
1 ml of 0.5 N HCl = 1 ml of 0.5 N KOH
(B – T) ml of 0.5 N HCL = (B – t) ml of 0.5 N KOH
1 ml of 0.5 N KOH = 28 mg of KOH
(B – T) ml of 0.5 N KOH = 28 (B – T) mg of KOH
Weight of oil = Volume × Density = 1.5 × 0.9 = 1.35 g.
Saponification number of 1.35 g of oil
$$= 28 \times (B - T) \text{ mg of KOH}$$

$$\text{Saponification number of 1 g of oil} = \frac{28 \times (B - T) \text{mg of KOH}}{1.35}$$

Significance - Saponification number is the best available index of the percentage of fat or fatty oil in a product. It measures both free and combined fatty acids. If it is desired to determine the amount of potassium hydroxide which corresponds to the combined acids, it is necessary to subtract from the saponification number the amount of KOH needed to neutralize the free acids originally present in 1 g of the oil. The saponification methods are not applicable to products which contain appreciable quantities of certain non-fatty compounds such as those of sulfur, phosphorus, the halogens, nitrogen and certain metals other than potassium or sodium, which consume alkali or acid under the conditions of the test.

Lubricating Oils - The saponification test is useful for identifying animal or vegetable oils and for determining the amount of these oils in compounded lubricants.

Gear Oils - Saponification number is useful for indicating the percentage of the compounding agent in a gear oil, if the fat or organic acid used in its preparation is known. In general, no relationship between saponification number and corrosion has been established.

Q.46. Write short note on saponification number. (R.G.P.V., March/April 2010, May 2019)

Or

Write short note on saponification value.(R.G.P.V., Dec. 2013)

Ans. Refer to Q.45.

Q.47. Write short note on SEN.(R.G.P.V., Dec. 2008, 2017)

Or

Why should a good lubricating oil possess a low SEN?(R.G.P.V., June 2011, 2014)

Or

Write note on steam emulsification number. (R.G.P.V., Dec. 2008, 2010)

Ans. It is the property of oils to get intimately mixed with water, forming a mixture, called emulsion. Certain oils form emulsions with water easily. Emulsions have a tendency to collect dirt, grit, foreign matter etc., thereby causing abrasion and wearing out of the lubricated parts of the machinery. So, a good lubricating oil should form an emulsion with water, which breaks off quickly. The time in seconds required for two constituents of an emulsion to separate from it is known as steam emulsion number (SEN).

The time in second required for two constituents of an emulsion with water is measured by the number of minute, taken by that liquid to separate itself from water and emulsion under given conditions is known as de-emulsification number. Good lubricant should possess a low SEN.

Q.48. Discuss following properties of lubricants - (i) S.E.N. (ii) Aniline point. (R.G.P.V., May 2018)

Ans. (i) S.E.N. - Refer to Q.47.

(ii) Aniline Point - Refer to Q.39.

Q.49. Define the following terms and explain their significance in case of lubricant oil

(i) Flash point and fire point (ii) Saponification number (iii) S.E.N. (R.G.P.V., June 2012)

Ans. (i) Flash Point and Fire Point - Refer to Q.29. (ii) Saponification Number - Refer to Q.45. (iii) S.E.N. - Refer to Q.47.

Q.50. Define and write the significance of the oiliness. (R.G.P.V., April 2009)

Ans. Oiliness is an important character of lubricant which is a measure o pressure its capacity to stick onto the surfaces of machine parts, under conditions t heavy pressure or load. If a lubricating oil with poor oiliness subjected to hig e then it has a tendency to be sequeezed out of the lubricated machin parts, thereby its lubrication action stops. On the other hand, lubricants, which have good oiliness stay in between the lubricated surfaces, when they subjected to high pressure. ar • l

Oiliness is very important property, particularly for extreme-pressu lubrication. Mineral oils have got very poor oiliness, while vegetable oils ha good oiliness, so in order to improve the oiliness of mineral oils additives lik vegetable oil and fatty acids (such as oleic and stearic acids) are added them. No direct test is available for measuring oiliness. V

Q.51. Define and write the significance of the following - (i) Oiliness (ii) Pour point. [R.G.P.V., Nov. 2018]

Ans. (i) Oiliness - Refer to Q.50.

(ii) Pour Point - Refer to Q.34 and Q.35.

Q.52. Explain the properties of lubricants and discuss their significance

Ans. To make a good choice of lubricant know certain properties lubricating oil i.e., for the use of lubricant one should know the characteristic of lubricant to decide the working conditions. Different lubricants are use according to different operating conditions.

The main properties of lubricants are as follows -

(i) Colour-Colour is the most important factor of a good lubrican which indicates its origin. The colour of lubricating oil vary from almos completely transparent to pitch black with all intermediate shades of yellow red and brown. The colour of on oil depends on its origin, paraffin based oi show greenish tinge while naphthanic based oils are bluish in appearance.

(ii) Specific Gravity - It is very helpful in identifying unknown o as it gives an indication of the type of crude from which the lubricant has bee prepared. Specific gravity is generally expressed in terms of "API (America Petrolium Institute) degree" which is defined as -

$$\text{API gravity} = \frac{141.5}{\text{Specific gravity at room temperature (60 degree F)}} - 1315$$

(iii) Specific Heat - The specific heat of most lubricant oils lies in the range of 0.44 to 0.49. Information on specific heat is required in heat transfer problem such as those pertaining to the design of plain bearings where the lubricating oil functions both as a lubricant and as a coolant.

(iv) Oiliness - Refer to Q.50.

(v) Volatility - When a lubricating oil is used in heavy machinery working at high temperature, a part of oil may be vaporize, leaving behind a residual oil, which have different lubricating properties. If a lubricant is highly volatile it will vapourize even at low temperature and the consumption of lubricant will be more than required. So, a good lubricant should have low volatility. The volatility of an oil is determined by an apparatus, called vaporimeter.

(vi) Cloud and Pour Points - Refer to Q.34 and Q.35. (vii) Carbon Residue - Refer to Q.37.

(viii) Corrosion Stability - Lubricating oils are frequently employed contact with system containing copper and brass. Hence, the corrosive properties of lubricating oils are ascertained by copper corrosion test and steel corrosion test. Corrosive substances like sulphur, H_2S, and polysulphides are found in petroleum and are removed or converted into relatively harmless organic sulphides by refining process. Refinery chemists usually test for sulphur both during refining and in the final products.

(ix) Decomposition Stability - Lubricating oils must be stable to decomposition at the operating temperatures. Oils are usually, broken up by three chemical actions -

(a) Oxidation - It is the main destructive influence encountered. It is usually, partially prevented by adding certain antioxidants, which act as inhibitors.

(b) Hydrolysis - The presence of moisture in the oil causes hydrolysis of such components as esters in the lubricant, releasing alcohols and destructive fatty acids.

(c) Pyrolysis - It is the cracking of petroleum chains, due to the high temperatures found within the engine bearings. Such a reaction is the main cause for the deposition of gummy and carbon sediments within the lubricants. These decomposition results in harmful lubricants contamination.

The harmful effects of contamination of the lubricant by these decomposition processes can be minimized by the use of an efficient system of oil filtration and periodic change of the oil.

(x) Aniline Point - Refer to Q.39.

(xi) Saponification Number - Refer to Q.45.

(xii) Neutralization Number - Refer to Q.44. and

(xiii) Precipitation Number - It is the percentage of asphalt presen in oil. A known weight of lubricant is dissolved in petroleum ether and centrifuged. The precipitated asphalt, if any, is filtered, washed, dried a weighed. Precipitation number is used for differentiating the different classe of lubricants.

(xiv) Drop Point - Drop point is the temperature at which grease passes from the semi-solid to the liquid state. So this temperature determines grease. The apparatus the upper temperature limit of the applicability of the used for determining drop point is called drop point apparatus.

(xv) Viscosity - Refer to Q.21.

(xvi) Viscosity Index - Refer to Q.22.

(xvii) Emulsification - Refer to Q.47.

UNIT 4

POLYMER & POLYMERIZATION

Q.1. What do you mean by polymer? (R.G.P.V., June 2010)

Ans. Polymer is a greek word (poly - many; mers - units or parts) which defined as "A high molecular mass or gaint molecule formed by linking together of large number of small molecules is called polymer". The small units of molecules which participates in the formation of polymer is called monomer and this reaction is called polymerization.

For example, polythene is a polymer which is formed by linking together a large number of small units of ethene monomer (C_2H4).

$$nCH_2 = CH_2 \xrightarrow{\text{Polymerization}} \{CH_2 - CH_2\}_n$$

$$\text{Ethene} \qquad\qquad \text{Polythene}$$
$$\text{(Monomer)} \qquad\qquad \text{(Polymer)}$$

Q.2. What is polymerization ?

Ans. The chemical reaction in which two or more simple and small (low weight) molecules combined in a regular manner and form a gaint (high weight) molecule is called polymerization reaction.

For example, small molecules of ethylene (monomer) gives polythene in the presence of high temperature and pressure, the polymerization reaction is represent as

$$nCH_2 = CH_2 \xrightarrow[\text{Polymerization}]{\text{High temp./pressure}} \{CH_2 - CH_2\}_n$$

$$\text{Ethylene (Monomer)} \qquad\qquad \text{Polythene (Polymer)}$$

In polymerization reaction, gaint molecule (high weight) formed is called polymer and small molecules (low weight) which are participate in polymerization is called monomer.

Q.3. Explain addition polymerization with two examples. (R.G.P.V., Dec. 2011)

Ans. The polymerization reaction in which the polymer formed by the direct addition of repeated monomer units is called addition polymerization, and the polymer formed is called addition polymer. In this type of polymerization, no molecule is released. For example, polythene, polyvinyl chloride, polypropylene, polystyrene etc.

The formation of polythene may be represented as -

$$nCH_2 = CH_2 \xrightarrow{\text{Polymerization}} +CH_2 - CH_2 \}_n$$
$$\text{Ethylene} \qquad\qquad\qquad \text{Polythene}$$

The formation of polypropylene –

$$nCH_3 - CH = CH_2 \xrightarrow{\text{Polymerization}} \left[CH_2 - \underset{\underset{CH_2}{|}}{C}H\right]_n$$
$$\text{Propylene} \qquad\qquad\qquad \text{Polypropylene}$$

Q.4. Define polymerization. List out various initiators used in addition polymerization. (R.G.P.V., June 2014)

Ans. Refer to Q.2 and Q.3.

Q.5. What are characteristics of polymers ?

Ans. Characteristics of polymers are as follows -

(i) Polymers have low densities, this leads to production of light weight products, hence cost of transportation and general handling are low. (ii) Polymers have low absolute strength and stiffness but their specific strength and specific stiffness values are favourable.

(iii) Polymers have excellent resistance to corrosions.

(iv) Polymers are usually thermal and electrical insulators.

(v) Polymeric materials are easily mouldable even into complex shapes with reproducible dimensions with a minimum fabrication and finishing cost.

(vi) Polymeric materials have the ability to take variety of colours, shades etc.

Q.6. Discuss the relationship between structure and following properties – (R.G.P.V., June 2013)

(i) Crystallinity

(ii) Elasticity

(iii) Polymer strength.

Ans. The degree of crystallinity and elastomeric properties of a polymer can be changed by controlling the length of polymer chains and the extent of branching (or cross-linking). The length and type of polymer chains also affect the strength of the polymer. Strength can be estimated with the help of stress-strain test. As the applied force (i.e., stress) increases, the amount of stretch is a measure of the strain.

Q.7. Write a note on tacticity of polymer.(R.G.P.V., June 2013)

Or

What is meant by tacticity of polymers? Explain. (R.G.P.V., June 2014)

Ans. The orientation of monomeric units in a polymer molecule can take place in an orderly or disorderly fashion with respect to the main chain. The difference in configuration (tacticity) do affect their physical properties.

(i) The head to tail configuration, in which the functional groups are all on the same side of the chain, is called isotactic polymer.

(ii) It the arrangement of functional groups are at random around the main chain, it is called atactic polymer, e.g., polypropylene.

(iii) If the arrangement of side groups is in a alternating fashion, it is called 'syndiotactic' polymer e.g., gutta percha.

Q.8. What is condensation polymerization ? Explain with example. (R.G.P.V., Jan./Feb. 2007)

Or

Explain condensation polymerization with two examples. (R.G.P.V., Dec. 2013)

Ans. The polymerization reaction in which the polymer is formed by the condensation of two or more monomers is called condensation polymerization and the polymer formed is called condensation polymer. In this type of polymerization simple molecules such as NH3, H_2O, R-OH etc., are released.

example, Nylon 6: 6, terylene, bakelite etc.

For The formation of Nylon 6 : 6 is a condensation polymerization reaction, which is formed condensation of hexamethylene diamine and adipic acid may be represented as

Adipic acid   Hexamethylenediamine $-H_2O$

Nylon 66

The formation of terylene may be represented as -

Dimethyl terephthalate   Dimethylene glycol

Terylene

Q.9. What is polymerization ? Explain condensation polymerization with the help of two examples.(R.G.P.V., Dec. 2012)

Ans. Refer to Q.2 and Q.8.

Q.10. Discuss mechanism of addition and condensation polymerization. (R.G.P.V., June,2011)

Or

Explain addition and condensation polymerization with suitable examples and important features.(R.G.P.V., Dec. 2010)

Ans. Depending on the nature of chemical reaction, polymerization is classified into two classes -

(i) Addition Polymerization - Refer to Q.3.

(ii) Condensation Polymerization - Refer to Q.8.

Q.11. Differentiate between addition and condensation polymeri zations with examples.

Ans. The differences between addition and condensation polymerizations are given below -

S.No.	Addition Polymerization	Condensation Polymerization
(i)	Only growth reaction adds repeating units one at a time to the chain.	Any two molecular species present can react.
(ii)	High molecular mass polymer is formed at once.	Polymer molecular mass rises steadily throughout the reaction.
(iii)	Number of units decreases steadily throughout the reaction.	Monomer disappears early in the reaction.
(iv)	Nothing is lost during polymerization.	Small molecules like H_2O, NH_3, HCl, R-OH are lost.
(v)	The monomers generally un-structured compounds.	The monomers generally contains two functional groups.
(vi)	Common examples are poly-ethylene PVC, polypropylene etc.	Common examples are Nylon 6:6, terylene, bakelite etc.

Q.12. What is co-polymerization ?

Ans. Co-polymerization is joint polymerization of two or more monomeric species and it usually leads to high molecular weight compounds. Such copolymers possess some properties advantageous for practical uses. For example, SBR, has good oil and petrol resistance. Polyacrylonitrile and vinyl chloride are soluble only in high boiling solvents.

For example, the formation of butadiene rubber may be represented as

$$n \, CH_2 = CH - CH = CH_2 + n \underset{\text{Styrene (1 part)}}{\overset{\overset{\displaystyle CH = CH_2}{|}}{\bigcirc}}$$

Butadiene (3 parts) $\Big\downarrow$ Styrene (1 part)

Na catalyst

$$\left[CH_2 - CH = CH - CH_2 - CH_2 - \underset{\underset{\bigcirc}{|}}{CH} \right]_n$$

Polybutadiene-co-styrene
or styrene-butadiene rubber (SBR)

Q.13. What are the monomer of butyl rubber? What would be its structure? (R.G.P.V., Dec. 2014)

Ans. Monomer of butyl rubber are isobutene and isoprene.

$$\underset{\text{Isobutene}}{CH_2 = \underset{\underset{CH_3}{|}}{C} - CH_3}, \qquad \underset{\text{Isoprene}}{CH_2 = \underset{\underset{CH_3}{|}}{C} - CH = CH_2}$$

Q.14. Explain why 'all organic molecules do not form polymers'. (R.G.P.V., June 2011)

Ans. A monomer is an organic or inorganic molecule which is at least bifunctional. For example, ethylene is bifunctional (i.e., it has two bonding sites per molecules), so it is capable of polymerizing to form polymer polyethylene. However, organic molecules like C_2H6, C_2H_2C1 etc., are only monofunctional, so they cannot form polymers. Hence, we can say that all organic molecules do not produce polymers.

Q.15. What are chain growth and step growth polymers ?

Ans. In chain growth and step growth polymerization, polymers have been classified according to mode of addition of monomers.

Chain Growth Polymerization - Chain growth polymerization involves a chain reaction successive addition of monomer units takes places and chain grows in length. This reaction requires an initiator like peroxide etc. In the beginning of reaction, a monomer react with an initiator to form an active intermediate. This active intermediate is added to another monomer forming another intermediate. In this way chain propagation continued and chain growth polymer is formed.

$$Peroxides \rightarrow Rad\bullet \qquad \text{Chain Initiating Step}$$

$$Rad \overset{\bullet}{} + CH_2 \overset{\bullet\bullet}{=} CH_2 \rightarrow Rad - CH_2 - \overset{\bullet}{C}H_2 \left] \begin{array}{l} \text{Chain} \\ \text{Propagating} \\ \text{Step} \end{array}\right.$$

$$Rad - CH_2 - \overset{\bullet}{C}H_2 + CH_2 \overset{\bullet\bullet}{=} CH_2 \rightarrow Rad - CH_2 - CH_2 - CH_2 - \overset{\bullet}{C}H_2$$

Reaction is terminated by steps which do not form free radicals an polymer is formed. Common examples of chain growth polymers are polythene, polypropylene, PVC, teflon etc.

Step Growth Polymerization - This type of polymerization occu through a series of condensation reaction of difunctional monomers, whic takes place in several steps. In this process no initiator is required and eac step involves same type of condensation reaction with the elimination of sma molecules like - H_2O, NH3, R-OH, HCl etc.

Since in this process polymers are formed in a stepwise manner, th process is known as step growth polymerization.

$$A + B \xrightarrow{\text{Condense}} A - B$$
$$A - B + A \rightarrow A - B - A$$
$$A - B - A + B \rightarrow A - B - A - B$$

Some common examples of step growth polymers are nylon 6: 6, bakelit dacron etc.

Q.16. What do you understand by polymer ? Write their various type

Ans. Polymer - Refer to Q.1.

Types of Polymers -

Types of Polymers – Polymers are of following types –

    (i) Homopolymers – Polymer which is formed by identical units monomer is called homopolymer and this reaction is called homopolymerization. Th

$$..... - M - M - M - M - \quad ....$$

Homopolymer

·   For example; polythene, PVC etc.

Depending upon the arrangement of side chains on main polymeric cha homopolymers are of three types –

    (a) Isotactic Polymers – In it all the functional groups ɛ present on the same side of chain.

$$- CH_2 - CH - CH_2 - CH - CH_2 - CH - CH_2 - CH - CH_2 -$$
$$\qquad\quad | \qquad\qquad | \qquad\qquad | \qquad\qquad |$$
$$\qquad\quad R \qquad\qquad R \qquad\qquad R \qquad\qquad R$$

    (b) Syndiotactic Polymers – In this type of arrangement si groups are oriented in alternating fashion

$$\qquad\qquad\qquad\qquad R \qquad\qquad\qquad\qquad\qquad R$$
$$\qquad\qquad\qquad\qquad | \qquad\qquad\qquad\qquad\qquad |$$
$$- CH_2 - CH - CH_2 - CH - CH_2 - CH - CH_2 - CH -$$
$$\qquad\quad | \qquad\qquad\qquad\qquad | $$
$$\qquad\quad R \qquad\qquad\qquad\qquad R$$

    (c) Atactic Polymers – In this type of arrangement groups ɛ attached in a random manner on main chain, joined together to form lo chains with side chains or branches of different length.

$$-CH_2-CH-CH_2-CH-CH_2-\overset{\overset{\displaystyle R}{|}}{CH}-CH_2-CH-CH_2-$$
$$\underset{R}{|}\qquad\underset{R}{|}\qquad\qquad\underset{R}{|}$$

(d) Crosslinked or Three Dimensional Polymers – These are the polymers in which monomer units are crosslinked together, to form a three dimensional network. These polymers are hard, rigid and brittle because of three dimensional network. Examples are bakelite, melamine formaldehyde resin etc.

(ii) Co-polymers – Molecules which are builtup of at least two different kinds of monomers are known as co-polymers. The chains of the co-polymer consist of repeating units derived from each monomer. Following are some common types of co-polymers –

(a) Alternating Co-polymers – In such co-polymers, the different repeating units alternate in each chain. It X and Y show two different repeating units, then an alternating co-polymer will be shown as –

$$-XYXYXYXYXYXY-$$

(b) Random Co-polymers – In such co-polymers, the different repeating units are not arranged in a systematic manner but are randomly arranged e.g.,

$$-XYXXXYXYXYYYXXXYX-$$

(c) Block Co-polymers – In such co-polymers, blocks of repeating units of one type alternate with blocks of another type e.g.,

$$-XXYYXXYYXXYYXXYY-$$
$$-XXXXYYYYXXXXYYYY-$$

(d) Graft Co-polymers – In such co-polymers, blocks of one repeating unit are attached or grafted to a backbone of a linear polymer e.g.,

$$-YYYYYYY-$$
$$\quad X\quad X\qquad\qquad X$$
$$\quad X\quad X\qquad\qquad X$$
$$\quad X\quad X\qquad\qquad X$$
$$\quad |\qquad\qquad\qquad -YYYYY-$$
$$\qquad\qquad\qquad\qquad X$$
$$\qquad\qquad\qquad\qquad X$$
$$\qquad\qquad\qquad\qquad |$$

Q.17. Write note on the classification of polymers. (R.G.P.V., Jan./Feb. 2006, March/April 2010)

Ans. Based on the mode of occurrence and chemical nature, the polymeric materials can be classified into several ways as described below -

(i) Natural Polymers - Those polymers which are obtained from natural sources (plant and animals) are known as natural polymers. For example, starch, rubber, cellulose, protein, silk etc.

$$n \, CH_2 = C - CH = CH_2 \longrightarrow \; +CH_2 - C = CH - CH_2 \underset{n}{\rightarrow}$$
$$\underset{\displaystyle CH_3}{|} \qquad\qquad\qquad \underset{\displaystyle CH_3}{|}$$

Isoprene   Natural Rubber

(ii) Synthetic or Organic Polymers - Synthetic polymers are man made polymers. Organic polymers include compounds containing apart from carbon, hydrogen, oxygen, nitrogen, sulphur and helogen atoms. Oxygen nitrogen or sulphur may also be present in the backbone chain or main chain Most common synthetic polymers are -

$$+CH_2 - CH_2\underset{n}{\rightarrow} \qquad +CH_2 - CH\underset{n}{\rightarrow} \qquad +CH_2 - CH\underset{n}{\rightarrow}$$
$$\qquad\qquad\qquad\qquad \underset{\displaystyle C_6H_5}{|} \qquad\qquad \underset{\displaystyle Cl}{|}$$

Polyethylene   Polystyrene   Polyvinyl Chloride

$$-C - NH - (CH_2)_x - NH - C - O - (CH_2)_y - O -$$
$$\underset{\displaystyle O}{\|} \qquad\qquad\qquad\qquad \underset{\displaystyle O}{\|}$$

Polyurethane

(iii) Inorganic Polymers - These are polymers having no carbo atoms. Their chains are composed of different atoms joined by chemical bond while weaker intermolecular forces act between their chains. Polysilicone silicon dioxide etc., are examples of inorganic polymers.

$$\begin{array}{cccc}
& & | & | \\
H \quad H \quad H \quad H & \quad & O & O \\
| \quad | \quad | \quad | & & | & | \\
-Si - Si - Si - Si - & \quad -Si - O - Si - O - \\
| \quad | \quad | \quad | & & | & | \\
H \quad H \quad H \quad H & \quad & O & O \\
& & | & | \\
\end{array}$$

Polysilicones   Silicon Dioxide

(iv) Semi-synthetic Polymers - Chemically modified natur polymers are known as semi-synthetic polymer. Nitrocellulose, cellulose aceta etc., are examples of semi-synthetic polymers. Relies on the physic characteristics, the polymers can be further classified as -

(a) Elastomers and Thermoplastic Polymers - These polyme primarily have long polymer chain. Such polymers when heated, becomes sc and more or less fluid, and then can be moulded into any desired shape. That why they can be remoulded, reshaped and used. Hence, they can be reclaime from wastes. These polymers are usually soluble in suitable solvents.

(b) Thermosetting Polymers - These are made from low mass substances. On heating these polymers become highly molecular crosslinked, thereby forming infusible and insoluble products. These polymers cannot be reprocessed.

0.18. Define the term polymer. Give classification of polymers. Discuss the role of functionality in polymerization. (R.G.P.V., June 2012)

Ans. Polymer - Refer to Q.1.

Classification of Polymers - Refer to Q.17.

Role of Functionality in Polymerization - Functionality is a very useful concept in polymer. Polymerization may occur only if the monomers involved in the reaction have the proper functionalities. The functionality of a molecule is the number of sites it has for bonding to other molecules under the given conditions of the polymerization reaction. Thus a bifunctional monomer, i.e. a with functionality 2, can link to two other molecules under suitable conditions. Styrene, $C_6H_2CH=CH_2$, for example, has functionality 2 because of the presence of a carbon-carbon double bond. The minimum functionality required for polymerization is 2. monomer

A polyfunctional monomer is one that can react with more than two bo molecules under the conditions of the polymerization reaction. Thus divinyl nds benzene is tetra-functional in reactions involving additions across carbonnes carbon double bonds while glycerol is trifunctional in polymerization reactions.

$$HC = CH_2$$
⬡
$$HC = CH_2$$
Divinyl benzene

$$HO - CH_2 - CH - CH_2OH$$
$$|$$
$$OH$$
Glycerol

Q.19. Discuss the classification of polymers on the basis of molecular forces. (R.G.P.V., Dec. 2013)
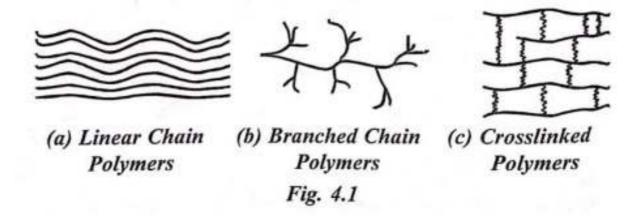
Ans. Depending upon the intermolecular forces the polymers are classified ura into following four types -

(i) Elastomers - The polymers, that have elastic character are called elastomers. In elastomer polymer chains are held together by weakest intermolecular forces. Due to pressure of these weak forces polymers can be easily stretched and regain original shape when stress is removed. Examples are natural and synthetic rubber.

(ii) Fibres These are the polymers, which have strong inter molecular forces between the chains. These forces are either hydrogen bonds or dipole-dipole interaction. For example, nylon 6: 6, decron, silk etc.

(iii) Thermoplastics - These are the polymers which can be eastimat softened repeatedly when heated and hardened when cooled, with little change in properties. The intermolecular forces are in between elastomers and fibre and no crosslinking is found between the chains. For example, polythe polyvinyl chloride, teflon etc.

(iv) Thermosetting Polymers - These are the polymers whic undergo permanent change on heating. They become hard and infusable thermosetti heating. When heated they get highly crosslinked to form hard plastic becomes permanently rigid. For example, bakelite, melamin formaldehyde etc.

Q.20. Give classification of polymers on the basis of structure.

Ans. Polymers are classified into several ways as described below.

(i) Natural and Synthetic Polymer - This classification is bas on the occurrence of polymers.

(a) Natural Polymers - These polymers are found as such nature. Most of them are found in living beings i.e., animals and plants. Examp protein, cellulose etc.

(b) Synthetic Polymers - These polymers are synthesized C men i.e., they do not occur as such in nature. Example, polythene, nylon e

(ii) Linear Branched and Crosslinked Polymers - On the basis structure, polymers can be classified into the following classes

(a) Linear Chain Polymers - The linear polymers are w packed and have high densities, high tensile strength and high melting poin For example, polythene, nylon and polyester etc.

(b) Branched Chain Polymers - These are polymers in whi monomers are joined to form long chains as well as side chains or branch of different lengths. These branches are irregularly packed and the polymers have low tensile strength and high melting point in comparis to linear polymers. For example, low density polythene, glycogen, star etc.

(a) Linear Chain Polymers (b) Branched Chain Polymers (c) Crosslinked Polymers

Fig. 4.1

(c) Crosslinked Polymers - In crosslinked polymers, units are crosslinked together to form a three dimensional network. are hard, rigid and brittle due to network structure. For These polymers monomers melamine formaldehyde resin etc.

(iii) Addition and Condensation Polymers - On the basis of synthesis, the polymers are classified into two classes -

(a) Addition Polymers - Addition polymers are formed by direct addition of repeated monomeric units, without the elimination of any product molecule. Monomers may be in the form of free radicals, cations or For example, formation of polypropylene

$$n\ CH_3 - CH = CH_2 \longrightarrow \left[CH_2 - CH \atop \underset{CH_3}{|} \right]_n$$

Propylene

Polypropylene

(b) Condensation Polymers - A polymer formed by the condensation of two or more than two monomers, with the elimination of simple molecules like water, ammonia, hydrogen chloride etc., is called condensation polymer. For example, Nylon 6:6 is obtained by the condensation of hexamethylene diamine and adipic acid.

$$n \, H_2N-(CH_2)_6-NH_2 + n \, HOOC-(CH_2)_4-COOH$$

Hexamethylene   Adipic Acid
Diamine

$$\xrightarrow[-2n \, H_2O]{\text{Condensation}} \left[NH-(CH_2)_6-NH-\overset{\overset{\displaystyle O}{||}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{||}}{C} \right]_n$$

Nylon 6:6 (A polyamide)

(iv) Elastomers,Thermoplastics and Thermosetting Polymers-Refer to Q.19. Fibres,

Q.21. Write short note on free radical polymerization. (R.G.P.V., June 2004, 2005, March/April 2010)

Or

Explain free radical polymerization with one example. [R.GP.V., Nov. 2018]

Ans. In free radical polymerization, monomer is activated by its transformation into radical by action of light, heat, ionizing radiation or by adding chemicals known as initiators which readily decompose into free radicals. The examples of well known initiators are benzoyl peroxide and azobis iso butyronitrile (AIBN). This mechanism involved following steps

It is considered to involve two reactions. First production of free radical, usually, by the homolytic dissociation of an initiat

(i) Initiation to yield a pair of radicals R*

$$I \rightarrow 2R^*$$

(Initiator) (Free radicals)

The second part of initiation involve the additions of this radical to firs monomer molecule (M) to produce the chain initiating species, M_1^*

$$R^* \quad + \quad M \quad \longrightarrow \quad M_1^{*\cdot}$$

(Free radical) (Monomer molecule) (Chain initiating speci

Thus polymerization of monomer, $CH_2 = CHY$, takes in the form –

$$R^* + CH_2 = CHY \rightarrow R - CH_2 - \overset{\overset{\displaystyle H}{\displaystyle |}}{\underset{\underset{\displaystyle Y}{\displaystyle |}}{C^*}}$$

where, R^* = Initiator radical or a primary radical.

(ii) Propagation - It consists of the growth of M_1^* by successiv additions of large numbers of monomer molecules according to equations -

$$M_1^* + M \rightarrow M_2^*$$
$$M_2^* + M \rightarrow M_3^*$$
$$M_3^* + M \rightarrow M_4^*$$

or in general terms $M_n^* + M \rightarrow M_{n\,+\,1}^*$

(iii) Termination - At some point the propagating polymer changes stops growing and terminates.

(a) By coupling or combination e.g.,

$$-CH_2 - \overset{\overset{\displaystyle H}{\displaystyle |}}{\underset{\underset{\displaystyle Y}{\displaystyle |}}{C^*}} + {}^*\overset{\overset{\displaystyle H}{\displaystyle |}}{\underset{\underset{\displaystyle Y}{\displaystyle |}}{C}} - CH_2 - \xrightarrow{\text{Coupling}} -CH_2 - \overset{\overset{\displaystyle H}{\displaystyle |}}{\underset{\underset{\displaystyle Y}{\displaystyle |}}{C}} - \overset{\overset{\displaystyle H}{\displaystyle |}}{\underset{\underset{\displaystyle Y}{\displaystyle |}}{C}} - CH_2 -$$

(b) By disproportionation in which a hydrogen atom of one radi centre is transferred to another radical centre, which results in the formation two polymer molecules as one saturated and one unsaturated e.g.,

$$-CH_2-\underset{\underset{Y}{|}}{\overset{\overset{H}{|}}{C^*}} + \underset{\underset{Y}{|}}{\overset{\overset{H}{|}}{^*C}}-CH_2- \xrightarrow{\text{Coupling}} -CH_2-\underset{\underset{Y}{|}}{\overset{\overset{H}{|}}{CH}} + \underset{\underset{Y}{|}}{\overset{\overset{H}{|}}{C}}=\overset{\overset{H}{|}}{C}-$$

$$\hspace{6cm}\text{(Saturated)} \quad \text{(Unsaturated)}$$

Q.22. Define polymerization. Explain free radical mechanism of polymerization. (R.G.P.V., Dec. 2013)

Ans. Refer to Q.2 and Q.21.

Q.23. Write a brief account of the classification of polymer and discuss the mechanism of free radical addition with suitable example. (R.G.P.V., June 2013)

Ans. Classification of Polymer - Refer to Q.17. Mechanism of Free Radical Addition Refer to Q.21. -

Q.24. Give the mechanism of addition polymerization.(R.G.P.V., Dec. 2012)

Ans. Mechanism of addition polymerization are of three types -

(i) Free radical polymerization

(ii) Ionic polymerization

(iii) Coordination addition polymerization or Ziegler-Natta polymerization.

(i) Free Radical Polymerization - Refer to Q.21.

(ii) Ionic Polymerization - It is of two types -

(a) Cationic Polymerization - It takeplace in the presence of acids e.g., H_2SO_4, HF or Lewis acids such as $AlCl_3$, $SnCl_4$, BF_3. Cationic catalysts are usually electrophilic reagents which acquire a share in a pair of pi electron from the double bond of the monomer.

Mechanism -

Mechanism – It involves following steps –

(1) Initiation – It initiated by a cation.

$$\underset{\substack{\text{An acid}\\\text{(A cation)}}}{Y^+} + \underset{\underset{X}{|}}{CH_2}=\overset{}{CH} \rightarrow Y-CH_2-\underset{\substack{\underset{X}{|}\\\text{A new cation}\\\text{(Carbocation)}}}{\overset{\oplus}{CH}}$$

(2) Propagation - In propagation the carbocations so form react with another molecule to give a new carbocation and reaction propagates.

$$Y-CH_2-\overset{\oplus}{\underset{X}{CH}}+CH_2=\underset{X}{CH} \rightarrow Y-CH_2-\underset{X}{CH}-CH_2-\overset{\oplus}{\underset{X \text{ A new } X}{CH}}$$

cation
(Carbocation)

$$\xrightarrow[+\text{n } CH_2=CHX]{\text{and so on}} Y \left[CH_2 - \underset{X}{CH} \right]_n CH_2-\overset{\oplus}{\underset{X}{CH}}$$

(3) Termination The reaction is terminated when carbocation come in contact with an anion.

$$Y\left[CH_2 - \underset{X}{CH} \right]_n CH_2-\overset{\oplus}{\underset{X}{CH}} \xrightarrow[\text{(An anion)}]{Z^-} Y\left[CH_2 - \underset{X}{CH} \right]_n CH_2-\underset{X}{CHZ}$$

Polymer

(b) Anionic Polymerization - In this polymerization, the end group of a growing macro molecule possess high activity and good stability. Polymerization process continues till all the available monomers are consumed.

Mechanism -

Mechanism – It involves following steps –

(1) **Initiation** – It is initiated by an anion.

$$Z:+CH_2=\underset{X}{CH} \rightarrow Z-CH_2-\overset{\ominus}{\underset{X}{CH}}:$$

A base
(An anion)

A new anion
(carbanion)

(2) Propagation - Carbanion react with another molecule and a new carbanion is form, which react with another molecule and chain propagates.

$$Z-CH_2-\overset{\ominus}{\underset{X}{CH}}:+CH_2=\underset{X}{CH} \rightarrow Z-CH_2-\underset{X}{CH}-CH_2-\overset{\ominus}{\underset{X}{CH}}:$$

$$\underset{A \atop new \atop anion}{}$$

$$\xrightarrow[+nCH_2=CHX]{and\ so\ on} Z\underbrace{\left[CH_2-\underset{X}{CH}\right]_n}_{Polymer} CH_2-\overset{\ominus}{\underset{X}{CH}}:$$

(3) Termination The chain terminates when carbanion combines with a cation.

$$Z\left[CH_2-\underset{X}{CH}\right]_n CH_2-\overset{\ominus}{\underset{X}{CH}}: \xrightarrow[\text{(A cation)}]{H^+} Z\underbrace{\left[CH_2-\underset{X}{CH}\right]_n CH_2-\underset{X}{CH_2}}_{Polymer}$$

(iii) Coordination Polymerization or Ziegler-Natta Polymerization - Ziegler(1953) and Natta (1955) discovered that in presence of a combination of transition metal halide (like TiCl4 or TiCl3, ZrBr3, TiCh2) with an organo-metallic compounds (like triethyl aluminium, trimethyl aluminium), steriospecific polymerization can be carried out is called coordination polymerization. Mechanism of coordination polymerization is as under

(a) Initiation - In the initiation step, л-cloud of alkene overlaps with an empty orbital of titanium then there is insertion of alkene molecules between the Ti-C bond

$$Cat-R' + CH_2 = CHR \longrightarrow Cat - CH_2.CH(R)\ R'$$
(Complex   (Monomer)
Catalyst)

$$> \overset{|}{\underset{|}{Ti}} - CH_2 - CH_3 \xrightarrow{\overset{CH_2-CH}{\underset{CH_3}{|}}} > Ti \overset{\overset{H\quad H}{\diagdown \diagup}}{\underset{\underset{CH_2}{\underset{|}{CH_3}}}{\overset{C}{\underset{C}{||}}}}\underset{HC\quad CH_3}{}$$

$$\longrightarrow > \overset{|}{\underset{|}{Ti}} - CH_2 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_3$$

(b) Propagation As intramolecular rearrangement again generates a vacant site on titanium, each time one monomer molecular can be added in the same fashion

$$Cat - CH_2 - \underset{\underset{R}{|}}{CH} - R' + nCH_2 = CHR' \rightarrow$$

$$Cat - CH_2 - \underset{\underset{R}{|}}{C} {\left[CH_2 - \underset{\underset{R}{|}}{CH} \right]}_n R'$$

(c) Termination - It can be done by the addition of molecules containing active hydrogen like HX.

$$Cat - CH_2 - CH \overline{} \begin{bmatrix} CH_2 - CH \end{bmatrix}_n R' + HX$$
$$\underset{R}{} \qquad \underset{R}{}$$

$$\longrightarrow Cat - X + CH_3 - CH \begin{bmatrix} CH_2 - CH \end{bmatrix}_n R'$$
$$\underset{R}{} \qquad \underset{R}{}$$

or

$$> Ti \begin{bmatrix} CH_2 - CH \end{bmatrix}_{n+1} CH_2 - CH_3 + HX$$
$$\underset{CH_3}{} \qquad \underset{H}{}$$

$$\longrightarrow > Ti - X + CH_3 - \underset{CH_3}{C} \begin{bmatrix} CH - CH_2 \end{bmatrix}_n CH_2 - CH_3$$
$$\underset{CH_3}{} \qquad \underset{CH_3}{}$$

Q.25. Write mechanism of polymerization. (R.G.P.V., Dec. 2015)

Ans. Refer to Q.24.

Q.26. Explain polymerization. Discuss mechanism of polymerization with suitable examples. (R.G.P.V., Nov. 2018)

Ans. Refer to Q.2 and Q.24.

Q.27. What are polymers? Discuss various types of polymerization processes. (R.G.P.V., May 2018)

Ans. Refer to Q.1 and Q.24.

Q.28. Describe the process of compression moulding. How does it compare with injection moulding ?

Ans. Compression moulding is a method which is used for both thermoplastic and thermosetting resins. The predetermined quantity of plastics ingradients in proper proportion get filled between the two half pieces of mould, which are capable of being moved relative to each other. Heat and pressure are used according to specifications. Thus, in case of injection moulding, it is capable only to thermoplastic resins. On this the moulding plastic

powder is fed into a heated cylinder from where it is injected at a controlled rate into the tightly locked mould by means of screw arrangement or by a piston plunger.

Q.29. Distinguish between the thermoplastic and thermosetting resins. (R.G.P.V., Jan./Feb. 2007, June 2010, 2012)

Or

Differentiate thermoplastic resins from thermosetting resins.(R.G.P.V., Dec. 2010, 2014)

Ans. The difference between thermoplastic and thermosetting polymers are given below

S. No.	Thermoplastic Polymers	Thermosetting Polymers
(i)	They soften on heating readily, because secondary forces between the individual chain can break easily by heat or pressure or both.	They crosslinks and bonds retain their strength on heating and hence, they do not soften on heating. On prolonged heating, however, charring of polymers is caused.
(ii)	These can be reclaimed from wastes.	These cannot be reclaimed from wastes.
(iii)	By reheating to a suitable temperature they can be softened, reshaped and thus reused.	They retain their shape and structure, even on heating. Hence they cannot be reshaped and reused.
(iv)	They are formed by addition polymerization.	They are formed by condensation polymerization.
(v)	They consists of long-chain linear polymers with negligible crosslinks.	They have three-dimensional network structure.
(vi)	These are, usually, soluble in some organic solvents.	These are insoluble in almost all organic solvents due to strong bonds and crosslinks structure.
(vii)	They are, usually, soft, weak and less brittle.	They are usually hard, strong and more brittle.

Q.30. Differentiate between giving examples - (R.G.P.V., Nov./Dec. 2007, Jan./Feb. 2008, April 2009, Dec. 2017)

(i) Thermoplastics and thermosettings

(ii) Addition and condensation polymerisation.

Ans. (i) Thermoplastic and Thermosetting Resins - Refer to Q.29.

(ii) Addition and Condensation Polymerizations - Refer to Q.11.

Q.31. Write short note on biopolymers.

Or

Write explanatory note on bio-polymerization. (R.GP.V., June 2017)

Ans. The polymers present in living matter, animals or plants, are termed as biopolymers. Broadly saying there are four types of biopolymers -

(i) Carbohydrates (Polysaccharides)

(iii) Nucleic acids (Polynucleotides)

(iv) Natural rubber (cis-1, 4-polyisoprene).

Characteristics of Biopolymers - A polymer, for use in medical applications, should be bio-compatible. It should have the following characteristics

(i) Easy sterilization, with no alteration in its properties.

(ii) Purity and reproducibility.

(iii) Biopolymers that are to come in contact with blood and tissues of the body must not destroy cellular elements of blood, enzymes, proteins, produce toxic and allergic reactions, and deplete electrolytes present in the body.

(iv) Optimum physical and chemical properties.

Q.32. Discuss in brief the biodegradable polymer.

Or
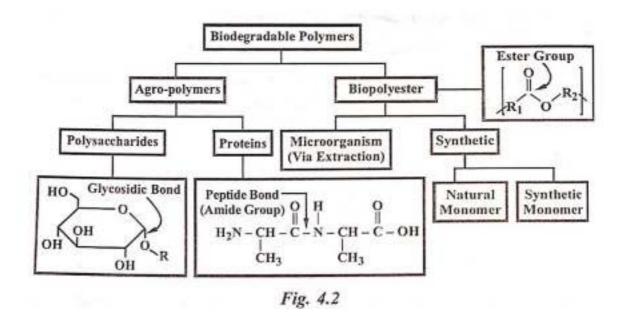
Write brief note on biodegradable polymers. (R.G.P.V., Nov. 2018)

Ans. Biodegradable polymers are specific type of polymers that breaks down after its intended purpose to result in natural bioproducts such as gases (N2, CO_2), biomass, water and inorganic salts. These polymers are found in both naturally and synthetically made, and largely consist of ester, amide and ether functional groups. Their properties and breakdown mechanism are determined by their exact structure. These polymers are often synthesized by condensation reactions, ring opening polymerization and metal catalysts.

Q.33. Give the structure of biodegradable polymers.

Ans. Generally, biodegradable polymers can be grouped into two large groups based on their structure and synthesis.

Fig. 4.2

Q.34. Give the properties and applications of biodegradable polymers.

Ans. Even though biodegradable polymers have numerous applications, there are properties that tend to be common among them. All biodegradable polymers should be stable and durable enough for use in their particular application, but upon disposal they should easily breakdown. Polymers, specifically biodegradable polymers, have extremely strong carbon backbones that are difficult to break, such that degradation often starts from the end groups. Since the degradation begins at the end, a high surface area is common as it allows easy access for either the chemical, light or organism. Biodegradable polymers also tend to have minimal chain branching as this cross linking often decreases the number of end groups per unit weight. Crystallinity is often low as it also inhibits access to end groups. A low degree of polymerization is normally seen, as hinted at above, as doing so allows for more accessible end groups for reaction with the degradation initiator. Another commonality of these polymers is their hydrophillicity. Hydrophobic polymers and end groups will prevent an enzyme from easily interacting if the water-soluble enzyme cannot easily get in contact with the polymer.

Other properties of biodegradable polymers that are common among those used for medicinal usages include -

(i) Non-toxic

(ii) Capable of maintaining good mechanical integrity until degraded

(iii) Capable of controlled rates of degradation.

Applications - Biodegradable polymers are of significant interest to a variety of fields including medicine, agriculture and packaging. One of the most active areas of research in biodegradable polymer is in controlled drug delivery and release.

UNIT 5

PHASE EQUILIBRIUM AND CORROSION

Q.1. Define the following terms (R.GP.V., Dec. 2015)

(i) Component , (ii) Phase , (iii) Degree of freedom.

Or

Define -(R.G.P.V., June 2017)

(i) Phase (ii) Component (iii) Degree of freedom.

Ans.

(i) Component - A component is defined as the "The minimum number of independently variable constituents by means of which the composition of each phase can be expressed either directly or in the form of chemical equation". The number of chemical individuals present in the system cannot be the components of the system. For example,

In the water system

$$\text{Ice} \rightleftharpoons \text{Water} \rightleftharpoons \text{Vapour}$$
$$\text{Solid} \quad \text{liquid} \quad \text{gas}$$

The chemical composition of all three phases is H_2O. Hence, it is one component system.

(ii) Phase Any heterogeneous system consists of two or more homogeneous parts which are separated from each other by bounding surface. This bounding surface is known as phase. The boundary between two phases is called an interface.

For example -

$$CaCO_3 \rightleftharpoons CaO + CO_2$$
$$\text{Phase} \quad \text{I} \qquad \text{II} \qquad \text{III}$$

This system has three phases i.e., solid ($CaCO_3$), solid (CaO), (gas) CO_2. (iii) Degree of Freedom - The factors such as temperature, pressure and composition of phases, which can affect the equilibrium of a systems are known as degree of freedom. Hence, the minimum number of the variable factors must be arbitrarily fixed in order to define the condition of the system completely, is known as degree of freedom of the system, For instance

$$\text{Ice} \rightleftharpoons \text{Water} \rightleftharpoons \text{Vapour}$$
$$\text{(solid)} \qquad \text{(liquid)} \qquad \text{(gas)}$$

The ice-water-vapour system can be in equilibrium only at one certain pressure and temperature. Therefore the system will have no degree of variance or zero varient.

Q.2. What is Gibb's phase rule ? Explain the meaning of the terms involved in it. What are the uses and limitations of phase rule ?

Ans. Phase Rule - Phase rule is an important generalization which finds wide applications in the study of heterogeneous systems. With the help of phase rule the effect of pressure, temperature and composition may be predicted for a heterogenous system in equilibrium. It was first of all put forward by an American Physicst Willard Gibbs and known as Gibb's phase rule, can be written as mathematically,

F = C-P+ 2

or   F+ P = C+2

Where F is the number of degree of freedom, P is the number of phases and C is the number of components for the system. So, according to phase rule, in a heterogeneous system in equilibrium, the number of components plus two is equal the number of degree of freedom plus the number of phases.

Terms Involved in it - Refer to Q.1.

Uses of Phase Rule - The uses of phase rule are as follows -

(i) With the help of terms phases, components and degrees of freedom the phase rule gives a convenient basis for classification of equilibrium state of systems.

(ii) The information about molecular structure is not necessary because it applies to macroscopic systems.

(iii) The phase rule shows that various systems having the same of freedom behave in a similar fashion.

(iv) It helps in deciding whether the given number of substances together would exist in equilibrium under a given set of conditions.

Limitations- The limitations of phase rule are given below -

(i) The phase rule is not applicable to the systems which are slow in reaching to equilibrium state.

(ii) In phase rule, there is no consideration of magnetic and electric influence since system is defined only the variables like pressure temperature and components force.

(iii) It is necessary that all phases must be present under pressure temperature and gravitational force.

(iv) Any liquid or solid present should not be in finally divided state otherwise the value of their vapour pressure will differ from their normal value.

Q.3. State and discuss phase rule and significance of triple point. (R.G.P.V., June 2016)

Ans. Phase Rule - Refer to Q.2.

Significance of Triple Point - A triple point is invariant. The triple point occurs at a unique set of values of the temperature and pressure for a given substance. If either volume or temperature is altered, even slightly, one of the three phases disappears and the system changes from invariant to univariant.

Q.4. Derive the expression F= C-P+ 2.

Or

Describe the derivation of Gibb's phase rule.

Ans. Consider a heterogeneous system consisting of C components distributed in P phases. The degree of freedom of the system is completely defined as the number of variables which must be arbitrarily fixed in order to define the system completely.

Hence, the total number of variable of the system minus the number of variables defined by the system. When a system is in equilibrium there may be only one temperature and one pressure, so these variables will be two in total. Thus the composition of the system is defined by (C-1) composition variables. Since the composition of the remaining components can be defined by difference. Thus for the system of P phases, the total numbers of composition or concentration variables will be P (C-1). Adding the temperature and pressure variables, we have the total number of variables,

$$= P (C-1)+2$$

On the basis of thermodynamic considerations, when a system is in equilibrium, the chemical potential (u) of the given component must be the same in every phase. Suppose the system consists of three phases (a), (b) and (c) in equilibrium at a definite pressure and temperature, then the chemical potential of the given components is same in each phase. If the components are designated by 1, 2, 3 then

$$\mu_1(a) = \mu_1(b)$$
$$\mu_2(a) = \mu_2(b)$$
$$\mu_3(a) = \mu_3(b)$$

and also,
$$\mu_1(a) = \mu_1(b) = \mu_1(c)$$

In general for the system of P phases and C components the fact of the system being in equilibrium may be given by

$$\mu_1(a) = \mu_1(b) = \mu_1(c) = \ldots\ldots = \mu_1(p)$$
$$\mu_2(a) = \mu_2(b) = \mu_2(c) = \ldots\ldots = \mu_2(p)$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$
$$\mu_c(a) = \mu_c(b) = \mu_c(c) = \ldots\ldots = \mu_c(p)$$

Which constitutes C (P-1) independent equations. Since chemical potential is a function of temperature, pressure and concentration, it means that each equation represents one variable of the kind mentioned above.

Hence, the number of unknown variables or degree at freedom will be

$$F = [P\,(C-1)+2] - [C\,(P-1)]$$
$$= PC - P + 2 - CP + C$$
$$F = C - P + 2$$

Which is phase rule as stated by W. Gibbs.

Q.5. Write the difference between phase and state.

Ans. Any homogeneous physically distinct and mechanically separable part of a heterogeneous system in equilibrium is known as phase, these are separated from each other by a boundary.

Physically appearance of a mater under ordinary conditions is its state two solids may form two phases none the less their state in one. Similarly two immiscible liquids form two phases but their state is one.

Q.6. What do you understand by one component three phase system? Give examples.

Or

Apply phase rule on ice-water vapour system.

Or

Draw and explain phase diagram for water system.

Or

Write short note on phase diagram of water. (R.G.P.V., Dec. 2016, June 2017, Nov. 2018)

Or

Write brief note on phase diagram of single component systems. (R.G.P.V., May 2019) (R.G.P.V., June 2016)

Ans. Water System - This is the most common example of the one component system. The water system consists of three phases i.e. ice, water and water vapour.

$$\text{Ice} \rightleftharpoons \text{Water} \rightleftharpoons \text{Vapour}$$
$$\text{(solid)} \quad \text{(liquid)} \quad \text{(gas)}$$

(liquid) (solid) It is single one component system because H_2O is the only chemical compound. When C = 1, the phase rule is as follows -

$$F = C - P + 2$$
$$F = 1 - P + 2$$
$$F = 3 - P$$
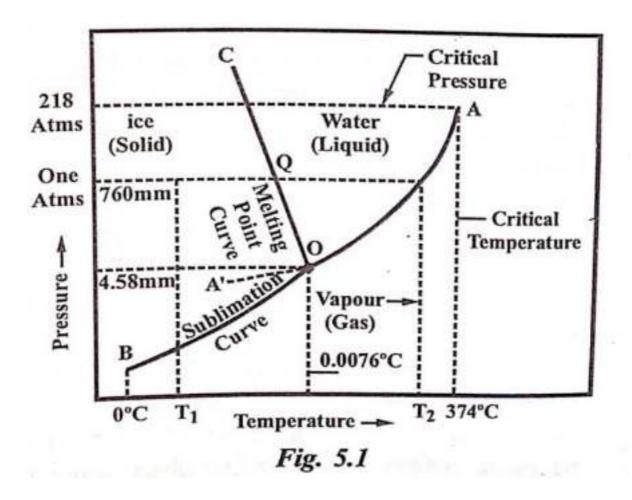
i.e., the degree of freedom based on the number of phases present at equilibrium. The various cases are possible -

(i) P = 1, F = 2 (bivarient system)

(ii) P = 2, F = 1 (univarient system)

(iii) P = 3, F = 0 (invarient system)

The maximum number of degrees of freedom is two for any one component system it is clear from above One cases. Therefore, such a system can be represented completely by a two dimensional diagram. The most convenient variable are the pressure and temperature. The water system is shown diagrammatically.

Fig. 5.1

The important features of the above phase diagram are listed below-

(i) The curve OA, OB, OC

(ii) The triple point O

(iii) The areas AOC, AOB, BOC

These three curves meet at the point O and divide the diagram into three regions.

Vapour Pressure Curve of Water, OA- It represents the vapour pressure of liquid water at different temperature. The two phases, water and water vapours co-exist in equilibrium along this curve. The curve OA terminates at A, the critical temperature (218 Atm. temperature 374°C), when the liquid and vapour are indistinguishable from each other and there is left one phase only.

When the vapour pressure is equal to one atmosphere, the corresponding temperature is the boiling point (100°C) of water.

Sublimation Curve of Ice-OB - It shows the vapour pressure of solid ice at different temperatures.

The two solid phases ice and vapour co-exist in equilibrium along the curve. At the lower limit, the curve OB terminates at absolute zero (-273°C) where no vapour exists.

The Fusion Curve of Ice OC- It depicts the effect of pressure on the melting point of ice. Here ice and water co-exists in equilibrium. The fact that OC slopes to the left indicates that the melting point of ice decreases with increase of pressure. Since the ice melts with decrease of volume so the melting points is lowered by an increase in pressure.

Along the curve OA, OB and OC there are two phases in equilibrium and one component. Therefore,

$$F = C-P+2$$

$$= 1-2 +2 = 1$$

Triple Point 'O' - In water system the point where three phases (water/ ice/vapour) are in equilibrium and curves OA, OB and OC meet from each other as shown in fig. 5.1. This point at 273.16 K (or 0.0075°C) and 4.572 mm pressure is known as triple point. Since three phases are co-exist, the system is invariant.

$$F = C-P + 2$$

$$=1-3+2=0$$

If either temperature or pressure be changed one of the three phases will disappear

Areas AOC, AOB, BOC - The areas or regions between the curves show the conditions of temperature and pressure under which a single phase ice, water of water vapour is capable of stable existence. Thus, Area AOC represents conditions for the one phase water liquid. Area AOB represents conditions for the one phase system water vapour. Area BOC represents conditions for the one phase system ice. In all the three areas, there being one and one component, we have, phase

$$F = C-P+ 2$$

$$= 1-1 + 2 = 2$$

Thus each system, water, water vapour or ice has two degrees of freedom the system is bivarient.

Metastable System, Super Cooled Water Vapour - The vapour pressure curve of water OA' can be continued past the triple point as shown by the dashed line OA'. That is water can be super cooled by carefully eliminating solid particles. The super cooled water vapour system is metastable. It at once reverts to the stable system ice/vapour on the slightest disturbance or introducing a crystal of ice.

Q.7. Explain the following -

(i) Maximum value of degree of freedom in a one component system is two.

(ii) A triple point in the phase diagram of a one component system is an invarient system.

Ans. **(i) Maximum Value of Degree of Freedom in One Component System is Two** - In a one component system like water system, when only one phase is existing under certain conditions then it could be described only by two variable factors which are temperature and pressure. When temperature and pressure are fixed then the volume become automatically constant. This also follows from the phase rule equation -

$$F = C-P+2$$

$$= 1-1+2=2$$

(ii) A Triple Point in the Phase Diagram of One Component System is an Invarient System - In a one component system the three phases are in equilibrium at triple point in phase diagram. If any of the variable like temperature or pressure is changed then one of the phase disappears. Thus at triple point in a one component system the degree of freedom is zero hence the system is termed as a invarient. This also follows from the phase rule equation.

$$F = C-P+2$$

$$F = 1-3 + 2 = 0$$

Q.8. What do you mean by eutectic system? Write its applications.

Ans. **Eutectic System** – An eutectic is a binary system which have two e substances, that are miscible in all proportions in the liquid state, but do not react chemically. For example, mixture of lead and silver.

Eutectic Mixture - It is a solid solution of fixed proportions of two or more substances which have the lowest freezing point. This is taken advantage of in "alloys of low melting point", which are normally eutectic mixtures.

Eutectic Point Point where the freezing point curves intersect each other is known as eutectic point. This point shows a fixed composition of two constitutents. The temperature at this point is called eutectic temperature and composition is called eutectic composition. In other words eutectic means lowest melting point.

Applications of Eutectic -

(i) It is used as safety devices like fire sprinklers, plugs in automobiles.

(ii) For freezing mixtures.

(iii) Very low melting alloys are obtained by suitable choice of metals.

Q.9. What is eutectic ? Describe formation of simple eutectic with general diagram.

Ans. The two components are completely miscible with one another in the liquid state, on solidification, only an intimate mixture of the pure components is called eutectic.

Formation of Simple Eutectic - Assume a general diagram of two component condensed systems belonging to type I.

It have completely miscible components A and B in the liquid phase and their solutions yield only pure A or B as solid states. Fig. 5.2 shows temperaturecomposition curve of this system.

The points A and B are the melting points of pure A and B respectively as shown in the fig. 5.2. The freezing point of A is lowered along AC when increasing quantities of B is added to A. Also, the freezing point of B is lowered along BC when increasing quantities of B

A are added to B.

The freezing point curve of the component A is the AC curve. The curve AC is the composition of the solutions saturated with solid A at temperatures between A and AC. Thus the two phases along this curve are solid A and solution of B in A. The freezing point curve of the component B is the BC curve. The curve BC is the composition of the solution

Temperature - A E Liquid Melt (Unsaturated Solution) C' Solid A + Solution Primary A k C A + B 1 D Composition100% A 0% B Solid B + Solution 1 Primary B t F 100% B 0% A

Fig. 5.2 Simple Eutectic System

saturated with solid B at temperatures between B and BC. Solid B is in equilibrium with solution of A in B along this curve.

These two curves show the two-phase equilibria which are univarient as be seen by applying reduced phase rule equation. can

F = C-P+1 = 2-2 + 1 = 1

Where both solids A and B are in equilibrium with the liquid phase these two curves intersect at the point C. Since there are three phases in equilibrium at this point. It is invarient in character. This can be simply followed from the reduced phase rule equation -

F = C-P+1 = 2-3 + 1 = 0

Hence, the temperature and composition of the solution must remain constant as long as three phases co-exist in equilibrium at this point. At least one of the phases will disappear when any of the two variables is changed. Moreover, as can be seen from the fig. 5.2, the point C is the lowest temperature at which any liquid mixture can exist. The system is completely solidified below this point. Temperature at point C is called eutectic temperature and composition is called eutectic composition point C is known as eutectic point.

As cooling continues till the eutectic temperature is reached, point k is obtained. The temperature now remains constant until all the liquids solidifies. On complete solidification, further decrease in temperature will cause the decrease in temperature of the mixed solids

along the line kl. When the process is done in reverse, that is solid / is heated until it liquefies completely about i the changes take place exactly in the reverse order.

Q.10. Describe silver-copper eutectic phase diagram for binary eutectic system.

Or

Write brief note on phase diagram of Cu-Ag system. (R.G.P.V., Nov. 2018)

Ans. Silver-copper alloys have eutectic phase diagram for binary eutectic system are as follows -

Silver solder is an alloy of silver (Ag) and copper (Cu). Solder is applied as a liquid that solidities to join two solid pieces of metal of without melting the two solid pieces Ag-Cu alloys have the eutectic phase diagram. In this diagram first three single phase regions are a, ß and liquid. The a-phase is a solid solution rich in copper, it has silver as the solute component and an FCC crystal structure. The 3-phase solid solution also has an FCC structure, but copper is the solute. Pure copper and pure silver are also considered to be a and ß phases.

Thus, the solubility in each of these solid phases is limited in that at any temperature below line BEG only a limited concentration of silver will dissolve in copper, and copper in silver similarly for a-phase and ß-phase. The solubility limit for the a-phase corresponds to the boundary line labelled CBA, between the a/(a + B) and a/(a + i) phase regions. It increases with temperature to a maximum at point B and decrease back to zero at the melting temperature of pure copper, point A. At temperature below 779°C the solid, solubility limit line separating the a. and a + ß phase regions is termed a solvus line, the boundary AB between the a. and a + ß phase regions is termed a solvus line. The boundary AB between the a and a + L fields is the solidus line, as shown in fig. 5.3. For the B-phase both solvus and solidus lines also exist Hg and GF, respectively as shown in fig. 5.3.

Fig. 5.3 Ag-Cu Eutectic Phase Diagram

Solubility in each of these solid phases is limited, in that at any temperature below line BEG only a limited concentration at silver will dissolve in copper (for the a-phase), and similarly for copper in silver (for ß-phase). The boundary line CBA is the solubility limit between a/(a + B) and a/(a + L) phase regions, it increases with temperatures to a maximum (8.0 wt% Ag At 779°C at point B and decreases back to zero at the melting temperature of pure copper, point A 1085°C. At temperatures below 779°C, the solid solubility limit line separating a and a + B phase regions is solvus line boundary AB between the a and a + L fields is

solidus line as shown in fig. 5.3. For the p-phase, both solvus and solidus line also exist HG and GF respectively. At 779°C the maximum solubility of copper in the B-phase. On point G (8.8 wt% Cu), also occurs. Horizontal line BGG parallel to the composition axis and extends between these maximum solubility positions may also be considered a solidus line, it represents the lowest temperature at which a liquid phase may exist for Cu-Ag alloy at equilibrium.

In this way three-two phase regions found for the copper-silver system in above fig. 5.3 like a + L, ß + L and a + ß. The a and ß-phase solid solutions co-exist for all compositions and temperatures within the a+ß phase field. a. + liquid and ß+ liquid phases also co-exist in their respective phase regions.

As silver is added to copper, the temperature at which the alloys become totally liquid decreases along the liquidus line, line AE; thus, the melting temperature of copper is lowered by silver additions. The same may be said for silver; the introduction of copper reduces the temperature of complete melting along the other liquidus line, FE. These liquidus lines meet at the point E on the phase diagram, through which also passes the horizontal isotherm line BEG. Point E is called an invariant point, which is designated by the composition CE and temperature TE; for the copper-silver system, the values of CE and TE are 71.9 wt% Ag and 779°C (1434°F), respectively.

An important reaction occurs for an alloy of composition CE as it changes temperature in passing through TE; this reaction may be written as given below -

L(CE) a(CaE) + B(CBE) ...(i)

On cooling, a liquid phase is transformed into the two solid a and B phases at the temperature TE; the opposite reaction occurs upon heating. This is called a eutectic reaction (eutectic means easily method), and CE and TE represent the eutectic composition and temperature, respectively; CaE and CBE are the respective composition of the a and ß phases at T_1. Thus, for the copper-silver system, the eutectic reaction. Equation (i) as written in this way

cooling heating

L(71.9 wt% Ag) = a(8.0 wt% Ag) + 3(91.2 wt% Ag)

Often, the horizontal solidus line at TE is called the eutectic isotherm.

The eutectic reaction, upon cooling, is similar to solidification for pure components in that the reaction proceeds to completion at a constant temperature, or isothermally, at TE. However, the solid product of eutectic solidification is always two solid phases, whereas for a pure component only

a single phase forms. Because of this eutectic reaction, phase diagrams similar to that in fig. 5.3 are termed eutectic phase diagrams; components exhibiting this behaviour comprise a eutectic system.

Q.11. Draw a phase diagram of copper-silver system.(R.G.P.V., Dec. 2015)

Ans. Refer to Q.10.

Q.12. Define corrosion. Write its causes and effects.

Or

What are the consequences of corrosion ? (R.G.P.V., Dec. 2015)

Ans. Corrosion - Any process of deterioration and consequent loss of solid metallic materials through an unwanted chemical or electrochemical attack by its environment starting at its surface, is called corrosion. Thus, corrosion is a process "reverse of extraction of metals". For example, rusting of iron.

Causes - Metals exist in nature in the form of carbonates, sulphides and sulphates. These chemically jointed states of metals known as ore has a low energy and is hence thermodynamically stable state of metal. The metals are extracted from these ores after supplying a enough amount of energy. Metals in the uncombined condition have a higher energy and are in an unstable state. Metals do this interacting chemically or electro-chemically with its environment to form compound at the surface and thus metal undergo corrosion.

Effects The following are the effects of corrosion -

(i) Loss of useful properties of metal.

(ii) Replacement of corroded equipment is time consuming.

(iii) Increase in maintenance and production cost.

(iv) Loss of efficiency.

(v) Contamination of product.

Q.13. Define corrosion of metals. Write factors influencing corrosion and explain any four.

Ans. Corrosion - Refer to Q.12.

Factors Influencing Corrosion - The rate and extent of corrosion,

depends on the following factors -

(i) Temperature

(ii) Humidity

(iii) Effect of pH

(iv) Presence of impurities

(v) Nature of ions present

(vii) Physical state of metal

(vi) Purity of metal

(viii) Nature of surface film.

(i) Temperature - Corrosion increases with temperature because chemical reactions rate and diffusion of ions rate increase with temperature. At a higher temperature passive metal may become active.

(ii) Humidity - Atmospheric corrosion increases in the presence of moisture. This is due to the fact that moisture works as the solvent for the in the air to furnish the electrolyte essential for setting up a corrosion ell. If the relative humidity of air reaches from 60 to 80%, rusting of iron oxygen increase.

(iii) Effect of pH - Generally, acidic media (i.e., pH <7) are more corrosive than alkaline and neutral media. However, atmospheric metals (like Al, Zn, Pb etc.) dissolve in alkaline solution as complex ions. If the pH of oxygen free water is below 5 then corrosion rate of iron is slow. The corresponding corrosion rate in presence of oxygen is much higher. Consequently, corrosion of metals, readily attacked by acids, can be reduced by increasing the pH of the attacking environment e.g., Zn.

(iv) Presence of Impurities - Atmosphere, in the vicinity of industrial areas, contains corrosive gases like CO_2, H_2S, SO_2 and fumes of HCl, H_2SO4 etc. In presence of these gases, the acidity of the liquid, adjacent to the metal surfaces, increases and its electrical conductivity also increases. This consequently, results in an increase of corrosions current flowing in the local electrochemical cells on the exposed metal surfaces.

Q.14. Explain electrochemical theory of corrosion with reference to iron. Discuss process of galvanization to protect iron. (R.G.P.V., May 2019)

Ans. Electrochemical Theory of Corrosion - Electrochemical corrosion, also known as immersed corrosion, occurs under the following two conditions -

(i) When a conducting liquid is in contact with the metal.

(ii) When two different metals or alloys are partially or completely immersed in a solution.

Various theories have been put forward to explain wet or immersed corrosion, but the most widely accepted theory is the electrochemical theory. Since iron metal is the most common which undergoes wet corrosion, the corrosion is explained by taking iron as an example.

According to electrochemical theory, the chemically non-uniform surfaces of metals behave like small electric cells in presence of water containing dissolved oxygen and carbon dioxide. Thus corrosion of a metal in aqueous solution is an electrochemical phenomenon which involves flow of electron current between the anodic and cathodic areas. The anodic reaction involves dissolution of metal as corresponding metal ions with the liberation of free electrons, while the cathodic reaction consumes the electrons, evolved in the anodic reaction, with the evolution of hydrogen or absorption of oxygen, depending upon the nature of corrosive environment. Thus, corrosion takes place as a result of local action.

(a) Evolution of Hydrogen - This type of corrosion generally occurs in acidic environments. Consider the case of iron metal, the anodic

reaction involves dissolution of Fe as Fe2+ ion with the liberation of electrons,

$Fe \rightarrow Fe^{2+} + 2e^-$

H* These electrons flow from anode to cathode through the metal and ions from the acid solution are reduced to hydrogen gas at the cathode.

$2H + 2e \rightarrow H_2$

Thus the overall reaction is

$Fe + 2H+ \rightarrow Fe^{2+} + H_2 \uparrow$ 2+

Thus this type of corrosion causes displacement of hydrogen ions from the acidic solution by metal ions.

(b) Absorption of Oxygen - The most important and common example of this type of corrosion is the rusting of iron. In neutral aqueous solution of electrolytes such as NaCl solution in present of atmospheric oxygen, iron surface is coated with a thin film of oxide. However, if this film of iron oxide develops some cracks, anodic areas are developed on the surface of the exposed iron metal while the rest metal surface forms cathode. Thus here, anodic area is small, while cathodic area is large.

At the anodic area, iron dissolves as ferrous ions with liberation of electrons (oxidation).

The liberated electrons flow from anodic to cathodic areas through the iron metal where electrons are taken up by the dissolved oxygen forming OHions (reduction).

At anode

$Fe \rightarrow Fe^{2+} + 2e^-$ $-O_2 + H_2O + 2e \rightarrow 20H$

At cathode -

The Fe2+ ions at anode and OH-ions at cathode diffuse and combine to form ferrous hydroxide, Fe(OH)2.

$Fe^{2+} + 2OH \rightarrow Fe(OH)2$

In case sufficient amount of oxygen is present, ferrous hydroxide is easily oxidised to ferric hydroxide.

$4Fe(OH)2 + 2H_2O + O_2 \rightarrow 4Fe(OH)3$

This product, called yellow rust, actually corresponds to $Fe_2O3.H_2O$.

In case, limited amount of oxygen is present, the corrosion product is the black anhydrous magnetite. 8:04.

Process of Galvanization - Galvanizing is the process of imparting a auting of zinc or iron or steel to prevent them from rusting. The process is carried out as follows

The iron or sheet article (e.g. sheet, pipe, wire) is first cleaned with dilute sulphuric acid for about 15-20 minutes at 60-90°C. Technically, this process is own as pickling and it also helps in removing any scale, rust (oxide layer) and her impurities present on the base metal. The article is then washed, dried and en dipped in a bath of molten zinc, maintained at 425-430°C. The surface of the uth is covered with a flux to prevent oxide formation. The article coated with the nk layer is then taken out of the bath and passed through a pair of hot rollers which removes any superfluous zinc and thus only a thin layer of zinc is adhered on the article. Finally, it is annealed at a temperature 650°C and then cooled slowly.

Fig. 5.4 Galvanizing of Steel Sheet
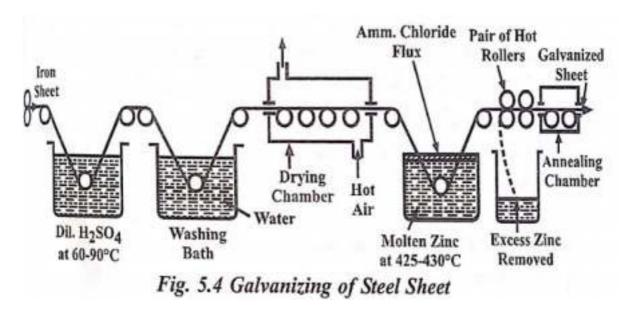
Fig. 5.4 Galvanizing of Steel Sheet

Galvanizing most widely used to protect roofing sheets, wire, pipes, bolts, nails, screws, buckets etc. from atmospheric corrosion. It should be remembered that zinc coated utensils should not be used for storing and cooking foods, especially acidic ones, because zinc dissolves in dilute acids to form highly toxic and even poisonous compounds.

Q.15. Explain electrochemical theory of corrosion.(R.G.P.V., Dec. 2016)

Ans. Refer to Q.14.

Q.16. Discuss various theories to explain corrosion.

Ans. The different theories of corrosion are as follows -

(i) Direct Chemical Attack - This theory is also known as chemical or dry corrosion. Chemical corrosion occurs mainly through the direct chemical action of environment or atmospheric gases like oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen or anhydrous inorganic liquid with metal surfaces in immediate proximity. Chemical corrosion follows adsorption mechanism. Chemical corrosion occurs in the dry state.

For example, chlorine and iodine attack silver generating a protective film of silver halide. Similarly, during de-tinning of tinned low-carbon steel cans using chlorine gas at high temperatures, volatile $SnCl_4$ is formed and so all the tin is readily removed from the metal

surface. However, the base metal iron is very little affected or attached by dry chlorine because if reacts with iron to form solid ferric chloride (non-volatile) which protects the rest of the metal.

(ii) The Electrochemical Theory - Refer to Q.14.

(iii) The Acid Theory - According to this theory, corrosion occurs in presence of an acid. This theory is particularly applicable to rusting of iron in the atmosphere. Rusting of iron is due to the continued action of oxygen, carbon dioxide and moisture, converting the metal into a soluble ferrous bicarbonate which is further oxidised to basic ferric carbonate and finally to hydrated ferric oxide.

$$Fe + 0 + 2CO_2 + H_2O \rightarrow Fe(HCO_3)_2$$

$$2Fe(HCO_3)_2 + H_2O + 0 \rightarrow 2Fe(OH)CO_3 + 2CO_2 + 2H_2O$$

$$2Fe(OH)CO_3 + 2H_2O \rightarrow 2Fe(OH)_3 + 2CO_2$$

This theory is supported by the following facts -

(a) Rust analysis generally shows the presence of ferrous and ferric carbonates along with hydrated ferric oxide.

(b) Retardation of rusting in presence of added lime or NaOH to the water in which iron is immersed.

Q.17. Differentiate between chemical corrosion and electrochemical corrosion. (R.G.P.V., June 2016)

Ans. Refer to Q.14 and Q.16 (i).

Q.18. Name the different types of corrosion. Explain any one type of corrosion.

Ans. Different types of corrosion are as follows -

(i) Galvanic corrosion

(ii) Pitting corrosion

(iii) Erosion corrosion

(iv) Crevice corrosion

(v) Stress corrosion

(vi) Water-line corrosion

(vii) Intergranular corrosion

(viii) Underground or soil corrosion

(ix) Microbiological corrosion

(x) Passivity. Water-line Corrosion - When water is stagnant in a steel tank, the concentration of oxygen above the water surface is greater than that under the surface. This generates an oxygen concentration cell. In this cell, the metal just above the water level is cathodic with respect to the metal below the water level.
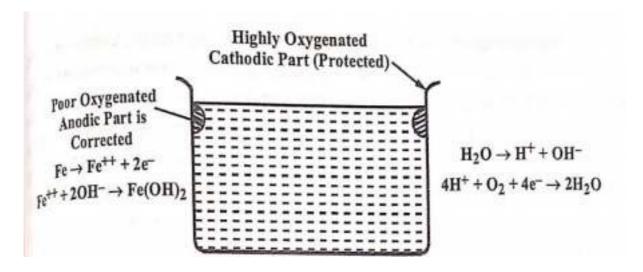

Highly Oxygenated Cathodic Part (Protected)

Poor Oxygenated Anodic Part is Corrected

$Fe \rightarrow Fe^{++} + 2e^-$

$Fe^{++} + 2OH^- \rightarrow Fe(OH)_2$

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

$4H^+ + O_2 + 4e^- \rightarrow 2H_2O$

Fig. 5.5 Water-line Corrosion Occurs Just Underneath the Meniscus and the Water Level

Corrosion occurs at the anodic part, the metal just below the water level. The cathodic area completely unaffected by corrosion.

Q.19. Write short note on intergranular corrosion.

Ans. Intergranular corrosion occurs due to the structures and defects due to metal surface heterogenity. In most of the metals, there are grain boundaries meeting the surface at different places. The plane of metal surface will usually be low atomic density plane in which various grains are separated by kinks. The grain boundaries become active under certain conditions and localized attack at these boundaries causes corrosion. The disadvantage of this type of corrosion is that it leads to reduction in mechanical strength of the metal. In some cases the metal convert to powder due to disintegration into separate grains. One the important parameter that makes the metals susceptible to intergranular is, heating it in the temperature range 800 to 1100 K. The il metals also become susceptible to intergranular corrosion when they are cooled slowly. It is believed that at high temperature, the carbon is completely dispersed through the metal or alloy, whereas, in the sensitizing temperature range it diffuses to the grains boundaries and form precipitate of chromium rich carbide at the boundaries. The chromium depleted zone near the grain boundary acts as anode and corrosion begins.

Q.20. What is galvanizing ? Galvanization of iron articles is preferred to tinning. Give reason.

Ans. The process of coating steel or iron sheets with zinc, generally by immersion in a bath of zinc, covered with a flux, at a temperature of 425-500°C. Galvanization (coating iron with zinc) is preferred to tinning (coating iron with tin) due to the following reason -

Zn, is more electropositive than iron, so zinc coating acts as anode, while the exposed iron portions of coating acts as cathode. If by chance, the zinc coating is broken at some place, the zinc (being more anodic than iron) undergoes corrosion, protecting iron (which is cathodic) from rusting. Thus, no attack, on the iron occurs, until practically all the zinc has been corroded in the vicinity of the exposed iron spot. So zinc coating protects iron 'sacrificially'.

On the other hand, tin is a noble metal (i.e., having higher electrode potential than iron), so it protects the iron due to its higher corrosion resistance than iron. Such a coating provides effective protection to iron only when the coating is completely continuous. If tin coating is punctured, much more corrosion damages can be done to the base metal (iron) than to iron metal without it. Since tin becomes cathode, while the exposed iron (which is above tin in the electromotive series) acts as anode, so a galvanic cell is set-up, thereby an intense corrosion at the small exposed iron part occurs.

Q.21. Write a brief note on passivity.

Ans. Passivity is the phenomenon in which a metal or an alloy exhibits a much higher corrosion resistance than expected from its position in the electrochemical series. Passivity is the result of the formation of a highly protective, but very thin and quite invisible film on the surface of metal or an alloy, which makes it more noble. This film is insoluble, non-porous and of such a 'self-healing nature' that when broken it will repair itself on the reexposure to oxidizing conditions.

Examples of passive metals and alloys are - Ti, Al, Cr and a wide variety of stainless steel alloys, containing Cr. These exhibit outstanding corrosion resistance in oxidizing environments, but in reducing environments, they become chemically active. Based on experiment, conducted in areated 0.5 M NaCl solution, the passivity of certain metals talls in the following order -

Ti→ Al → Cr→ Be→Mo→ Mg→Ni →Co→Fe→→Mn → Zn → Cd → Sn→ Pb→ Cu.

Passivity is not a constant state, but exists only in certain environment condition, which tend to maintain thin protective oxide films on their surfaces. In the presence of oxygen, the oxide film is automatically repaired whenever any damage occurs, but in oxygen absence, the passive metals and alloys become chemically active and are rapidly corroded. For example, the austentic stainless steels are quite good resistant to the action of aerated dilute sulphuric acid, but show low resistance in air-free acid.

The action of more concentrated solution of HNO3 on active metals (Fe and Al) produces a thin protective oxide film, thereby stifling the anodic reaction and making them passive.

Q.22. Describe the mechanism, causes and prevention of pitting corrosion.(R.G.P.V., June 2016)

Ans. Pitting corrosion is, usually due to the breakdown or cracking of the protective film on a metal at specific points. Pitting corrosion is a localized accelerated attack, resulting in the formation of cavities around which the metal is relatively unattached. Therefore, pitting corrosion results in the formation of pinholes, pits and cavities in the metal. This gives rise to

the mation of small anodic and large cathodic areas. Breakdown of the protective be caused by -

(i) Surface roughness or non-uniform finish

(ii) Scratches or cut edges (iii) Sliding under load

(iv) Alternating stresses

(v). Local straining of metal due to non-uniform stresses

(vi) Chemical attack

(vii) Impingement attack.

A pure and homogeneous metal with a highly polished surface will be a uch more resistant to pitting than the one with many inclusions, defects and rough surface. Surface cleanliness and selection of proper materials known to be resistant to pitting in the given environment are the usual methods to y combat this problem.

Owing to the differential amount of oxygen in contact with the metal (see f 1 fig. 5.6), the small part (underneath the impurity) become the anodic areas e and the surrounding large parts become the cathodic areas. Intense corrosion thus start just underneath the impurity. Once a small pit is formed, the rate of corrosion will be increased.
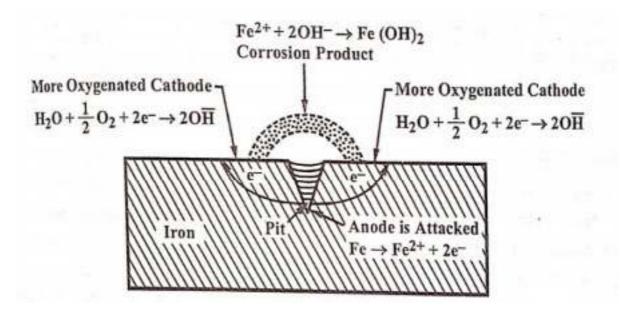
Fig. 5.6

Q.23. Corrosion of water filled steel tasks occurs below the water-line. Give reason.

Ans. This is because the area above the water-line is highly-oxygenated and acts as cathodic, while the fully immersed part is poorly oxygenated and acts as anodic. So the anodic part (below the water-line) gets corroded, due to electrochemical corrosion, while the cathodic part (above the water-line) remains completely unaffected by corrosion.

Q.24. Write mechanism of electrochemical corrosion.(R.G.P.V., Dec. 2015)

Ans. Electrochemical corrosion involves flow of electron-current between the anodic and cathodic areas.

(i) Anodic Reactions - At the anode, the metal atoms lose their electrons to the environment and pass into the solution in the form of positive ions, i.e.,For example,

$M(s) \rightarrow M^{n+} (aq) + ne^-$

This continuous as long as the electrons and ions are removed from the environment. In case they are not removed, the corrosion will not proceed further. Thus, the extent of corrosion of the metal anode depends upon the reactions at the cathode which mop-up electrons flowing from the anode and convert the metal ions formed at the anode into insoluble corrosion product.

$Fe(s) \rightarrow Fe^{2+} (aq) + 2e^-$

$Fe^{2+} (aq) + 2OH^- (aq) \rightarrow Fe(OH)_2$

(ii) Cathodic Reactions - The electrons released at the anode are conducted to the cathode and are responsible for the various cathodic reactions as given below -

(a) Electroplating - At the cathode, the metal ions collect the electrons and deposit on the cathode surface.

$Cu^{2+} (aq) + 2e \rightarrow Cu(s)$

(b) Liberation of Hydrogen - In acid solution, (in absence of oxygen) hydrogen ions acquire electrons and hydrogen gas is formed.

$2H_2O^1(aq) + 2e \rightarrow H_2(g) + 2H_2O(1)$

In neutral and alkaline media and in the absence of oxygen, the reaction taking place will be Such type of corrosion in which hydrogen is evolved is known as hydrogen i type corrosion. reaction is

$2H_2O + 2e \rightarrow H_2\uparrow + 2OH$

(c) Formation of Hydroxyl Ion -

(1) In presence of dissolved oxygen and in neutral or alkaline medium, the reaction is

$2H_2O + O_2 + 4e \rightarrow 4OH$

(2) In presence of dissolved oxygen and in acid medium, the

$4H^+ + O_2 + 4e \rightarrow 2H_2O$

Such type of corrosion involving oxygen is known as oxygen type corrosion.

Q.25. What is corrosion of metals ? Describe the mechanism of electrochemical corrosion by oxygen absorption. (R.G.P.V., June 2017)

Ans. Refer to Q.12 and Q.24. ¿ i 1

Q.26. Explain the methods of corrosion control.

Ans. There are various methods for protecting metal from corrosion or corrosion control. Some of the important methods are discussed as follows - (i) Design and Material Selection - Important design principles are given below1

(a) The contact of different metals in the presence of a corroding solution should be avoided. Corrosion is localized on the more active metal in the absence of this principle, while the less active metal remains protected. If an active metal is used, it should be insulated from more cathodic metals. (b) If two metals are to be in contact, they should be so selected that their oxidation potentials are as near as possible.

(c) The anodic material should have as large area as possible and the cathodic material should have as small area as possible when two dissimilar metals are to be in contact.

(d) If contact of dissimilar metals is unavoidable, suitable insulator should be inserted between them to reduce current flow and attack on the anode. (e) If a structure consists of two dissimilar metals, it is beneficial to use a more active third metal in contact so that the structure is saved from corrosion at the expense of the third metal.

(f) As far as possible, the equipment should be supported on legs to permit free circulation of air and preve the formation of stagnent pools or dam areas.

(g) A proper design should prevent condition subjecting some areas of structure to stress. Such a area could setup a galvanic couple with non stressed areas of the metal.

(ii) Cathodic and Anodic Protection - In situation where it is impossible or impractical to change the nature of the corrosion medium, corrosion control may be achieved by cathodic protection or by anodic protection. When electrical current flows between the anodic or cathodic areas on a corroding metal surface, the higher the current, the greater and faster will be the corrosion at the anode. The rate of corrosion can be controlled by imposing additional current on the metal using an external circuit. If an opposing current is applied to nullify corrosion, it is known as cathodic protection. If the potential of the metal is so adjusted that the corrosion is appreciably suppressed because the metal is rendered passive, then it is known as anodic protection. The principle involved in cathodic protection is to force the metal to behave like a cathode. Since there will not be any anodic area on the metal, corrosion will not occur. While in anodic protection, metal is passivated by applying current in a direction that renders it more anodic.

(iii) Inorganic Non-metallic Coatings - The inorganic non-metallic protective coating include surface conversion or chemical dip coating, anodized oxide coating and vitreous enamel coating.

(iv) Metallic Coatings - Metallic coatings are mostly applied on iron and steel because they are the cheap and most commonly used construction materials and are also the most

susceptible ones for corrosion. The metallic coatings often used are of Zn, Sn, Ni, Cr, Al, Pb and Cu. In general, the following methods are used for metallic coatings -

(a) Electroplating

(b) Metal cladding (d) Hot dipping

(c) Metal spraying

(e) Vapourising

(f) Cementation.

(v) Organic Coatings - Protection of a metal surface from corrosion by using organic protective coatings is an established practice. Important organic protective coatings include paints, varnishes, enamels and lacquers. When applied on cleaned metal surfaces, they act as effective inert barriers which not only protect the metal from corrosion but also afford decorative and aesthetic appeal.

(vi) Modifying the Environment - The corrosive nature of the environment can be reduced either by, (a) the removal of harmful constituents or (b) the addition of specific substances, which neutralize the effect of corrosive constituents of the environment.

Q.27. What is corrosion ? Discuss various theories to explain corrosion with suitable examples. How corrosion may be prevented ?(R.G.P.V., Nov. 2018)

Ans. Corrosion - Refer to Q.12.

Theories of Corrosion - Refer to Q.16. Prevention of Corrosion - Refer to Q.26.

UNIT 6

SPECTROSCOPIC TECHNIQUES AND APPLICATIONS

Q.1. Define spectroscopy. (R.G.P.V., Dec. 2013)

Ans. The term spectroscopy was originally applied to the branch of science that was based upon the resolution of visible radiation into its component wavelength. With the passage of time, however, the meaning of the term has been broadened to encompass studies involving the entire electromagnetic spectrum and even some techniques which do not at all involve electromagnetic radiation e.g., mass, electron and acaustic spectroscopy.

Q.2. What are the merits and demerits of instrumental analysis ? (R.G.P.V., Jan./Feb. 2006)

Ans. The merits and demerits of instrumental analysis are given below

Merits -

(1) In instrumental method, small sample can be used.

(ii) High sensitivity in results is obtained.

(iii) Measurements or results obtained by instrumental methods are reliable.

(iv) The determination is very fast.

(v) By instrumental method even complex samples can be easily handled.

Demerits -

(i) An initial or continuous calibration of the instrument is required.

(ii) Sensitivity and accuracy depends a lot on the instrument.

(iii) The cost of equipment is very high.

(iv) It works accurately in between a particular concentration range.

(v) Specialized training to handle the instrument is needed.

(vi) Sizable space is required.

Q.3. Most absorption bands in the visible UV-spectra Give reason. are very broad.

Ans. Visible-UV spectra involve electron energy level associated with its vibrational and rotational levels. The electron transition may occur from a of several vibrational and

rotational states of one electronic level to any of several vibrational and rotational states of a higher level. Since a large number of transitions are possible, so a large number of absorptions will take place corresponding to different wavelengths. Hence spectra are very broad

Q.4. Write informative note on U.V. visible spectroscopy. (R.G.P.V., Dec. 2006, June 2007)

Or

Write short note on U.V. spectroscopy.(R.G.P.V., Dec. 2012)

Ans. Principle - When electromagnetic radiations of ultraviolet region (2= 200-400 nm) or visible region (2= 400-800 nm) are passed through a compound with multiple double bonds, some part of the incident radiations is absorbed. The quantity of absorbed radiation depends on the wavelength of incident light as well on the nature of compound. Due to absorption of light radiations, the bonded electrons go to higher energy levels. The quantity of absorbed radiations can be determined by spectrometer.

The modes of electronic energy changes which occur, when radiation in U.V. and visible region is absorbed by an organic compound are - (i) Transition between Bonding Orbitals and Antibonding Orbitals

For example,

$$\sigma \rightarrow \sigma^* \ \text{or} \ \pi \rightarrow \pi^*$$

The excited state closely resembles the polar character

C = C- →C+ -C

(ii) Promotion of Non-bonding Electron (i.e., Unshared Pair, n) into Antibonding Sigma or Antibonding Pi i.e., noor n→*- These involves transitions of non-bonding lone pair of hetero atoms (e.g., o, n) to an empty non-bonding molecular orbital. The absorption bonds for such transitions occur in longer wavelength with low intensity.

Structural units which absorb selective wavelengths and even small structural changes bring about perceptible changes in wavelength of radiation absorbed is called chromophores,

$$C = C, -C = C-, -C \equiv N, -N = N-, -\overset{|}{C} = 0$$

undergo í→ * transitions in the short wavelength regions of U.V. radiations. Polar groups such as - OH, - OR, -NH$_2$, - SH and - X (halogen) having unshared pair of electrons and may show absorption above 190 nm such groupings are called auxochrome.

It may be noted that energy gap between non-bonding and antibonding M.O. of ethene is greater than that between the corresponding M.O. in 1, 3butadiene. Consequently, 1, 3-butadiene has its max at 171 nm (of higher energy) than that of ethene at 217 nm (of lower energy). Thus, in general, the greater the number of double bonds present in a given compound the longer is the wavelength at which it absorbs U.V. radiations.
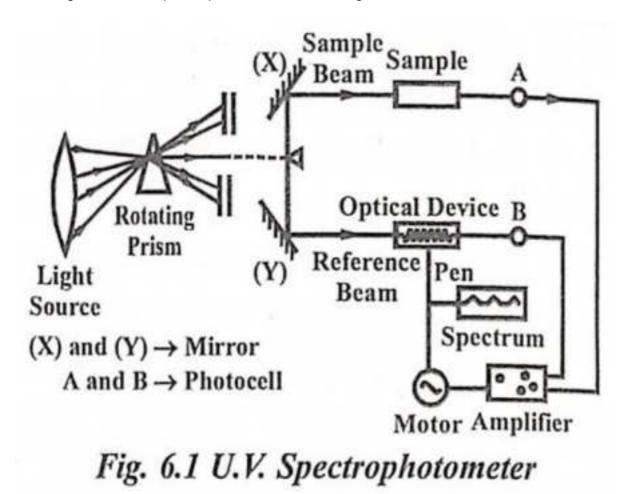
Compounds containing carbon-oxygen double bond also absorb light in the U.V. region.

Q.5. Explain the instrumentation and working of the U.V. spectrophotometer.

Ans. Instrumentation of U.V. Spectrophotometer - The following are the important components of the U.V. spectrophotometer.

(i) Source of Radiation - The following are the most common radiation sources used in U.V. spectrophotometer

(a) Hydrogen discharge lamps (b) Deuterium lamps (c) Xenon discharge lamps (d) Mercury arcs.

(ii) Monochromators - Monochromators are used to disperse the radiation according to the wavelength. The essential component of the monochromator are an entrance slit, a dispersing element and an exist slit. The prism is generally of quartz or fused silica. The dispersing element disperse the heterochromatic radiation into its component, wavelengths where the exit slit allow the nominal wavelength to pass through.

(iii) Detectors - The following types of detectors are commonly used -

(a) Photovoltaic or Barrier Layer Cell - In this cell, light striking surface of a semiconductor such as selenium leads to generates the electric current. The magnitude of the current generated in proportional to the intensity of the light beam falling on it.

(b) Photocell or Photoemission Cell - This cell consists of a glass bulb coated internally with a thin, senstive layer of calcium and potassium oxide or silver oxide. This layer limit electron when light fall on it, this layer is cathod. A metal ring insert near the centre of the bulb forms the anode.

(c) Photomultiplier Tube-It consists of an electrode covered with a photo-emissive material and a series of positively charged plates, each charged at a successively higher potential. The plate is covered with a material such as Be-Cu or Cs-Sb, which limit several electron for each electron collected on its surface. This is extremely very sensitive and very fast in response.

(iv) Recorders - This signal from the detector is received by the recording system provided with a recorder pen.

(v) Sample and Reference Cells - Matched pair of cells made of quartz or fused silica are used. Generally quartz cells are used in the ultraviolet region, and also visible region. Single beam and double beam U.V. spectrophotometers are available commercially.

Working of Double Beam U.V. Spectrophotometer - The U.V. radiation emitting from the source is allowed to pass through a monochromator unit via a mirror system. The radiation of narrow range of wave lengths coming out of the monochromator is received by the rotator system which divides the beam into two identical beams, on passing through a sample cell and other through reference cell are focussed on detector. The output from the detector is connect to phase sensitive amplifier. The signal transmitted by the amplifier are transmitted and recorded which is connected to recorder. The chart device is coupled to the rotation of the prism. Thus, the absorbance or transmittance of the sample is recorded as a function of wavelength. The U.V. spectro photometer shown in fig. 6.1.

Fig. 6.1 U.V. Spectrophotometer

Q.6. Explain briefly the applications of U.V. spectroscopy. (R.G.P.V., Dec. 2003, Feb. 2005)

Or

Write short note on applications of U.V. spectroscopy.(R.G.P.V., Dec. 2013)

Ans. Applications of U.V. spectroscopy are given below -

(i) Qualitative Determinations Analysis - U.V. spectroscopy is used for characterizing aromatic compounds and conjugated olefins and identification is done by comparing the U.V.

absorption spectrum of the sample with the U.V. spectra of known compounds available in reference books.

(ii) Quantitative Analysis - U.V. absorption spectroscopy can be used for quantitative analysis of such compounds, which absorb ultraviolet radiation, the determination can be done on the basis of Beer-Lambert's law, according to which absorbent

$$A = \log I/I = \log T = \epsilon / c$$

For the quantitative determination of an organic compound the wavelength at which its solution has the maximum absorption is identified. It is also used in mixture analysis.

(iii) Determination of Molecular Weight - U.V. spectroscopy can be used for determining the molecular weight of compound if it can be converted into suitable derivatives which shows an absorption band in spectrum. For example, many hydrocarbons and amines form picrates the absorption spectra of picric acid is not effected by complex formation.

(iv) Study the Tautomeric Equilibria - U.V. spectroscopy can be ed for determine the percentage of keto and enol form present in compound, ch as ethyl acetylacetate, by measuring the strength of the respective sorption bands.

(v) Study of Kinetics of Chemical Reaction - It can be done by suring the change in concentration of reactant or product with time provided of the reactants or product exhibit suitable absorption in the U.V. visible ion. As absorbance is directly proportional to concentration.

(vi) Detection of Impurities - The impurities present in organic mpounds can be easily detected by U.V. absorption spectroscopy. The main easons for the superiority of this method are -

(a) The band due to impurities are very intense.

(b) The organic compound can be classified into saturated compounds having little absorption, while the unsaturated compounds have trong absorption bands.

Q.7. What are the essential parts of U.V.-visible spectrometer. Give its important applications in analytical chemistry. (R.G.P.V., March/April 2010)

Or

Describe U.V. spectroscopic instrument and mention its applications. (R.G.P.V., June 2013)

Ans. Refer to Q.5 and Q.6.

Q.8. Discuss brief introduction of electronic spectroscopy.(R.G.P.V., May 2019)

Or

Write brief note on electronics spectroscopy.

Or

selectronic excitation of bonded electrons from lower to higher energy levels, U.V. spectra arise. This phenomenon is called electronic transition. The possible transitions in electronic (R.G.P.V., Jan./Feb. 2007)

Ans. Origin of Electronic Absorption Bands - In organic molecules, electrons of o, or n bonding orbitals may get excited with the absorption of electronic radiations.

So, whenever, thereo* (Antibonding)T* (Antibonding)Energyn-o*n (Non-bonding)n→π*π (Bonding) (Bonding) hergy levels is shown in Fig. 6.2 Transition in Simple Organic Molecules fig. 6.2. *b↑5 T-T*

(i) $\sigma \rightarrow \sigma^*$ Transition - This type of electronic transition requires large amount of energy. So compounds having single covalent bond or o-bond cannot absorb in U.V. or viz., region in other words these compounds are transparent for these radiations.

halogen grouping CH3-Cl shows atoms can have this type of electronic transition because these atoms have atleast one lone pairs of electrons so, organic compounds with or shows this type of transitions, C-OH, C-OR, $C-NH_2$, C-X etc. This transition requires lesser amount of energy CH3OH or absorption in U.V. region due to this type of transition. (ii) no Transition - Compounds having O, N, S or

(iii) n→* Transition - This transition is possible in still lower energy. Carbonyl compounds with >CO grouping shows absorption in

U.V. region due to this type of transition. (iv) → Transition - Two types of bands arise by this transitions, whose energy is in between the energies of n→ o* and n→ * transitions (a) K-band - Those organic compounds which have conjugated system give K-band. Due to conjugation, red shift is observed with increased intensity of absorption. The following table shows some K-bands -

Table 6.1

S.No.	Compounds	K-band	
		λ_{max} (mμ)	$\varepsilon_{max} \times 10^3$
(i)	$CH_2=CHCH=CH_2$	217	21
(ii)	$CH_3CH=CHCHO$	217	16
(iii)	$CH_2=CHCH=CHCH=CH_2$	258	35
(iv)	$CH_3(CH=CH)_4CH_3$	296	52

(b) B-band - Benzene has a broad absorption peak at 254 nm. If a chromophore is present in benzene ring, we get absorption bands with large bathochromic shift as compared to K-bands. The B-bands in aromatic compound are given in following table -

Table 6.2

S.No.	Compounds	B-band	
		$\lambda_{max}(m\mu)$	ε_{max}
(i)	Benzene	254	204
(ii)	Naphthaline	312	250
(iii)	Phenanthrene	330	250

Q.9. Define R. value. [R.G.P.V., June 2008, Nov. 2018]

Ans. The ratio of distance moved by the pure substance and the distance oved by the solvent front is called R1 value.

$$R_f \text{ value} = \frac{\text{The distance moved by the pure substance}}{\text{The distance moved by the solvent front}}$$

Q.10. Discuss chromophores. [R.G.P.V., Nov. 2018]

Or

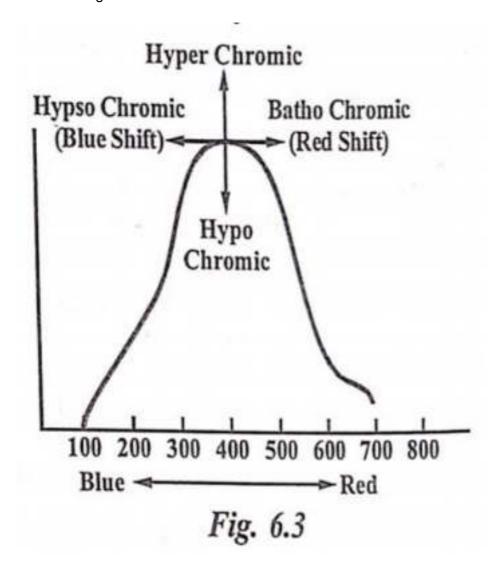**Write short note on chromophores. (R.G.P.V., Dec. 2013)**

Or

Define chromophore with example. (R.G.P.V., June 2014)

Ans. Some groups when present in a compound, make it coloured. In other words, due to presence of such groups, the absorption takes place in visible range. These groups are known as chromophores. For example, Or

> C=C <, > C=0,- N=N-, -NO₂

0 == 0 etc.

Electronic excitation in these group can be made easily.

The position and intensity of an absorption band of a chromophore may be modified by the attachment of substituent group in place of hydrogen on the basic chromophore structure. The absorption maxima may be shifted to longer or shorter wavelengths depending upon the substituent and its position with respect to the chromophore some shifts in the absorption maxima are given characteristic names

Fig. 6.3

(i) Batho Chromic Shift (Red Shift) - It is a shift of max to longer wavelength.

(ii) Hypso Chromic Shift (Blue Shift) - It is a shift of max to shorter wavelength.

(iii) Hyper Chromic Shift - It is accompanied by increase in intensity of absorption.

(iv) Hypo Chromic Shift - It is accompanied by decrease in intensity of absorption.

Q.11. Write a note on Beer-Lambert's law. (R.G.P.V., Nov./Dec. 2007) (R.G.P.V., June/July 2006, 2007, Dec. 2012) (R.G.P.V., Dec. 2013)

Or

Write short note on Lambert-Beer law. Or Discuss Beer-Lambert's law. (R.G.P.V., Dec. 2017)

Ans. Lambert's Or State and derive Beer-Lambert's law of colorimetry. (R.G.P.V., Sep. 2009) Or Write short note on Beer and Lambert's law.

Law - When a monochromatic light is passed through a transparent medium, then the intensity of transmitted radiation is given by

$I_1 = I_o \times 10^{-kl}$

where Io is the intensity of incident radiation and l is the thickness of transparent substance.

Beer's Law - Beer found that the Lambert's law is also applicable to the solutions now the concentration of solution is to be considered. Hence

$I_t = I_0 \times 10^{-k'C}$

Lambert-Beer's Law --When a beam of monochromatic radiation is passed through a homogeneous solution, the decrease in the intensity with the thickness of medium is proportional to the intensity of radiation and concentration of the solution. So

$$-\frac{dI}{dl} \propto I.C$$

So that $\quad -\frac{dI}{dl} = \varepsilon . I.C \quad$ or $\quad -\frac{dI}{I} = \varepsilon C. dl$

or $\quad I_t = I_0 \times 10^{-\varepsilon.C.l}$

or $\quad \dfrac{I_0}{I_t} = 10^{\varepsilon Cl} \quad$ or $\quad \log_{10}\dfrac{I_0}{I_t} = \varepsilon Cl = A$

where $\varepsilon = k/2.303$ is called the *molar absorptivity coefficient*, and

$\log_{10}\dfrac{I_0}{I_t} = A$ is called the absorbance.

$\therefore \qquad\qquad A = \varepsilon Cl$

where C is molar concentration, and l is the thickness of the medium.

Q.12. Derive Beer-Lambert's law and application of U.V. spectroscopy[R.G.P.V., Nov. 2018)

Ans. Beer-Lambert's Law - Refer to Q.11.

Q.13. State and derive Beer-Lambert's law giving its applications and limitations. (R.G.P.V., June 2009)

Ans. For Beer-Lambert's law, refer to Q.11.

Application From this equation, we can determine the concentration of species absorbing in ultraviolet or visible region. We measure the absorbance Ag, of a solution of known concentration or called a standard solution. In this case,

$$A_s = \varepsilon C_s l$$

$$\frac{A_s}{C_s} = \varepsilon l$$

where s Standard solution of known concentration.

Now, we measure absorbance A, of a solution of unknown concentration Cu

:: & and I are constant, so for unknown solution, we have

$$A_u = \varepsilon C_u l$$

$$\frac{A_u}{C_u} = \varepsilon l \qquad \qquad ...(ii)$$

From equations (i) and (ii), we get

$$\frac{A_s}{C_s} = \frac{A_u}{C_u} \quad \text{or} \quad C_u = \frac{A_u}{A_s}.C_s \qquad \qquad ...(iii)$$

Since C, is known, and A_1, A, are experimentally determined values, so C_1 can be calculated from equation (iii).

Limitations - This law possess following limitations -

(i) These cells are less sensitive in the blue region as compared to other regions of the visible spectrum.

(ii) The current output of the cells depends upon the wavelengths of the incident light.

(iii) These cells show tendency to fatigue.

(iv) The current produced photovoltaic cells cannot be readily amplified by the conventional electronic circuit because of the low internal resistance.

Q.14. State Beer-Lambert's law. Explain how this law can be used to determine the concentration of coloured solution. (R.G.P.V., June 2013)

Ans. Refer to Q.11 and Q.13.

Q.15. Name and state the basic laws of photochemistry. How the laws may be used to determine the concentration in solution? (R.GP.V., June 2012)

Ans. The basic laws of photochemistry are as follows -

(i) Grothus-Draper law, also referred to as the first law of photochemistry, states that "only light which is absorbed can be effective in producing chemical change.

(ii) Stark-Einstein law or Einsteins law of photochemical equivalence states that "in the primary process, each reacting molecule is activated by one quantum of effective light".

(iii) Lambert's Law - According to it "equal fractions of incident radiation are absorbed by successive layers of equal thickness of the absorbing substance".

Q.16. State Beer-Lambert's law. Discuss instrumentation and experimental technique of colorimetry. (R.G.P.V., June 2010)

Ans. Beer-Lambert's Law - Refer to Q.11.

Instrumentation - In a colorimeter a narrow beam of light pass through the solution under test through filter or diffraction grating. The current generated in the photocell is proportional to the amount of light transmitted by the solution. The current generated in the photocell will be the greatest when the light transmitted by the solution is the greatest i.e., the coloured solution is most dilute.
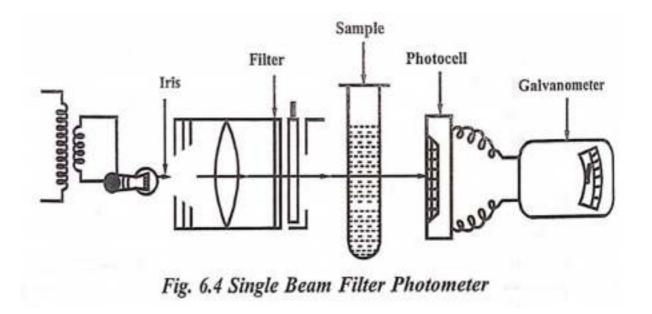

Fig. 6.4 Single Beam Filter Photometer

Fig. 6.4 Single Beam Filter Photometer

Experimental Technique -

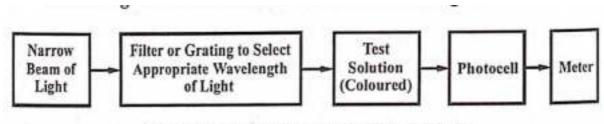**Block Diagram of Colorimeter** - It is shown in fig. 6.5.

Fig. 6.5 Block Diagram of Colorimeter

Fig. 6.5 Block Diagram of Colorimeter

Working - In a colorimeter, a narrow beam of light (of proper wavelength) passes through the solution under test towards a sensitive photocell. Generally, colorimeters are provided with arrangement of filter or diffraction grating. Consequently, it is possible to select the most appropriate wavelength (or frequency) by choosing a particular/filter grating. The current generated in the photocell is, of course, proportional to the amount of light transmitted by the solution. This-in-turn depends upon the depth of colour of substance under test. Thus, the current from the photocell will be greatest when the light transmitted by the solution is greatest. This occurs when the coloured solution is most dilute. However, the general meter is calibrated to show not the fraction of light transmitted, but the fraction of light absorbed. This will be proportional the concentration of the coloured substance in the test solution.

Q.17. What are the main parts of an infrared spectrometer ? Explain each part in brief.

Ans. The instrument used for recording infra and spectra is called infrared or infrared spectra photometer. Most of the instrument have a spectrometer range of 2u to 15µ (5000 to 667 cm-^{1}).

The instrument which is used in infrared spectroscopy consists of following parts

(i) Source of Radiation The main sources of mid infrared radiation are - -

(a) Nichrome wire wound on a ceramic support.

(b) Nernst-glower is a filament which containing oxide of zirconium, thorium, yittrium and cerium held together with a binder.

(c) Globar, which is bonded silicon carbide rod, when heated electricity at 1200 to 2000°C, they glow and produce mid-I.R. radiation.

(ii) Monochromator - Prism and Grating are commonly used for this purpose. The prism materials used commonly are Sodium-chloride, potassium bromide, lithium fluoride etc., the most commonly used prism materials NaCl or KBr are hygroscopic.

Advanced infrared spectrophotometers produce the I.R. spectra by a procedure based upon interferometry. This is known as Fourier transform infrared spectroscopy.

(iii) Detectors - The I.R. detector generally convert thermal radiant energy into electrical energy. Two types of I.R. detectors are in use, (a) selective (b) non-selective. In selective detectors, the response depends upon the wavelength of incident radiation. Example - Photocells, photoconductive cells, I.R. phosphorus.

(iv) Sample Holder - Gaseous samples are collected in a gas cells equipped with mirrors. The simplest gas cells consists of a glass or metal cylinder 10 cm long and closed with appropriate windows.

Liquid samples are collected in a variety of absorption cells like cavity cell, demountable cell, sandwich cell etc. Cavity céll is made by matching a parallel sides holes in a salt black. The demountable cell consists of a pair of salt plates separated by a gasket mode of metal or teflon.

Solid samples are analysed by in cooperating them into a pressed plate of alkali halide usually potassium bromide.

Q.18. How a sample can be analyze by infrared spectrometer?

Ans. In infrared spectrometer a source of infrared light emitting radiation One beam of such light is passed through the sample to be examined. If the is present, which gives radiation to the whole frequency range of the instrument, frequency of vibration of the sample molecules fells within the range of to be examined. If the frequency of vibration of the sample molecules fells within the range of instrument it will absorb energy from this light. The spectrum is scanned by comparing the intensities of the beams before and after passing through the sample, the wavelength range over which the comparison is made can be sprayed out by using a prism or grating. The spectrum consists of a chart showing downwards peaks corresponding to absorption plotted against wavelength or frequency. These spectrums are obtained after passing the corresponding wavelength through detectors, which detect the presence of substances in the sample.

Compounds canbe examined in the vapour phase, as pure liquid, in solution and in solid state,

(i) In the Vapour Phase-In vapour phase analysis, analysis is done after removing water vapours from the sample. The vapour is introduced in a special cell of about 10 cm length. This cell is placed directly in the path of infrared beams. The end walls of the cells generally made of sodium chloride which is transparent to infrared radiation.

(ii) As a Liquid-The liquid drop is measured after squeezing between the two flat plates of salts separated by a gasket made of metal or teflon. A variety of absorption cell for liquid are available, they are cavity cell, demountable cell, sandwich cell etc.

(iii) In the Solution - The compound is dissolved to give I to 5% solution in CCL, or alcohol free $CHCl_3$. The solution is taken into a special cell with 0.1 to 1 mm thick cell wall, made up of sodium chloride. A second cell with equal wall thickness, containing pure solvent is placed in the path of other beam in the spectrometer to balance solvent absorption. In dilute solution spectrum, are desirable because intermolecular forces, which are strong in crystalline state becomes minimum.

(iv) In Solid State When the sample is in solid state it can be examined by following two methods

(a) In it I mg of a solid is finally grounded with a drop of liquid hydrocarbon or is C II vibrations are to be examined with hexachloro butadiene. The mould thus obtained is pressed between two flat plates of sodium chloride. (b) In i't the solid is grounded with 10-100 times in quantity with pure KBr, the mixture is pressed into a special mould by means of a hydraulic press. These KBr pallets containing sample gives better spectra,

Q.19. "IR spectra is often characterised as molecular finger prints". Justify this statements.

Ans. This is because different functional groups produce recognisable peaks at nearly definite positions in IR spectra. Most of the peaks can be assigned due to the presence of specific groups in the molecule. So IR spectra also be used in establishing the identity of the compounds.

Q.20. Explain in brief I.R. spectroscopy. (R.G.P.V., June 2005, 2007)

Or

Write short note on I.R. spectroscopy. (R.G.P.V., Dec. 2017, May 2018)

Ans. Infrared spectroscopy is also known as vibrational spectroscopy. The infrared spectrum yields the most informations concerning the structure of organic molecules. A molecule is constantly vibrating, its bond cach, contract and bend w.r.t. each other. Furthermore, given bond may undergo several different type of vibratory motions. Each mode of vibration, a different amount of energy and accordingly absorb radiation of different wavelengths. Hence, each bond give rise to several bands.

Therefore, infrared spectroscopy is based on the absorption of infrared radiations by the molecules. Infrared spectroscopy is employed for qualitative and quantitative analysis of chemical compounds and are most widely used for the identification of organic compounds.

The infrared radiation lies between the visible and microwave regions of the electromagnetic spectrum. This region may be divided into following types

(i) Near Infrared Region - It is the region which extends from 0,8 to 2.5 μm (12500 to 4000 cm ^{1}). It is also known as vibration-rotation region.

(ii) Far Infrared Region - It is the region which extends from 15 to 200 μm (667 to 50 cm). It is also known as rotation region.

(iii) Ordinary Infrared Region-It is the region which extends from 2.5 to 15 μm (4000 to 667 cm),

Working of I.R. Spectrophotometer - The instruments are of two types single beam and double beam. The single beam instruments measures directly the amount of energy transmitted by the sample and the spectrometer optics, It yields most accurate transmittance

measurements and is particularly useful for quantitative analysis. The layout of the single beam infrared spectrophotometer is shown in fig. 6.6.
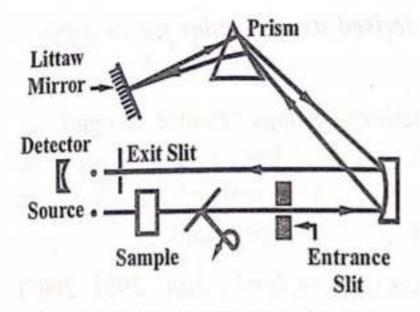

Fig. 6.6 Layout of a Single Beam Infrared Spectrophotometer

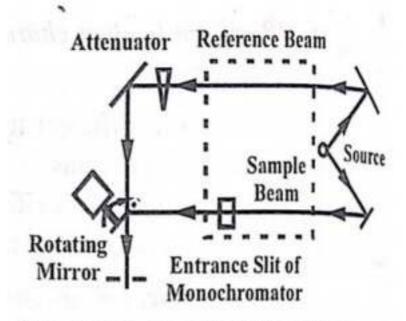Fig. 6.6 Layout of a Single Beam Infrared Spectrophotometer

Fig. 6.7 Optical Null Double Beam Spectrometer

Fig. 6.7 Optical Null Double Beam Spectrometer

Double beam instruments are particularly useful in qualitative analysis. Two designs of double beam instruments, which are widely used are optical null system and electric beam rotating system. The double spectrometer is shown in fig. 6.7.

Q.21. Write note on applications of I.R. (R.G.P.V., March/April 2010)

Or

State the applications of I.R. spectroscopy. (R.G.P.V., Dec. 2011)

Ans. The important applications of I.R. spectroscopy are as follows -

(i) Qualitative Analysis - I.R. spectroscopy is particularly useful in the qualitative determination of compound or component in a mixture. I.R. spectroscopy was successfully used in identification of various organic compounds such as alkynes, aromatic, inorganic ions.

(ii) Quantitative Analysis - The quantitative determination of given compound is based on the determination of concentration of one of functional group of compound being estimated. Suppose there is a mixture of hexane and hexanol and then concentration of hexanol can be determined by measuring absorption of OH bond. The following formula is used for calculating the concentration.

$A = \log I/I_o = abc$

where, A Absorbance

I = Intensity of radiation after leaving the sample

Io = Intensity of radiation before entering the sample

a = Absorptivity of cell

b = Initial path length of same cell and

C = Concentration of solution.

If a and b are constant then,

$$A \propto c$$

Hence, c can be measured by knowing A.

(iii) In Identifying the Compounds - The I.R. spectrum of the compound is compared with that of known compound and from the resemblance of the two spectra, the nature of the compound can be established due to the particular group of atoms give to characteristics absorption band in the I.R. spectrum i.e., A particular group absorb light of certain wavelength in I.R. spectrum no matter to which compound it belongs.

(iv) In Detecting Impurities in a Sample - I.R. spectroscopy is useful to detect impurities of the sample. I.R. spectra of impure sample will show some extra absorption bands, by comparison with I.R. spectra of pure compound. Hence these extra bands if impure sample indicates the impurity of given sample.

(v) To Distinguish between Intra and Inter Molecular Hydrogen Bonding - We know that generally, it is not possible to distinguish between intra and inter molecular hydrogen bonding. This can be done by taking a series of I.R. spectra of the compound at different concentration as the concentration is increased, the absorption of bond, due to hydrogen bonding increases. While that due to H-bonding remains unchanged.

(vi) Elucidation of Structure - Elucidation of structure is possible by I.R. spectroscopy because it gives valuable information regarding molecular symmetry, dipole moments, bond lengths, bond strength etc.

(vii) In the Study of Reaction Kinetics - We know that any reaction, there is always bond breaking and making in the reactants. I.R. spectra arises from the different modes of vibrations in bonds, so if we withdraw the sample from reaction mixture in a regular interval of time, and study its I.R. spectra, we can draw some inference regarding the kinetics of reaction.

(viii) Study of Polymers - Infrared techniques have been used in the detection of end groups and chain branching found in polymers. Use of polarise infrared radiation has been made in the study of certain properties of polymers. Example, stretching of rubber.

Q.22. Write short note on significance of IR spectroscopy.

Ans. Refer to Q.21.

Q.23. Discuss instrumentation and applications of IR spectroscopy.(R.GP.V., Dec. 2013)

Ans. Refer to Q.17 and Q.21.

Q.24. Discuss principle, instrumentation and applications of vibrational spectroscopy. (R.G.P.V., Nov. 2018)(R.G.P.V., June 2011)

Ans. Refer to Q.20, Q.17 and Q.21.

Q.25. What is spectroscopy? Discuss IR spectroscopy giving principle, instrumentation and applications. (R.G.P.V., May 2019)

Ans. Refer to Q.1., Q.20, Q.17 and Q.21.

Q.26. Discuss in brief the type of molecular vibrations. (R.G.P.V., Jan./Feb. 2006, Dec. 2013)

Ans. Various observations indicate that the atoms in a molecules are always in motion, which may be of different types. Consider a simple diatomic molecule A-B. The only

vibrations which can occur in such a molecule are the compression or extension, along the A-B bond. Molecular vibrations are mainly two types -

(i) Stretching vibration

(ii) Bending vibration.

(i) Stretching Vibrations - In this type of vibration the distance between two atoms increases or decreases, but the atoms remain in the same bond axis.

Stretching vibrations are of two types -

(a) Symmetric Stretching Vibrations - When stretching and compression occurs in a symmetrical form, we call it symmetric stretching vibration.

(b) Asymmetric Stretching Vibrations - When one bond is compressing, while the other bond is stretching, then we call it asymmetric stretching vibration.

Both symmetric and asymmetric stretching vibrations are shown in fig. 6.8.
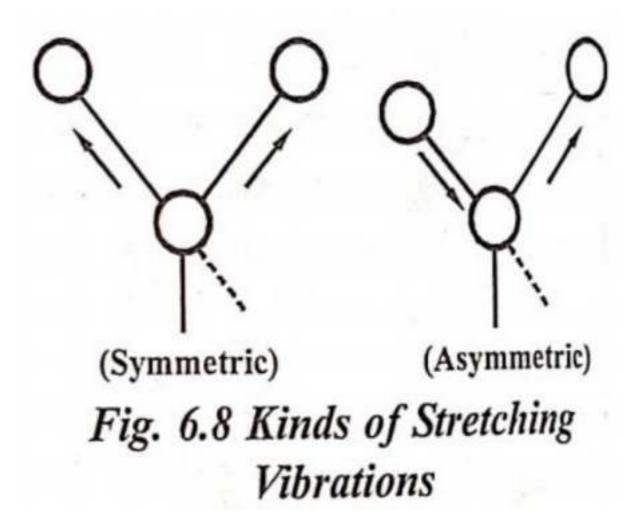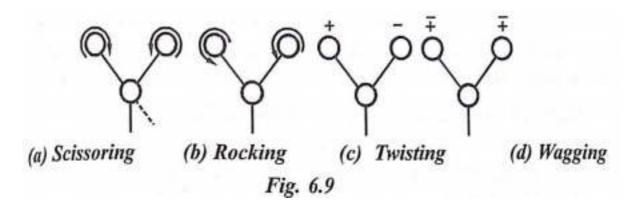

(Symmetric)   (Asymmetric)

Fig. 6.8 Kinds of Stretching Vibrations

Fig. 6.8 Kinds of Stretching Vibrations

(ii) Bending Vibrations - In these types of vibrations, atoms move in and out of the bond axis plane. Hence, these vibrations involve change in bond angle.

The bending vibrations mostly are of four types -

(a) Scissoring - In this vibration, two atoms joined to a central atom, and move towards away from each other, is called scissoring vibration. In this vibration bond angle changes.

(b) Rocking - In this vibration, two atoms joined a central atom and both atoms move back and forth in the plane of the molecule is called rocking vibration. In this vibration bond angle does not change.

(c) Twisting - In this vibration, the structural unit rotates about the bond which joins it to the rest of molecule is called twisting vibration. Bond angle does not change.

(d) Wagging - In this vibration the structural unit moves back and forth, out of the plane of molecule is called wagging vibration.

All of four bending vibrations are shown in fig. 6.9.

(a) Scissoring   *(b) Rocking*   *(c) Twisting*   *(d) Wagging*

Fig. 6.9

Q.27. Write short note on stretching and bending vibrations.

Ans. Refer to Q.26.

Q.28. Differentiate between IR and UV spectroscopy.(R.G.P.V., Dec. 2013)

Ans. The difference between U.V. and I.R. spectroscopies are given below

S.No.	U.V. Spectroscopy	I.R. Spectroscopy
(i)	The region of U.V. spectroscopy extends from 10-800 nm.	The region of I.R. spectroscopy extends from 800-20000 nm.
(ii)	As U.V. radiations passes more energy they are strong and so can cause electronic transition.	I.R. radiations are weak and so cannot produced electronic excitation. They cause bending and stretching vibrations of organic bonds.
(iii)	Unsaturated and especially conjugated group only absorb in this region.	All organic bonds and groups absorb in this region.
(iv)	U.V. absorption spectrum exhibits broad absorption bands.	I.R. spectrum exhibits sharp peaks.
(v)	This spectroscopy gives an idea about the presence of carbonyl group and no conjugate system.	This spectra give an idea about the nature of the molecule. It help identifying the complete structure of the compound.
(vi)	The spectra are usually expressed terms of wavelength.	The spectra are usually expressed in terms of frequency in wave number (v) units.

Q.29. Write short note on rotational (or microwave) spectroscopy.

Ans. Rotational or microwave spectra is due to the result of transitions between the rotational levels of a gaseous molecule containing permanent dipole moments i.e., HCl, HBr, NH3, CO, NO, H_2O vapour etc. on the absorption of radiations falling in the microwave region. Homonuclear diatomic molecules i.e., H_2, Cl_2, O_2, N_2, etc. and non-polar polyatomic molecules i.e., CO_2 do not show microwave spectra.

UNIT 7

PERIODIC PROPERTIES

EFFECTIVE NUCLEAR CHARGE, VARIATIONS - s, p, d & f ORBITAL ENERGIES OF ATOMS IN PERIODIC TABLE, ELECTRONICS CONFIGURATION, ATOMIC & IONIC SIZES, ELECTRON AFFINITY & ELECTRONEGATIVITY, POLARIZABILITY & OXIDATION STATES

Q.1. Write introduction of periodic table in brief.

Ans. Upto the end of seventeenth century, only a few elements ware known. Thus it was easy to study and remember their individual properties. However, with the discovery of a large number of new elements, it was realized that there should be some simple way to study the properties of these elements and a large number of their compounds. After numerous attempts the scientists were finally successful in arranging the elements in various groups. This arrangement of elements is called classification of elements. Such a classification of the elements has resulted in the formulation of periodic table. Thus, periodic table may be defined as the arrangement of all the known elements according to their properties in a tabular form.

The periodic classification of elements has extremely simplified the study of the properties of various elements and their compounds.

Q.2. What is Mendeleef's periodic law ?

Ans. Mendeleef proposed a law before classifying elements in 1869, which is known as periodic law. According to him, physical and chemical properties of elements are periodic functions of their atomic masses that is, on placing elements in increasing order of their atomic masses elements having similar properties are repeated after a regular interval. This law means that on placing the elements in sequence of their atomic masses. their properties change but after a definite interval elements of approximately same properties are repeated. On the basis of this law, Mendeleef arranged all elements in the increasing order of their atomic masses in a table called periodic table and this type of classification is known as periodic classification.

Q.3. State modern periodic law.

Ans. According to Moseley, physical and chemical properties of elements do not depend upon atomic weight but on atomic number, that is, number of electrons and atomic number is the basic property of elements and not the atomic weight. Therefore, Moseley considered atomic number as the basis of classification and not the atomic weight. He gave the following definition of modern periodic law -

"The physical and chemical properties of elements are a periodic function of their atomic numbers" i.e., if the elements are arranged in order of their increasing atomic numbers, the elements with similar properties are repeated after certain regular intervals. As a result of

this arrangement all the elements fall in various groups. This arrangement of elements is called the long form of the periodic table.

Q.4. What do you understand by long form of periodic table ?

Ans. Long form of the periodic table is based upon the modern periodic law. This is also called Bohr's table as it is based on the Bohr's scheme for the arrangement of various electrons around the nucleus. Some important structural features of the long form of periodic table are given below -

(i) The first period is the shortest period. It consists of only two elements namely $_1$H and $_2$He corresponding to filling of electrons in the first energy shall i.e., n = 1. Since first period has only one orbital (i.e., 1s) therefore it can accommodate maximum two electrons or in turn two elements.

(ii) The second and third periods are short periods each consisting of 8 elements namely 3Li to 10Ne and 11Na to 18Ar. These periods have only four orbitals to be filled by 8 electrons and thus can accommodate eight elements each.

(iii) The fourth and fifth periods are long periods each consisting of 18 elements namely 19K to 36Kr and 37 Rb to 54Xe. Thus in each period, 18 elements are accommodated in nine orbitals (i.e., one s, three p and five d orbitals). These periods consist of d-block elements and thus called transition series.

(iv) The sixth period is the longest period and consist of 32 elements. The filling of electrons takes place in sixteen orbitals (i.e., one 6s, seven 4f, five 5d and three 6p). It consists of inner transition series known as lanthanide series.

(v) The seventh period is considered to be incomplete period. It is also expected to contain 32 elements corresponding to the filling of 16 orbitals (ie., one 7s, seven 5f, five 6d and three 7p). It has elements starting with 87Fr onwards. Elements from atomic number 93 onwards are purely synthetic and known as transuranium elements. are The number of elements and the corresponding orbitals are compiled in the following table

Table 7.1 Number of Elements and Number of Orbitals Filled in

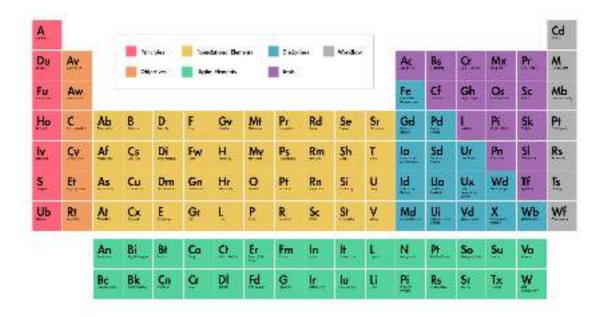| Period (n)	Orbitals being Filled up	Number of Electrons	Elements in the Period
First (1)	1s	2	2
Second (2)	2s, 2p	2 + 6	8
Third (3)	3s, 3p	2 + 6	8
Fourth (4)	4s, 3d, 4p	2 + 10 + 6	18
Fifth (5)	5s, 4d, 5p	2 + 10 + 6	18
Sixth (6)	6s, 4f, 5d, 6p	2 + 14 + 10 + 6	32
Seventh (7)	7s, 5f, 6d, 7p	2 + 14 + 10 + 6	32

Q.5. Write down the characteristics of modern periodic table.

Ans. Characteristics of modern periodic table are as follows - (i) Metallic and non-metallic elements have been separated. (ii) On the basis of filling of electrons in elements, all elements can be divided into s-block, p-block, d-block and f-block elements. (iii) Two subgroups of the same group are placed separately. (iv) Hydrogen is placed in group 1. (v) Fe, Co, Ni are placed with transition elements. (vi) Lanthanides and actinides are given appropriate places in modern periodic table.

(vii) Strongly metallic elements (s-block elements) are placed on left side of transition elements (d-block elements) in groups 1 and 2, transition elements are placed between groups 3 to 12 and non-metallic elements (pblock elements) at the right of transition elements from groups 3 to 17.

Q.6. Draw the long form of periodic table or modern periodic table.

Ans.

0.7. Classify elements according to the type of orbital.

Ans. The elements, as arranged in the long form of the periodic table, can so be divided into four blocks known as s-, p-, d- and f-block elements. This assification depends upon the type of the orbital (s, p, d or f) into which the st electron of the atom of the element enters.

(i) s-Block Elements - Elements in which the last electron enters es orbital are known as s-block elements. For example, among elements of tomic numbers 10, 11, 12 and 13 since the last electron enters the s-orbital ly in elements with atomic numbers 11 and 12, only these are said to be the embers of the s-block elements.

$$_{10}Ne \ 1s^2, \ 2s^2p^6$$

$$_{11}Na \ 1s^2, \ 2s^2p^6, \ 3s^1 \quad \text{s-block element (member of groups IA)}$$

$$_{12}Mg \ 1s^2, \ 2s^2p^6, \ 3s^2 \quad \text{s-block element (member of groups IIA)}$$

$$_{13}Al \ 1s^2, \ 2s^2p^6, \ 3s^2p^1$$

Since an s-orbital can accommodate a maximum number of two electrons, e s-block comprises of only two groups of the periodic table, i.e., group IA alkali metals) having one electron in the outermost s orbital and group IIA alkaline earth metals) having two electrons in the outermost s orbital. Thus he electronic configuration of group IA and IIA elements may be represented s ns and ns² respectively where n is the number of the outermost shell. Their (n-1) s, p and d orbitals are completely filled. Thus only the outermost erbital of these elements is incomplete.
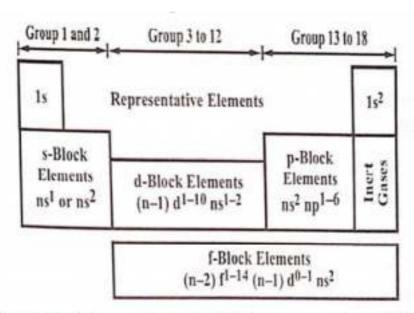
Fig. 7.1 Division of Periodic Table into s, p, d and f-Blocks

(ii) p-Block Elements - Elements in which p-orbitals are being progressively filled (i.e., elements in which last electron enters the p-orbital) are known as p-block elements. For example,

$_5B \quad 1s^2, 2s^2p^1 \qquad _8O \quad 1s^2, 2s^2p^4$

$_6C \quad 1s^2, 2s^2p^2 \qquad _9F \quad 1s^2, 2s^2p^5$

$_7N \quad 1s^2, 2s^2p^3 \qquad _{10}Ne \quad 1s^2, 2s^2p^6$

In the long form of the periodic table, p-block consists of elements of IIIA, IVA, VA, VIA, VIIA and zero groups whose outermost energy levels have the configurations ns^2np^1, ns^2np^2, ns^2np^3, ns^2np4, ns^2np5 and ns^2np6 respectively. Thus the general configuration of these elements is ns^2 pl-6 where n is the number of the outermost shell. Their (n-1) s, p and d orbitals are completely filled. Thus only the outermost orbital of these elements is incomplete. Since their properties are dependent on the presence of p-electrons, they are known as p-block elements. Elements having ns^2p6 configuration are also grouped separately as inert gases.

Elements of s- and p-blocks are called normal or representative elements.

(iii) d-Block Elements (Transition Elements) - Elements in which last electron enters the d-orbital (i.e. elements in which d-orbitals are being progressively filled) are known as d-block elements. In these elements, the last electron is added to the penultimate shell (inner to the outermost shell). Their two outermost orbitals are not complete or full. In the long form of the periodic table, d-block consists of elements of IIIB, IVB, VB, VIB, VIIB, VIII,

IB and IIB whose two outermost energy levels have the configurations varying from $(n - 1)$ $s^2p^0d^1$, ns^2 (in group IIIB) to $(n - 1)$ $s^2p^0d^{10}$, ns^2 (in group IIB). Since the properties of these elements are midway between those of s-block and p-block elements, they are known as transition elements. Their general electronic configuration is $(n - 1)d^{1-10}$ ns^{1-2}. - -

Transition (d-block) elements may again be divided into three series each having 10 elements -

(a) First Transition Series - In these elements, the last electron is added in the 3d orbital. This includes elements of fourth period from scandium (21Sc) to zinc (30Zn).

(b) Second Transition Series - In these elements, the last electron is added in the 4d orbital. This includes elements of fifth period from yttrium (39Y) to cadmium (48Cd).

(c) Third Transition Series - In these elements, the last electron is added in the 5d orbital. This includes elements of sixth period i.e. lanthanum (57La) and hafnium (72Hf) to mercury (80Hg).

(iv) f-Block Elements - Elements in which the last electron is added to any one of the seven f-orbitals (i.e. f-orbitals are being progressively filled) are called f-block elements. In all these elements, the last electron is added in the antepenultimate (third orbit from the outermost i.e. $n - 2$) shell. Thus f-block elements have their three outermost orbits incomplete. In these elements, the outermost shell (n) has only two electrons in s-orbital, the penultimate $(n-1)$ shell has 0 or 1 electron in the d-orbital and the antepenultimate $(n-2)$ hell has 1 to 14 electrons in the f-orbital. Thus the outer shell electronic configuration of f-block elements is given as -

$$(n - 2)f^{1-14} (n - 1) d^{0-1} ns^2$$

The f-block elements are also known as inner transition elements because iterally speaking they constitute transition series within transition series. There e two series of f-block elements each containing 14 elements classified on basis of the number of f-orbital (4f or 5f) being progressively filled. the

(a) Lanthanides or Rare Earths - In these elements, the last electron is being progressively added in the 4f orbital. This includes elements from cerium (58Ce) to lutetium (71Lu) which form a part of sixth period.

(b) Actinides - In these elements, the last electron is being progressively added in the 5f orbital. This includes elements from thorium (Th) to lawrencium (103Lw) which form a part of seventh period.

Q.8. What are the general characteristics of s-block and p-block elements?

Ans. **General Characteristics of s-Block Elements-**

(i) They are soft metals with low melting and boiling points.

(ii) They are highly reactive metals and provide univalent and bivalent ions by losing one or two valence electrons respectively.

(iii) They have low ionization energies and thus are highly electropositive.

(iv) They act as strong reducing agents.

(v) Most of the elements of this block impart characteristic colours to the flame.

(vi) They form ionic compounds.

General Characteristics of p-Block Elements -

(1) p-block elements include both metals and non-metals. The metallic character decreases and non-metallic nature of elements increases as we move along a period from left to right.

(ii) Their ionization energies are relatively higher as compared to s-block elements.

(iii) They form covalent compounds.

(iv) Majority of them show more than one oxidation state in their compounds.

(v) Their reducing character increases from top to bottom in a group and their oxidising character increases from left to right in a period.

Q.9. Write the characteristics of d-block and f-block elements,

Ans. **General Characteristics of d-Block Elements-**

(i) They are hard metals having high melting and boiling points.

(ii) They exhibit several oxidation states.

(iii) Their ionization energies lie between s- and p-block elements.

(iv) They form both the ionic and covalent compounds.

(v) They are good conductor of heat and electricity.

(vi) They form coloured ions and complexes. in nature.

(vii) Metals and their ions having unpaired electrons are paramagnetic

(viii) Most of the transition metals such as V, Mn, Fe, Co, Ni, Cu etc. act as catalyst.

(ix) Transition elements form alloys.

General Characteristics of f-Block Elements

(i) They are heavy metals.

(ii) They show high melting and boiling points.

(iii) They show variable oxidation states.

(iv) They have the tendency to form complexes.

(v) Their ions and complexes are generally coloured.

(vi) Elements of actinide series are radioactive in nature.

Q.10. What are the advantages and disadvantages of long form of the periodic table?

Ans. Advantages - Since long form of the periodic table classifies the elements on the basis of electronic configuration of their atoms, it has the following advantages -

(i) This classification is based on the atomic number of the elements, which is their fundamental property.

(ii) The elements in the same group show marked similarities in properties due to their similar outer electronic configuration.

(iii) It is easy to remember them and reproduce.

(iv) The systematic grouping of elements into four blocks i.e. s, p, d and f has made the study of these elements quite simple.

(v) Same position to the isotope of an element can be justified as have same atomic number but different atomic mass.

(vi) The position of few elements, which were misfit in Mendeleef's the basis of their atomic mass is now justified on the basis of atomic mber. For example, argon is assigned position before potassium because gon has atomic number 18 and potassium has 19.

(vii) The transition elements of fourth, fifth, sixth and seventh periods e assigned proper positions in the periodic table.

(viii) Three triads consisting of nine elements have been placed in oups 8, 9 and 10.

(ix) The lanthanides and actinides have been placed separately at the ottom of the table.

Disadvantages - Although the long form of the periodic table has simplified he study of chemistry of elements yet it suffers from the following sadvantages -

(i) Position of hydrogen is not properly settled. It has been placed longwith alkali metals (group I) and halogens (group VII) as it resembles oth in chemical properties.

(ii) 14 elements each of lanthanides and actinides have not been accommodated in the main body of the periodic table.

Q.11. How electronic configuration is useful to place an element in periodic table? Write the definition and trends of following in periodic table.

(i) Electron affinity (ii) Ionization energy. (R.GP.V., Nov. 2018)

Ans. The electron configuration of an atom is the representation of the arrangement of electrons distributed among the orbital shells and subshells. Commonly, the electron configuration is used to describe the orbitals of an atom in its ground state, but it can also be used to represent an atom that has ionized into a cation or anion by compensating with the loss of or gain of electrons in their subsequent orbitals. Many of the physical and chemical properties of elements can be correlated to their unique electron configurations. The valence electrons, electrons in the outermost shell, are the determining factor for the unique chemistry of the element.

(i) Definition and Trends of Electron Affinity - Electron affinity is defined as the change in energy (in kJ/mole) of a neutral atom (in the gaseous when an electron is added to the atom to form a negative ion. In other words, the neutral atom's likelihood of gaining an electron.

Electron affinity increases upward for the groups and from left to right across periods of a periodic table because the electrons added to energy levels become closer to the nucleus, thus a stronger attraction between the nucleus and its electrons. Remember that greater the distance, the less of an attraction; thus, less energy is released when an electron is added to the outside orbital. In addition, the more valence electrons an element has, the more likely it is to gain electrons to form a stable octet. The less valence electrons an atom has, the least likely it will gain electrons.

Electron affinity decreases down the groups and from right to left across the periods on the periodic table because the electrons are placed in a higher energy level far from the nucleus, thus a decrease from its pull. However, one might think that since the number of valence electrons increase going down the group, the element should be more stable and have higher electron affinity. One fails to account for the shielding affect. As one goes down the period, the shielding effect increases, thus repulsion occurs between the electrons. This is why the attraction between the electron and the nucleus decreased as one goes down the group in the periodic table.

As we go down the group, first electron affinities become less. Fluorine breaks that pattern, and will have to be accounted for separately. The electron affinity is a measure of the attraction between the incoming electron and the nucleus - the stronger the attraction, the more energy is released. The factors which affect this attraction are exactly the same as those relating to inonization energies - nuclear charge, distance and screening. The increased nuclear charge as we go down the group is offset by extra screening electrons. Each outer electron in effect feels a pull of 7+ from the centre of the atom, irrespective of which element you are talking about.

(ii) Definition and Trends of Ionization Energy-Ionization energy is the energy required to remove an electron from a gaseous atom or ion. The first or initial inonization energy or E, of an atom or molecule is the energy required to remove one mole of electrons from one mole of isolated gaseous atoms or ions.

Ionization, together with atomic and ionic radius, electronegativity, electron affinity and metallicity, follows a trend on the periodic table of elements.

Ionization energy generally increases moving from left to right across an element period (row). This is because the atomic radius generally decreases moving across a period, so

there is a greater effective attraction between the negatively charged electrons and positively-charged nucleus. Ionization is at

minimum value for the alkali metal on the left side of the table and a maximum the noble gas on the far right side of a period. The noble gas has a filled tence shell, so it resists electron removal.

S S Ionization decreases moving top to bottom down an element group (column). is is because the principal quantum number of the outermost electron increases oving down a group. There are more protons in atoms moving down a group reater positive charge), yet the effect is to pull in the electron shells, making em smaller and screening outer electrons from the attractive force of the cleus. More electron shells are added moving down a group, so the outermost ectron becomes increasingly distance from the nucleus.

Q.12. Write brief note on electron affinity.(R.G.P.V., May 2019)

Ans. Refer to Q.11 (i).

Q.13. What do you understand by periodic properties of elements ? Discuss its important properties.

Ans. Most of the properties of the elements such as valency, atomic size, cnisation energy and electron affinity and electronegativity are directly related to te electronic configuration of atoms. These properties undergo periodic variation ith the change in atomic number within a period or a group. These properties directly control the physical properties such as melting point, boiling point, density c. of elements. Some important properties are discussed below - 1

(i) Valency and Oxidation State-Combining capacity of an element 3 1 > r s known as its valency. It is generally expressed in terms of the number of hydrogen atoms or the number of chlorine atoms or double the number of oxygen atoms that combine with an atom of the element. As discussed earlier, the properties of an element usually depend upon the number of electrons present in the valence shell i.e., the number of electrons present in the last orbit. Therefore, the electrons present in the outermost shell are called valence 1 electrons and these electrons determine valency of the atom.

1 ; 1 In case of s-block and d-block elements (known as representative elements) the valency is generally equal to the either the number of valence electrons or equal to eight minus the number of valence electrons. However, the transition elements (d-block elements) and inner transition elements (fblock elements) exhibit variable valency.

(a) Variation of Valency in the Periodic Table - The number of valency electrons increases from 1 to 8 on moving across a period from left to right. However, valency of element along a period with respect to hydrogen or chlorine increases from 1 to 4 and then decreases to zero. This may be illustrated by taking the elements of second and third periods as shown below in table 7.3.

Table 7.3 Variation of Valency of Elements of Second and Third

Periods

Elements of Second Period								
Elements of 2nd period	Li	Be	B	C	N	O	F	Ne
Compounds with hydrogen	LiH	BeH_2	BH_3	CH_4	NH_3	H_2O	HF	–
Compounds with chlorine	LiCl	$BeCl_2$	BCl_3	CCl_4	NCl_3	Cl_2O	ClF	–
Valency w.r.t. H or Cl	1	2	3	4	3	2	1	0

Elements of Third Period								
Elements of 3rd period	Na	Mg	Al	Si	P	S	Cl	Ar
Compounds with hydrogen	NaH	MgH_2	AlH_3	SiH_4	PH_3	H_2S	HCl	–
Compounds with chlorine	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	SCl_2	Cl_2	–
Valency w.r.t. H or Cl	1	2	3	4	3	2	1	0

(b) Variation of Valency in a Group - On moving down a group, the number of valency electrons remain the same, therefore, all the elements in a group exhibit same valency. For example, all elements of group 1 (i.e. alkali metals) and of group 2 (i.e. alkaline earth metals) have valency 1 and 2 respectively. Similarly, all noble gases present in group 18 are chemically inert and exhibit zero valency.

The arbitrary charge assigned to an atom in a compound is known as its oxidation number or oxidation state. Transition and inner transition metals exhibit variable oxidation numbers.

(ii) Atomic and Ionic radii - The radius of an atom (known as atomic radius) is the distance between the centre of its nucleus and electron in the outermost orbit. Although atomic radius or atomic size is very important property of an atom because most of the chemical and physical properties shown by an atom are related to its atomic size yet it is not possible to find out the exact radius of the atom because of the following reasons.

(a) Size of an atom is very small and hence it is not possible to isolate a single atom to measure its radius.

(b) According to probability distribution of electrons, an atom does not have well defined boundary. Furthermore, the probability of finding the electron is never zero even at large distance from the nucleus.

(c) The probability distribution is also affected by the presence of other atoms in its neighbourhood.

(d) Atomic radius also changes from one bonding state to another.

(iii) Ionization Energy (or Ionization Potential) - When an atom sorbs energy, the electrons from the outermost orbit are promoted to higher ergy levels. If supplying of energy is continued, the electron goes off mpletely from the influence of nucleus. Such removal of electron from an om will result in the formation of a cation (i.e. a positive ion) and the amount energy required for ionization of electron is termed as ionization energy or nization potential.

$M(g) + Energy\ M^*(g) + e$

here $M(g)$ and $M^*(g)$ represent metal atom and metal cation in gaseous ate.

Thus, ionization energy may be defined as the amount of energy required remove an electron from the outermost orbit of an isolated atom in the seous state.

Successive Ionization Energy - The energy corresponding to the onization of the most loosely bound electron from an atom in gaseous state is called its first ionization energy denoted by IE_1 e.g.,

$M(g) + IE_1 \rightarrow\rightarrow\rightarrow\rightarrow M^*(g) + e$

Similarly, the amount of energy required to remove one more electron from unipositive ion is termed second ionization energy. it is denoted by IE_2. Likewise the energy required to knock out third and fourth electrons from dipositive and tripositive ions are called IE3 and IE4 respectively.

$$M^*(g) + IE_2 \rightarrow M^2+(g) + e$$

$$M^2+(g) + IE3 \rightarrow\rightarrow\rightarrow\rightarrow M^3+(g) + e$$

$$M^3+(g) + IE4 \rightarrow\rightarrow M4+(g) + e$$

It may be noted that $IE4 > IE3 > IE2 > IE_1$

(iv) Electron Affinity- It is defined as the amount of energy released when an extra electron is taken up by a neutral gaseous atom to form monovalent gaseous anion, e.g.,

$X(g) + e- \rightarrow\rightarrow\rightarrow\rightarrow X-+ Energy$

The magnitude of electron affinity is the force with which the atom can hold an extra electron i.e. greater the electron affinity value greater is the tendency of atom to accept the electron.

Units of Electron Affinity - Electron affinity values are expressed either in electron volt (eV) or kJ mole-^{1}. Its values are determined indirectly with the help of Born-Haber cycle.

Successive Electron Affinities - When an electron is added to gaseous atom, the energy is released and the atom becomes negative iron or anion. However, the addition of second electron to an anion is opposed by electrostatic repulsion and hence the energy has to be supplied for the addition of second electron. Therefore, the second and successive electron affinities of an element are negative. For example,

First E.A. O(g) + e- = + 141.0 kJ mole-¹ (Energy is released) (g); EA₂ 780.0 kJ mole-1
Second E.A. - 0→ O¯ (g); EA₁ + e == (Energy is absorbed)

(v) Electronegativity - The tendency of an atom in a compound to attract a pair of bonded electrons towards itself is known as electronegativity of the atom. It is important to note that electron affinity and electronegativity both measure the electrons attracting power but the former refers to an isolated gaseous atom while the latter to an atom in a compound. Thus electron affinity is attraction for a single electron while electronegativity is for a pair of bonded electrons. Further, electron affinity is energy while electronegativity is a tendency.

Electronegativity depends upon (a) the size of the atom and (b) electronic configuration.

Small atoms attract electrons more than the larger one and are therefore more electronegative. Secondly, atoms with nearly filled shells of electrons, will tend to have higher electronegativity than those which are sparsely occupied.

(a) Variation of Electronegativity in a Period-Along a period electronegativity increases from left to right. This is due to decrease in size and increase in nuclear charge. Thus alkali metals possess the lowest values, while halogens have the highest. Inert gases have zero electronegativity.

(b) Variation of Electronegativity in a Group - Within a group electronegativity decreases from top to bottom. This is due to increase in atomic size.

If an element exhibits various oxidation states, the atom in the higher oxidation state will be more electronegative due to greater attraction for the electron, i.e., Sn II (1.30) and Sn IV (1.90).

Concept of electronegativity may predict following properties -

(a) If the two atoms have similar electronegativities, the bond between them will be covalent (i.e., a weak bond), while a large difference in electronegativities leads to an ionic bond (i.e., a strong bond). It is observed at when the difference between the electronegativities of the two atoms is 1, the bond formed between them will be 50% ionic in character.

(b) Since a covalent bond is a weaker bond, while an ionic bond a stronger bond, greater the ionic percentage character of a bond more is its ability. Percent ionic character of a bond may be calculated using Hannay d Smyth equation.

$$\text{\% Ionic character} = 16 (X_A - X_B) + 3.5 (X_A - X_B)^2$$

here ($X_A - X_B$) are electronegativities difference between A and B. For example, e percent ionic character between H and F bond can be calculated as follows.

Electronegativities of F and H are 4.0 and 2.1 respectively.

$$\text{\% Ionic character in HF} = 16 (4.0 2.1) + 3.5 (4.0 - 2.1)^2 = 43\%$$

(c) Greater the electronegativity of an element, greater is its endency to gain electrons (greater oxidising power) and hence more is its on-metallic properties.

Conversely, the electropositive character (the tendency of an atom to se its valence electrons) decreases across the period and increases down the soups. Alkali metals (group 1) are the most electropositive followed by alkaline arth metals (group 2). Oxides of these elements become increasingly acidic cross a period, but increasingly basic down a group.

Since electronegativity is a relative property, it has no units. Electronegativity may be expressed on the Mulliken's scale.

Mulliken's Scale - Mulliken regarded electronegativity as the average value of ionization potential and electron affinity of an atom.

$$\text{Electronegativity} = \frac{\text{Ionization potential} + \text{Electron affinity}}{2}$$

Q.14. Explain the types of atomic radius or size.

Ans. In order to explain various chemical properties of different elements in terms of atomic or ionic radii, three operational concepts of atomic radius are widely in use.

(i) Covalent Radius It is defined as one half of the distance between the centres of nuclei of two covalently bonded atoms of the same element. Thus covalent radius of carbon in a compound having C-C single bond (i.e. homonuclear diatomic molecule) can be determined by dividing the bond length by two i.e. -

$$r_{covalent} = \frac{1}{2} [\text{Internuclear distance between two covalently bonded atoms}]$$

Since the internuclear distance between two bonded atoms is known as bond length,

$$r_{covalent} = \frac{1}{2} [\text{ Bond length}]$$

or r_{H-H} covalent $= \left[\dfrac{H-H}{2}\right]$ i.e. $\dfrac{1}{2}$ [Bond distance between two H atoms]

or $H - H$ bond distance $= 2r_{covalent}$

For example, the internuclear distance between two hydrogen atoms in H_2 molecule is 0.74 Å (or 74 pm). Hence the covalent radius of hydrogen atom is equal to 0.37 Å (or 37 pm). Similarly, atomic radius of fluorine is

$$\frac{\text{Bond distance between } F-F}{2} = \frac{144}{2}$$

$$= 72 \text{ pm (or } 0.72 \text{ Å)}$$

|←—1.44 Å—→|

Covalent Radius
$= \dfrac{1.44}{2} = 0.72 \text{ Å}$

Fig. 7.2 Covalent Radius of Fluorine Atom

$$\text{Atomic radius of chlorine} = \frac{\text{Bond distance between } Cl - Cl}{2}$$

$$= \frac{198}{2} = 99 \text{ pm (or } 0.99 \text{ Å)}$$

(ii) Vander Waal's Radius - It is defined as one-half of the distance between the centres of nuclei of two adjacent non-bonded atoms belonging to two neighbouring molecules of an element in the solid state.

For example, the internuclear distance between two adjacent chlorine atoms of the two neighbouring Cl_2 molecules in the solid state is 360 pm.

Therefore, the Vander Waal's radius of chlorine atom is 360 pm = 180 pm or 2 1.8 Å.

Similarly, the internuclear distance between two adjoining H-atoms of neighbouring hydrogen molecules in the solid state is 240 pm (or 2.4 Å).

Therefore, Vander Waal's hydrogen radii 240 120 pm or 1.2 Å.

(iii) Metallic Radius - It is defined as one half of the internuclear distance between the centres of two adjacent atoms in the metallic crystal. The internuclear distance between the two adjacent atoms in a metallic crystal is longer than the internuclear distance between the two atoms linked by a covalent bond. Due to overlapping of atomic orbitalsthe covalent bond

ecomes short. It suggests that metallic bond is weaker than a covalent ond. Therefore, metallic radius of an element is greater than its covalent adius. For example, metallic and covalent radius of potassium are 2.31 and 1.03 Å respectively.

Q.15. Compare covalent radius with Vander Waal's radius.

Ans. Vander Waal's forces between two non-bonded isolated atoms is veak and its magnitude depends upon the packing of atoms when the element s in the solid state. Contrary to it, a covalent bond is formed by overlapping of tomic orbitals and the overlap region becomes common between the two atoms, therefore, the covalent radii is always shorter than the atomic radii of non-bonded adjoining atoms (i.e. Vander Waal's radii).
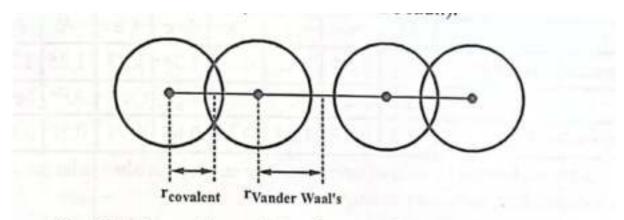

$r_{covalent}$ $r_{Vander\ Waal's}$

Fig. 7.3 Comparison of Covalent and Vander Waal's Radius

Q.16. Write explanatory note on ionic radii.

Ans. Ions are formed when neutral atoms either lose or gain electrons. When a neutral atom loses one or more electrons a cation is formed whereas gain of one or more electrons by a neutral atom results in the formation of anion. Thus radius of an ion decreases by lose of electron and increases by gain of electron. Therefore, ionic radius may be defined as the effective distance from the centre of the nucleus of the ion upto which it exerts its influence on its electron cloud.

A cation (formed by the removal of one or more electrons from an atom) is always much smaller than the corresponding atom. Further, greater the number of electrons removed smaller will be the size of the resulting positive ion. For example,

$$Atomic\ radius\ of\ Fe = 1.26\ Å$$

$$Ionic\ radius\ of\ Fe^{2+} = 0.76\ Å$$

$$Ionic\ radius\ of\ Fe^{3+} = 0.64\ Å$$

This is due to following two factors -

(i) A cation formed by the loss of electrons may result in the complete disappearance of the outer shell and since the remaining inner shells

do not extend so far in space, the cation is much smaller than the metal atom. For example,

Sodium atom (Na) → Sodium ion (Na+)

(2, 8, 1)   (2,8)

(ii) Whenever a cation is formed, the ratio of nuclear charge to the number of electrons (Z/e ratio) is increased with the result the effective nuclear charge is increased and electrons are pulled towards the nucleus. Consequently, the cation becomes smaller. Table 7.4 illustrates the comparative size of atoms and their cations.

Table 7.4 Comparative Size of Atoms and their Cations

Atom	Li	Na	K	Be	Mg	Ca	Al	Fe
Atomic radii (Å)	1.23	1.54	2.02	0.89	1.36	1.97	1.25	1.26
Corresponding cation	Li^+	Na^+	K^+	Be^{2+}	Mg^{2+}	Ca^{2+}	Al^{3+}	Fe^{3+}
Ionic radii (Å)	0.60	0.95	1.33	0.39	0.65	0.99	0.50	0.64

An anion (formed by gain of one or more electrons) is always larger than the corresponding atom. For example,

Atomic radius of Cl = 0.99 Å

Ionic radius of Cl- = 1.81 Å

The reason for increase in ionic radius is due to following factors.

(i) Due to addition of one or more electrons, the electron cloud expands and the ionic size increases.

(ii) In the formation of anion the effective nuclear charge decreases which results in expansion of electron cloud. Thus the anion becomes larger than the corresponding atom.

Comparative sizes of atoms and their anions may be illustrated in table 7.5.

Table 7.5 Comparative Sizes of Atoms and their Anions

Table 7.5 Comparative Sizes of Atoms and their Anions

Atom	F	Cl	Br	I	O	S	N
Atomic radii (Å)	0.72	0.99	1.14	1.33	0.74	1.02	0.75
Corresponding anion	F^-	Cl^-	Br^-	I^-	O^{2-}	S^{2-}	N^{3-}
Ionic radii (Å)	1.36	1.81	1.95	2.16	1.42	1.84	1.71

Q.17. Give the reason for increase the units of ionization energy. Write of successive ionization energy.

Ans. After the removal of first electron, the atom changes to unipositive ion. In unipositive ionic state, the number of electrons have reduced but the

nuclear charge remains the same. As a result of this the effective nuclear charge per electron increases and the electrons are held more firmly by the nucleus. Therefore, greater amount of energy is required to remove the second electron i.e. $IE_2 > IE_1$. Similarly, successive removal of electrons further increases the effective nuclear charge per electron and hence successive ionization energies increase. Thus, $IE3 > IE_2 > IE_1$.

The values of IE_1, IE2 and IE3 for the first ten elements are tabulated in table 7.6.

Table 7.6 Values of IE_1, IE_2 and IE_3 for the First Ten Elements

Atomic Number	Symbol	Valence Configuration	Ionization Potential		
1	H	$1s^1$	13.6	–	–
2	He	$1s^2$	24.0	54.5	–
3	Li	$2s^1$	5.4	75.6	122.4
4	Be	$2s^2$	9.3	18.2	153.8
5	B	$2s^2\ 2p^1$	8.3	25.1	38.0
6	C	$2s^2\ 2p^2$	11.2	24.3	48.0
7	N	$2s^2\ 2p^3$	14.5	29.6	57.0
8	O	$2s^2\ 2p^4$	13.6	35.1	55.0
9	F	$2s^2\ 2p^5$	17.4	35.0	63.0
10	Ne	$2s^2\ 2p^6$	21.6	41.0	64.0

Units of Ionization Energy - Ionization energy is measured in units of <ilocalories/mole or kilojoules/mole. It is also measured in units of electron volts (eV) where one electron volt is the energy acquired by an electron while noving under a potential difference of one volt. These units are interrelated to each other as follows -

$$1 \text{ electron volt (eV) per atom} = 23.05 \text{ kCal mol}^{-1} = 96.49 \text{ kJ mol}^{-1}$$

Q.18. Discuss various factors affecting the values of ionization energy.

Ans. Ionization energy depends upon the following factors -

(i) Atomic size or radius

(ii) Nuclear charge

(iii) Penetration effect of the electron

(iv) Screening effect

(v) Stable electronic configuration.

(i) Atomic Size or Radius - The larger the atomic size, smaller is the ionization energy. As the size of the atom increases down the the outer electrons lie farther away from the nucleus and thus exert less attraction towards the nucleus. Hence electron can be easily removed. Similarly, as we move along a period from left to right, atomic size decreases and the nuclear charge increases. As a result of this ionization energy increases along a period. Ionization energies of alkali metals are given in table 7.7.

Table 7.7 First I.E. of Alkali Metals in kJ mole⁻¹

Element	Li	Na	K	Rb	Cs
I.E. (kJ mole⁻¹)	520	495	418	403	374

(ii) Nuclear Charge - The effective nuclear charge of a neutral atom or ion is defined as the net nuclear attraction towards the valence shell electrons. Greater is the effective nuclear charge, more tightly the electrons are held with the nucleus and thus more energy will be required to remove electrons from the atom.

On moving along the period the charge on nucleus increases as the atomic number increases while the valence shell remains the same and thus effective nuclear charge increases which leads to higher ionization energy. Therefore, ionization energy increases along the period with some disorders.

Increase in positive charge on the ion increases the effective nuclear charge which in turn increases the ionization energy. On the other hand, increase in negative charge on the ion decreases the effective nuclear charge which in turn decreases the ionization energy.

First I.E. of the elements of second period are compiled in table 7.8.

Table 7.8 First I.E. of Second Period Elements

Elements	Li	Be	B	C	N	O	F	Ne
Nuclear charge	+3	+4	+5	+6	+7	+8	+9	+10
I.E. (kJ mole^{-1})	520	900	800	1086	1403	1314	1681	2081

First ionization energies (in eV) of representative elements are given in table 7.9.

Table 7.9 First Ionization Energies of Representative Elements

Group	s-block		p-block Elements					
Period	1	2	13	14	15	16	17	18
1	H 13.6							He 24.6
2	Li 5.4	Be 9.3	B 8.3	C 11.2	N 14.5	O 13.6	F 17.4	Ne 21.6
3	Na 5.1	Mg 7.6	Al 6.0	Si 8.1	P 11.0	S 10.4	Cl 13.0	Ar 15.8
4	K 4.3	Ca 6.1	Ga 6.0	Ge 7.8	As 9.8	Se 9.8	Br 11.8	Kr 14.0
5	Rb 4.2	Sr 5.7	In 5.7	Sn 7.3	Sb 8.6	Te 9.0	I 10.4	Xe 12.1
6	Cs 3.9	Ba 5.2	Tl 6.1	Pb 7.4	Bi 7.2	Po 8.4	At –	Rn 10.7

(iii) Penetration Effect of Electrons - Ionization energy increases as the penetration effect of electrons increases in an atom. In a multielectron atom, the electrons of s-orbital is more close to nucleus than the p-orbital of the same orbit. Therefore, s electrons will experience more attraction than p-electrons. Hence their removal is difficult leading to higher I.E. Likewise I.E. of p-electrons will be more than I.E. of d-electrons and so

In general, the ionization energy follows the following order.

s>p>d> forbital of the same orbit.

Mg. This difference in For example, first I.E. of Al is lower than that I.E. can be explained due to penetration effect of the outermost electron.

12 Mg = 1s² 2s²2p6 3s²

13Al = 1s² 2s²2p6 3s² 3p¹

Hence, during ionization of one electron from Al to form Al*, is ionized from p-orbital whereas in case of Mg the electron is knocked out from s-orbital of the same energy shell. Since the energy required to remove p-electron is less than the s-electron of the same energy shell, the first I.E. of Al is lower than that of Mg. Similarly, the first I.E. of B (1s² 2s² 2p') is lower than that of Be (1s² 2s²). shielding

(iv) Screening Effect (or Shielding Effect) - Screening or effect is defined as the effect caused by inner electrons on the attraction of the outermost electrons by the nucleus. As the screening effect increases, the ionization energy decreases.

Larger the number of electrons in the inner shell, greater is the screening effect on the electrons in the outer (valency) shell. Thus electron experiences less attraction from the nucleus and can be easily removed leading to the lower value of ionization potential. Now as we move down a group, the number of inner shells increases and hence the ionization potential tends to decrease.

The actual charge felt by the valence shell electrons is called effective nuclear charge (Z_{eff}). Therefore, the effective nuclear charge is given as

Z_{eff} = Total nuclear charge (Z) - Screening constant (S)

where screening constant (S) takes into account the number of electrons present in the inner shell. Thus greater the number of electrons in the inner shells, more will be the screening effect. Obviously it will result in less attraction by the nucleus for the valence shell electrons and hence I.E. decreases.

Slater gave a set of empirical rules for calculating S, i.e. screening constant in a polyelectronic system. The Slater rules are as under -

(a) Electrons present in higher quantum shells are incapable of shielding electrons in the lower shells and thus give no contribution towards screening constant.

(b) All electrons in the ns, np group contribute to the extent of 0.35 each to screening constant (S).

(c) All electrons in the (n-1)th shell contribute 0.85 each to the screening factors (S).

(d) All electrons in (n - 2)th shell or lower shells shield the electrons in the nth shell completely. Their contribution to the screening constant is 1.0 each.

(e) All the electrons in the groups lying left to the nd or nf orbital shield the d or f electrons completely and contribute 1.0 each to S.

(v) Stable Electronic Configuration - According to Hund's rule, atoms containing exactly half filled or completely filled orbitals have extra stability. Obviously the removal of an electron from such an atom requires more energy than expected. For example,

(a) I.E. of Be> I.E. of B-Since Be has fully filled orbitals (i.e. $1s^2 2s^2$), the knocking of electron needs higher ionization energy. Similarly, I.E. of Mg is greater than I.E. of Al.

(b) I.E. of N> I.E. of O- Electronic configuration of nitrogen ($1s^2 2s^2 2p1 2p 2p$) shows that its valence electrons are exactly half filled

which provide extra stability to the atom. As a result, the removal of electron from N becomes difficult and its I.E. becomes higher than that of oxygen. Similarly, I.E. of P is greater than I.E. of S.

(c) Inert Gas Electronic Configuration of Atom or Ion - If an atom or an ion has $ns^2 np6$ configuration, its ionization energy is extremely high due to the presence of the so-called octet arrangement. To sum up, we can say that greater the stability of electronic configuration of atom, greater is the ionization energy.

Q.19. What are the factors influencing the value of electron affinity?

Ans. Important factors which influence the electron affinity of an atom are discussed below -

(i) Size of the atom

(ii) Nuclear charge

(iii) Electronic configuration.

(i) Size of the Atom - With the increase in size of the atom, the distance between the nucleus and the last orbit which receives the incoming electron also increases. As a result of this the force of attraction between the nucleus and the incoming electron decreases. Thus the electron affinity decreases with increase in size of atom.

(ii) Nuclear Charge - Greater the magnitude of nuclear charg greater will be the force of attraction between the nucleus and incoming electron. Thus, electron affinity increases with increase in nuclear charge.

(iii) Electronic Configuration - Atoms having stable electronic configuration (i.e. half filled or completely filled orbitals) show no tendency to accept additional electron. Hence their electron affinity is almost zero.

Q.20. Distinguish between electron affinity and electronegativity.

Ans. Difference between electron affinity and electronegativity are follows.

Electronegativity	Electron affinity
It is the chemical property that decides the tendency of atom to attract electros in a covalent bond	It is the amount of energy the atom exerts when the electrons is added to neutral atom or molecule to make it into negative ion
Example: Cl-F In this molecule the most electronegative atom is F	Example: $Cl + e^- \rightarrow Cl^-$ -349KJ/mole Negative charge shows the release of energy
Concept of electronegativity used to explain covalent bond and bond polarity	It is the energy and can easily be measured by measuring the amount of energy released when an e is added
It is a property	It is a measurement.

Q.21. What is polarizability? Give its examples.(R.G.P.V., May 2019)

Or

Write short note on polarizability.

Ans. Polarizability is a measure of how easily an electron cloud is distorted by an electric field. Typically the electron cloud will belong to an atom or molecule or ion. The electric field could be caused, for example, by an electrode or a nearby cation or anion.

If an electron cloud is easy to distort, we say that the species it belongs to is polarizable. Polarizability, which is represented by the Greek letter, alpha, a, is experimentally measured as the ratio of induced dipole moment p to the electric field E that induces it -

$$\alpha = \frac{p}{E}$$

The units of a are cm^2V^{-1}..

Examples -

(i) Large, negatively charged ions, like I and Br, are highly polarizable. (ii) Small ions with high positive charge, like $Mg2+$ and $A1^{3+}$ have low polarizability, but they have a high ability to polarize polarizable species, like I and Br.

(iii) In ordinary usage polarizability refers to the mean polarizability, i.e., the average over the x, y, z axes of the molecule. Polarizabilities in different directions (e.g. along the bond in Cl_2, called longitudinal polarizability, and in the direction perpendicular to the bond, called transverse polarizability) can be distinguished, at least in principle.

Q.22. What are the factors that affect polarizability?

Ans. The relationship between polarizability and the factors of electron density, atomic radii and molecular orientation is as follows -

(i) The greater the number of electrons, the less control the nuclear charge has on charge distribution, and thus the increased polarizability of the atom.

(ii) The greater the distance of electrons from nuclear charge, the less control the nuclear charge has on the charge distribution, and thus the increased polarizability of the atom.

(iii) Molecular orientation with respect to an electric field can affect polarizability (labeled orientation-dependent), except for molecules that are - tetrahedral, octahedral or icosahedral (labeled orientation-independent). This factor is more important for unsaturated molecules that contain areas of electron dense regions, like 2-4 hexadiene. Greatest polarizability in these molecules is achieved when the electric field is applied parallel to the molecule rather than perpendicular to the molecule.

Q.23. Write generic definition of oxidation state.

Ans. The oxidation state is the atom's charge after ionic approximation of its bonds. The terms to be clarified are the atom's charge, its bonds, and the ionic approximation.

The atom's charge is the usual count of valence electrons relative to the free atom. The oxidation state is a quantitative concept that operates on integer values of counted electrons. This may require idealizing visual representations or rounding off numerical results.

Approximating all bonds to be ionic may lead to unusual results. If the N= N bond in N_2O were extrapolated to be ionic, the central nitrogen atom would have an oxidation state of +5 and the terminal one-3. To obtain less extreme values, bonds between atoms of the same element should be divided equally upon ionic approximation.

Several criteria were considered for the ionic approximation -

(i) Extrapolation of the bond's polarity -

(a) from the electronegativity difference

(b) from the dipole moment

(c) from quantum-chemical calculations of charges.

(ii) Assignment of electrons according to the atom's contribution to the molecular orbital (MO).