# QUESTION BANK

## XII STANDARD CHEMISTRY

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# UNIT – 1 METALLURGY

## I. TEXT BOOK QUESTIONS AND ANSWERS

**1. What is the difference between minerals and ores? (SEPT-2020, MAY-2022)**

| S No. | Minerals | Ores |
|---|---|---|
| 1 | Naturally occurring substances obtained by mining which contain the metals in free state or in the form of compounds like oxides, sulphides, etc. are called minerals. | Minerals that contain high percentage of metal from which it can be extracted conveniently and economically are called ores. |
| 2 | Mineral of A*l* is Bauxite ($Al_2O_3\ nH_2O$ ) and China clay ($Al_2O_3\ SiO_2\ .2H_2O$ ) | Ore of A*l* is Bauxite ($Al_2O_3\ nH_2O$ ) |

**2. What are the various steps involved in extraction of pure metals from their ores?**

i) Concentration of the ore

ii) Extraction of the crude metal.

iii) Refining of the crude metal.

**3. What is the role of Limestone in the extraction of Iron from its oxide $Fe_2O_3$? (JULY-2020)**

Lime stone ($CaCO_3$) is a basic flux

Limestone decomposes to form CaO

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

Impurity silica ($SiO_2$) react with CaO form fusible slag calcium silicate.

$CaO_{(s)} + SiO_{2(s)} \rightarrow CaSiO_{3(s)}$

Flux Gangue Slag

**4. Which type of ores can be concentrated by froth flotation method? Give two examples for such ores. (JULY-2020)**

Sulphide ores - concentrated - froth flotation method. (eg) Galena (PbS), Zinc blende (ZnS)

**5. Out of coke and CO, which is better reducing agent for the reduction of ZnO? why?**

Coke is better reducing agent than CO for the reduction of ZnO.

$ZnO_{(s)} + C \rightarrow Zn_{(s)} + CO_{(g)}\uparrow$

In Ellingham diagram formation ZnO line lies above the formation C→ CO at low temperature ($T_1$), and above the CO → $CO_2$ but at high temperature

Hence carbon can be used as a better reducing agent than CO for the reduction of ZnO.

Below the temperature $T_1$ both Coke and CO cannot reduce ZnO

**6. Describe a method for refining nickel. (Mond's process) (MAY-2022)**

Impure nickel is heated in a stream of carbon monoxide at around 350K. Nickel reacts with CO to form a highly volatile nickel tetracarbonyl. The solid impurities are left behind.

$Ni_{(s)} + 4CO_{(g)} \xrightarrow{350\ K} Ni[CO]_{4\,(g)}$

On heating nickel tetra carbonyl around 460K, decomposes to give pure nickel.

$Ni[CO]_{4\,(g)} \xrightarrow{460\ K} Ni_{(s)} + 4CO_{(g)}$

**7. Explain zone refining process with an example (MARCH-2020)**

The principle is fractional crystallisation.

When an impure metal is melted and allowed to solidify, the impurities will prefer to remain in the molten region. ie; impurities are more soluble in the melt than in the solid state metal.

In this process the impure metal is taken in the form of a rod. One end of the rod is heated using a mobile induction heater, melting the metal on that portion of the rod.

When the heater is slowly moved to the other end pure metal crystallises while impurities will move on to the adjacent molten zone formed due to the movement of the heater.

As the heater moves further away, the molten zone containing impurities also moves along with it.

This process is repeated several times by moving the heater in the same direction again and again to achieve the desired purity level.

This process is carried out in an inert gas atmosphere to prevent the oxidation of metals.

Germanium, Silicon and Gallium which are used as semiconductor are refined by this process.

**8. Using the Ellingham diagram given below.**

**A) Predict the conditions under which**

**i) Aluminium might be expected to reduce magnesia.** **ii) Magnesium could reduce alumina.**

**B) Carbon monoxide is more effective reducing agent than carbon below 983K but, above this temperature, the reverse is true - Explain.**

**C) It is possible to reduce $Fe_2O_3$ by coke at a temperature around 1200K**

**A)** **i)** Ellingham diagram for the formation of $Al_2O_3$ and MgO intersects around 1600K. Above this temperature aluminium line lies below the magnesium line. Hence we can use aluminium to reduce magnesia above 1600K.

**ii)** In Ellingham diagram below 1600K magnesium line lies below aluminium line. Hence below 1600K magnesium can reduce alumina.

**B)** The two lines for $CO \rightarrow CO_2$ and $C \rightarrow CO$ cross at about 983K. Below this temperature the reaction to form $CO_2$ is energetically more favourable hence CO is more effective reducing agent than carbon. But above 983K the formation of CO is preferred, hence carbon is more effective reducing agent than CO above this temperature.

**C)** In Ellingham diagram above 1000K carbon line lies below the iron line. Hence it is possible to reduce $Fe_2O_3$ by coke at a temperature around 1200K.

**9. Give the uses of zinc.**

1. Metallic zinc is used in galvanisation to protect iron and steel from rusting and corrosion.
2. Zinc is used to produce die - castings in the automobile, electrical and hardware industries.

3. Zinc oxide is used in the manufacture of paints, rubber, cosmetics, pharmaceuticals, plastics, inks, batteries, textiles and electrical equipment.
4. Zinc sulphide is used in making luminous paints, fluorescent lights, and x - ray screens.
5. Brass an alloy of zinc is used in water valves and communication equipment as it is highly resistant to corrosion

**10. Explain the electrometallurgy of aluminium.**

Hall - Herold Process

Cathode: Iron tanked lined with carbon

Anode: Carbon blocks

Electrolyte: 20% solution of alumina obtained from bauxite + Molten Cryolite + 10% calcium chloride (lowers the melting point of the mixture)

Temperature: Above 1270K

Ionisation of Alumina $Al_2O_3 \rightarrow 2Al^{3+} + 3O^{2-}$

Reaction at cathode : $2Al^{3+}(melt) + 6e^{-} \rightarrow 2Al_{(l)}$

Reaction at anode : $6O^{2-}(melt) \rightarrow 3O_2 + 12e^{-}$

Since carbon acts as anode the following reaction also takes place on it.

$C_{(s)} + O^{2-}(melt) \rightarrow CO + 2e^{-}$

During electrolysis anodes are slowly consumed due to the above two reactions.

Pure aluminium is formed at the cathode and settles at the bottom.

Net electrolysis reaction is

$4Al^{3+}(melt) + 6O^{2-}(melt) + 3C_{(s)} \rightarrow 4Al_{(l)} + 3CO_{2(g)}$

**11. Explain the following terms with suitable examples. i) Gangue ii) Slag (SEPT-2020)**

**i) Gangue:**

The non-metallic impurities, rocky materials and siliceous matter present in the ores are called gangue. (eg): $SiO_2$ is the gangue present in the iron ore $Fe_2O_3$ .

**ii) Slag:** Slag is a fusible chemical substance formed by the reaction of gangue with a flux.

$$\underset{\text{Flux}}{CaO_{(s)}} + \underset{\text{gangue}}{SiO_{2(s)}} \rightarrow \underset{\text{slag}}{CaSiO_{3(s)}}$$

**12. Give the basic requirement for vapour phase refining.**

The metal is treated with a suitable reagent to form a **volatile compound.**

Then the **volatile compound is decomposed to give the pure metal** at high temperature.

**13. Describe the role of the following in the process mentioned.**

**i) Silica in the extraction of copper.**

**ii) Cryolite in the extraction of aluminium.**

**iii) Iodine in the refining of Zirconium.**

**iv) Sodium cyanide in froth floatation.**

**i)** In the extraction of copper, silica acts as an acidic flux to remove FeO as slag $FeSiO_3$.

$$FeO_{(s)} + \underset{\text{Flux}}{SiO_{2(s)}} \rightarrow \underset{\text{Slag}}{FeSiO_{3(s)}}$$

**ii)** As $Al_2O_3$ is a poor conductor, cryolite improves the electrical conductivity and lowers the melting point of the electrolyte.

**iii)** Impure zirconium metal is heated in an evacuated vessel with iodine to form the volatile zirconium tetraiodide ($ZrI_4$). The impurities are left behind, as they do not react with iodine.

$$Zr_{(s)} + 2I_{2(s)} \rightarrow ZrI_{4(Vapour)}$$

volatile zirconium tetraiodide vapour is passed over a tungsten filament, decomposes to give pure zirconium.

$$ZrI_{4(Vapour)} \rightarrow Zr_{(s)} + 2I_{2(s)}$$

**iv)** Sodium cyanide acts as a depressing agent in froth floatation process, sodium cyanide selectively prevent other metal sulphides coming to the froth. eg: NaCN depresses the floatation property ZnS present in Galena (PbS) by forming a layer of Zinc complex $Na_2 [Zn(CN)_4]$ on the surface of Zinc sulphide (ZnS).

**14. Explain the principle of electrolytic refining with an example. (JULY-2022)**

Crude metal is refined by electrolysis carried out in an electrolytic cell.

Cathode: Thin strips of pure metal.

Anode: Impure metal to be refined.

Electrolyte: Aqueous solution of the salt of the metal with dilute acid.

As current is passed, the metal of interest dissolves from the anode and pass into the electrolytic solution.

At the same time same amount of metal ions from the electrolytic solution will be deposited at the cathode.

Less electro positive impurities in the anode settle down as anode mud.

eg : Electro refining of silver:

Cathode: Pure silver

Anode: Impure silver rods.

Electrolyte: Acidified aqueous solution of silver nitrate.

When current passed, the following reactions will take place.

Reaction at anode: $Ag_{(s)} \rightarrow Ag^{+}_{(aq)} + e^{-}$

Reaction at cathode: $Ag^{+}_{(aq)} + e^{-} \rightarrow Ag(s)$

At anode silver atoms lose electrons and enter the solution. From the solution, silver ions ($Ag^{+}$) migrate towards the cathode. At cathode silver ions get discharged by gaining electrons and deposited on the cathode.

**15. The selection of reducing agent depends on the thermodynamic factor: Explain with an example.**

A suitable reducing agent is selected based on the thermodynamic considerations.

For a spontaneous reaction $\Delta G$ should be negative.

Thermodynamically, the reduction of metal oxide with a given reducing agent can occur if ΔG for the coupled reaction is negative.

Hence the reducing agent is selected in such a way that it provides a large negative ΔG value for the coupled reaction.

Ellingham diagram is used to predict thermodynamic feasibility of reduction of oxides of one metal by another metal.

Any metal can reduce the oxides of other metals that are located above it in the diagram.

Ellingham diagram for the formation of FeO and CO intersects around 1000K. Below this temperature the carbon line lies above the iron line.

Hence FeO is more stable than CO and the reduction is not thermodynamically feasible.

However above 1000K carbon line lies below the iron line. Hence at this condition FeO is less stable than CO and the reduction is thermodynamically feasible. So coke can be used as a reducing agent above this temperature.

Following free energy calculation also confirm that the reduction is thermodynamically favoured.

From the Ellingham diagram at 1500K

$2Fe_{(s)} + O_{2(g)} \rightarrow 2FeO_{(g)}$ $\Delta G_1 = -350\ kJmol^{-1}$ ............1

$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)}$ $\Delta G_2 = -480\ kJmol^{-1}$ ............2

Reverse the reaction 1

$2FeO_{(s)} \rightarrow 2Fe_{(s)} + O_{2(g)}$ $\Delta G1 = 350\ kJmol^{-1}$ ............3

Couple the reactions 2 and 3

$2FeO_{(s)} + 2C_{(s)} \rightarrow 2Fe_{(s)} + 2CO_{(g)}$ $\Delta G_3 = -130\ kJmol^{-1}$ ............4

The standard free energy change for the reduction of one mole of FeO is $\frac{\Delta G_3}{2} = -65\ kJmol^{-1}$

**16. Give the limitations of Ellingham diagram.**

Ellingham diagram is constructed based only on thermodynamic considerations.

1. It gives information about the thermodynamic feasibility of a reaction.
2. It does not tell anything about the rate of the reaction.
3. It does not give any idea about the possibility of other reactions that might be taking place.
4. The interpretation of ΔG assumes that the reactants are in equilibrium with the product which is not always true.

**17. Write a short note on electrochemical principles of metallurgy.**

Reduction of oxides of active metals such as sodium, potassium etc. by carbon is thermodynamically not feasible. Such metals are extracted from their ores by using electrochemical methods.

In this method the metal salts are taken in fused form or in solution form.

The metal ion present can be reduced by treating the solution with suitable reducing agent or by electrolysis.

Gibbs free energy change for the electrolysis is

$\Delta G^o = - nFE^o$

n = number of electrons involved in the reduction

F = Faraday = 96500 coulombs       $E^o$ = electrode potential of the redox couple.

If $E^o$ is positive, $\Delta G^o$ is negative, and the reduction is spontaneous.

Hence a redox reaction is planned in such a way that the e.m.f of the net redox reaction is positive.

A more reactive metal displaces a less reactive metal from its salt solution.

eg: $Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$

Zinc is more reactive than copper and displaces copper from its salt solution.

## II. EVALUATE YOURSELF

**1. Write the equation for the extraction of silver by leaching with sodium cyanide and show that the leaching process is a redox reaction.**

In the metallurgy of silver metal is leached with a dilute solution of NaCN in the presence of air ($O_2$)

$4Ag + 8CN^- + 2 H_2O + O_2 \rightarrow 4[Ag(CN)_2] + 4OH^-$

In this reaction, $Ag \rightarrow Ag^+$ oxidation number of Ag increases from 0 to +1, hence oxidation

$O_2 \rightarrow {}^-OH$ (oxidation number of oxygen decreases from 0 to -2, hence reduction)

Hence Leaching of silver is a redox reaction.

**2. Magnesite (Magnesium carbonate) is calcined to obtain magnesia, which is used to make refractory bricks. Write the decomposition reaction**

Magnesite (Magnesium carbonate) is heated in the absence of oxygen decomposes to form Magnesium oxide ( Magnesia)

$MgCO_3 \rightarrow MgO + CO_2 \uparrow$

**3. Using Ellingham diagram indicate the lowest temperature at which ZnO can be reduced to Zinc metal by carbon. Write the overall reduction reaction at this temperature**

Ellingham diagram for the formation of ZnO and CO intersects around 1233K Below this temperature, Carbon line lies above Zinc line. Hence ZnO is more stable than CO so the reduction is thermodynamically not feasible at this temperature range. However above 1233K carbon line lies below the zinc line, hence carbon can be used as a reducing agent above 1233K.

$2Zn + O_2 \rightarrow 2ZnO$ ...........1

$2C + O_2 \rightarrow 2CO$ ..........2

Reversing 1 and adding with equation 2

$2ZnO \rightarrow 2Zn + O_2$

$2C + O_2 \rightarrow 2CO$

$2ZnO + 2C \rightarrow 2Zn + 2CO$

4. **Metallic Sodium is extracted by the electrolysis of brine (aq. $NaCl$ ). After electrolysis, the electrolytic solution becomes basic in nature. Write the possible electrode reactions.**

If an aqueous solution of NaCl is electrolysed, $H_2$ is evolved at cathode and $Cl_2$ is evolved at anode. NaOH is obtained in the solution.

$2NaCl_{(aq)} \xrightarrow{\text{Electrolysis}} 2Na^{+}_{(aq)} + 2Cl^{-}_{(aq)}$

Cathode: $2H_2O_{(l)} + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}_{(aq)}$

Anode: $2Cl^{-}_{(aq)} \rightarrow Cl_{2(g)} + 2e^{-}$

Na + and $OH^{-}$ ions to form NaOH . Hence solution is basic in nature

Net reaction: $2NaCl_{(aq)} + 2H_2O_{(l)} \rightarrow H_{2(g)} + Cl_{2(g)} + 2NaOH_{(aq)}$

## IV. ADDITIONAL QUESTIONS AND ANSWERS

1. **What is concentration of ores?**

The removal of non-metallic impurities, rocky materials, and siliceous matter (called as gangue) from the ores is known as concentration of ores.

2. **What is leaching?**

Crushed ore is allowed to dissolve in a suitable solvent to form a soluble metal salt or complex leaving the gangue undissolved is called leaching.

3. **What is ammonia leaching?**

Crushed ore containing nickel, copper and cobalt is treated with aqueous ammonia under suitable pressure. Ammonia selectively leaches these metals by forming their soluble complexes namely $[Ni(NH_3)_6]^{2+}$, $[Cu(NH_3)_4]^{2+}$ and $[Co(NH_3)_5H_2O]^{3+}$ from the ore.

The gangue left behind are iron (III) oxides / hydroxides and alumino silicate.

4. **What is acid leaching? (AUG-2022)**

Sulphide ores ZnS, PbS can be leached with hot aqueous sulphuric acid.

In this process the insoluble sulphide is converted into soluble sulphate and elemental sulphur.

$2ZnS_{(s)} + 2H_2SO_{4\,(aq)} + O_{2\,(g)} \rightarrow 2ZnSO_{4(aq)} + 2S_{(s)} + 2H_2O$

5. **What are the steps involved in the extraction of crude metal?**

    1. Conversion of the ore into metal oxide either by roasting or calcination.
    2. Reduction of the metal oxide into metal.

6. **In the extraction of metal, ore is first converted into metal oxide before reduction into metal. Why?**

From the principles of thermodynamics, the reduction of oxide is easier compared to the reduction of other compounds of metal.

Hence before reduction the ore is first converted into metal oxide.

7. **Write about the extraction of metal by the process of reduction by hydrogen.**

This method can be applied to the oxides of the metals (Fe, Pb, Cu) which are less electropositive than hydrogen.

$Ag_2O_{(s)} + H_{2(g)} \rightarrow 2Ag_{(s)} + H_2O_{(l)}\uparrow$

Nickel oxide is reduced to nickel by a mixture of hydrogen and carbon monoxide(water gas)

$2NiO_{(s)} + CO_{(g)} + H_{2(g)} \rightarrow 2Ni_{(s)} + CO_{2(g)} + H_2O_{(l)}\uparrow$

**8. What is auto reduction of metallic ores?**

Roasting of some of the metallic ores give the crude metal. Use of reducing agent is not necessary because of low thermal stability (eg) Cinnabar is roasted to give mercury.

$HgS_{(s)} + O_{2\,(g)} \rightarrow Hg_{(l)} + SO_{2(g)}\uparrow$

**9. Write the applications of copper.**

1. Copper is the first metal used by humans and extended use of its alloy bronze resulted in a new era, ‘Bronze age’.
2. Used for making coins and ornaments along with gold and other metals.
3. Copper and its alloys are used for making wires, water pipes and other electrical parts.

**10. Write the applications of gold.**

1. Gold is one of the expensive and precious metals.
2. Used for coinage and has been used as standard for monetary systems in some countries.
3. Extensively used in jewellery in its alloy form with copper.
4. Used in electroplating to cover other metals with a thin layer of gold, which are used in watches, artificial limb joints, cheap jewellery, dental fillings and electrical connectors.
5. Gold nanoparticles are used for increasing the efficiency of solar cells.
6. Used as a catalyst.

**11. Write about alumino thermite process.**

In this method a metal oxide such as $Cr_2O_3$ is reduced to metal by aluminium.

Metal oxide ($Cr_2O_3$) is mixed with aluminium powder in a fire clay crucible.

The reduction process is initiated by ignition mixture of Magnesium powder and barium peroxide.

$BaO_2 + Mg \rightarrow BaO + MgO$

It is an exothermic process where heat is liberated. Temperature = 2400°C Heat liberated = $852 kJmol^{-1}$

This heat initiates the reduction of $Cr_2O_3$ by Al.

$Cr_2O_3 + 2Al \xrightarrow{\Delta} 2Cr + Al_2O_3$

**12. What is refining process of a metal?**

Metals extracted from its ore contains impurities such as unreacted oxide ore, other metals, non-metals etc ; Removal of such impurities from crude metal is known as refining process of a metal.

**13. Write about distillation process of refining a metal?**

This method is used for low boiling volatile metals like zinc and mercury.

In this method impure metal is heated to evaporate and the vapours are condensed to get pure metal.

**14. Write about liquation process of refining a metal?**

This method is used to remove the impurities with high melting points from metals having relatively low melting points.

(eg) Tin, lead, mercury, bismuth.

The impure metal is placed on sloping hearth of a reverberatory furnace, and it is heated just above the melting point of the metal in the absence of air, the molten metal flows down and impurities are left behind .The molten metal is collected and solidified.

**15. Give example for the following 1. Frothing agent 2. Collector 3. Depressing agent**

**Frothing agent** : Pine oil , eucalyptus oil
**Collector** : Sodium ethyl xanthate
**Depressing agent** : Sodium cyanide , sodium carbonate

**16. What is cementation ?**

Gold can be recovered by reacting the deoxygenated leached solution with Zinc. In this process Gold is reduced to its elemental state ( zero oxidation state) and the process is called cementation

$Zn_{(S)} + 2[Au(CN)_2]^{-}_{(aq)} \rightarrow [Zn(CN)_4]^{2-}_{(aq)} + 2Au_{(S)}$

**17. Why Fe, Pb , Cu are reduced by hydrogen ?**

The oxides of metal Fe, Pb, Cu having less electropositive character than hydrogen, these metal oxide can be reduced by hydrogen.

$Ag_2O_{(S)} + H_{2\,(g)} \rightarrow 2Ag_{(S)} + H_2O_{(l)} \uparrow$

$Fe_3O_{4\,(S)} + 4H_{2\,(g)} \rightarrow 3Fe_{(S)} + 4H_2O_{(l)} \uparrow$

**18. Write about gravity separation or hydraulic wash? (MAY-2022)**

Ore with high specific gravity is separated from gangue with low specific gravity by simply washing with running water.

Finely powdered ore is treated with rapidly flowing current of water.

Lighter gangue particles are washed away by the running water.

This method is used for concentrating native ore such as gold and oxide ores such as haematite($Fe_2O_3$), tin stone($SnO_2$).

**19. Write about magnetic separation.**

This method is applicable to ferromagnetic ores.

It is based on the difference in the magnetic properties of the ore and the impurities.

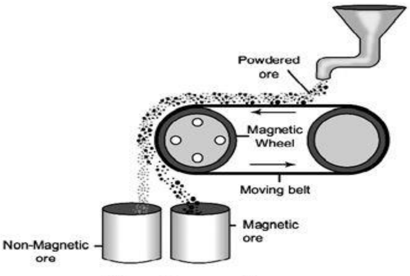
Nonmagnetic tin stone can be separated from the magnetic impurities wolframite.

Similarly magnetic ores chromite, pyrolusite can be removed from nonmagnetic siliceous impurities.

The crushed ore is poured on, to an electromagnetic separator with a belt moving over two rollers of which one is magnetic.

Magnetic part of the ore is attached towards the magnet and falls as a heap close to the magnetic region.

Nonmagnetic part falls away from it.



Magnetic separation

**20. Write about calcination.**

Calcination is the process in which the concentrated ore is strongly heated in the absence of air.

During this process water of crystallisation present in the hydrated oxide escapes as moisture.

Any organic matter present also get expelled leaving the ore porous.

This method can also be carried out with a limited supply of air.

During calcination of carbonate ore is decomposed to metal oxide and carbon dioxide is liberated.

$PbCO_3 \xrightarrow{\Delta} PbO + CO_2\uparrow$ $CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow$

$Al_2O_3.2H_2O \xrightarrow{\Delta} Al_2O_{3(s)} + 2H_2O_{(g)}\uparrow$

**21. Write about Van – Arkel method for refining zirconium/titanium?**

This method is based on the thermal decomposition of gaseous metal compounds to metals.

(eg) Titanium and Zirconium.

Impure titanium is heated in an evacuated vessel with iodine at 550K to form volatile titanium tetra iodide.

The impurities do not react with iodine.

$Ti(s) + 2I_2(s) \xrightarrow{550\ K} TiI_4(vapour)$

Volatile titanium tetraiodide is passed over a tungsten filament at 1800K.

Titanium tetraiodide is decomposed to pure titanium which is deposited over the filament.

Iodine is reused.

$TiI_{4(vapour)} \xrightarrow{1800\ K} Ti_{(s)} + 2I_{2(s)}$

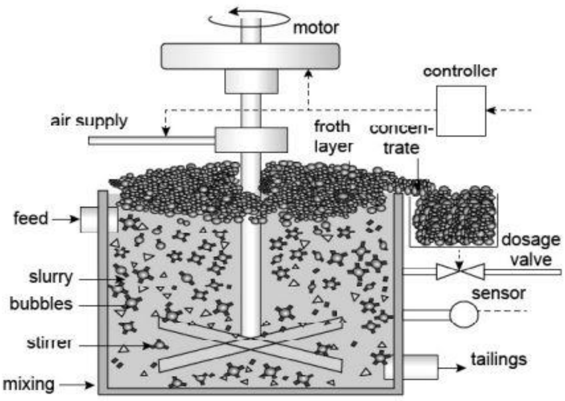
**22. Write the applications of aluminium.**

1. Used for making heat exchangers/sinks.
2. Used for making our day-to-day cooking vessels.
3. Used for making aluminium foils for packing, food items.
4. Alloys of aluminium with copper, manganese, magnesium, silicon are light weight and strong hence used in design of aeroplanes and other forms of transport.
5. Due to its high resistance to corrosion, it is used in the design of chemical reactors, medical equipment's, refrigeration units and gas pipelines.
5. It is a good electrical conductor and cheap, hence used in electrical overhead cables with steel core for strength.

**23. Write the applications of iron.**

1. Iron is used everywhere including bridges, electricity
2. pylons, bicycle chains, cutting tools and rifle barrels.
3. Cast iron is used to make pipes, valves, and pump stoves etc.
4. Magnets can be made from iron , its alloys, and compounds.
5. alloy of iron is stainless steel which is very resistant to corrosion.
5. It is used in architecture, bearings, cutlery, surgical instruments, and jewellery.

**24. Explain froth floatation method**. **(AUG-2021)**



This method is used to concentrate sulphide ores such as galena ($PbS$) Zinc blende ($ZnS$) etc.

Metallic ore particles preferentially wetted by oil can be separated from gangue.

Crushed ore is mixed with water and a frothing agent like pine oil or eucalyptus oil.

A small amount of sodium ethyl xanthate is added as a collector.

A froth is formed by blowing air through the mixture.

The collector molecules attach to the ore particles and make them water repellent.

As a result ore particles wetted by the oil rise to the surface along with the froth.

The froth is skimmed off and dried to recover the concentrated ore.

Gangue particles preferentially wetted by water settle at the bottom.

When sulphide ore contains other metal sulphides as impurities, depressing agents such as sodium cyanide, sodium carbonate etc. are used to selectively prevent other metal sulphide coming to the froth

For example , when impurities such as $ZnS$ is present in Galena ($PbS$) , Sodium cyanide $NaCN$ is added to depresses the flotation property of $ZnS$) by forming a layer of zinc complex $Na_2[Zn(CN)_4]$ on the surface of $ZnS$.

# UNIT 2 p-BLOCK ELEMENTS

## I TEXT BOOK QUESTION AND ANSWERS

**1 Write a short note on anomalous properties of the first element of p-block. (SEPT-20, AUG-2021)**

- Small size of the first member
- High ionization enthalpy and high electronegativity
- Absences of d-orbital in their valence shell

**2 Describe briefly allotropism in p-block elements with specific reference to carbon.**

Some elements exist in more than one crystalline or molecular forms in the same physical state. This phenomenon is called allotropism and the different forms of an element are called allotropes.
**Eg:** carbon exist as diamond, graphite, graphene, fullerenes and carbon nanotubes

**3 Give the uses of borax. (AUG-2021)**

- Borax is used for the identification of coloured metal ions
- It is used as a flux in metallurgy.
- It act as a preservative

**4 What is catenation? Describe briefly the catenation property of carbon. (SEPT-20, JULY-22)**

Catenation is an ability of an element to form chain of atoms.
Conditions for catenation: (**MAR-20)**

- The valency of element is greater than or equal to two.
- Element should have an ability to bond with itself.
- The self-bond must be as strong as its bond with other elements.

Carbon possesses all the above properties and forms a wide range of compounds with itself and with other elements such as H, O, N, S and halogens.

**5 Write a note on Fisher tropsch synthesis.**

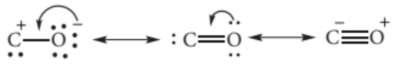
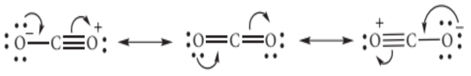
The reaction of carbon monoxide with hydrogen at pressure of less than 50 atm using metal catalysts at 500 – 700K yields saturated and unsaturated hydrocarbons

$$\mathrm{nCO} + (2\mathrm{n}+1)\mathrm{H_2} \rightarrow \mathrm{C_n H_{2n+2}} + \mathrm{nH_2O}$$

$$\mathrm{nCO} + 2\mathrm{nH_2} \rightarrow \mathrm{C_nH_{2n}} + \mathrm{nH_2O}$$

Carbon monoxide forms complex compounds with transition metals.
**Eg**: Nickel tetra carbonyl.

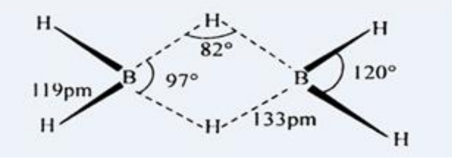
**6 Give the structure of CO and $CO_2$.**

| Structure of CO | Structure of $CO_2$ |
|---|---|
| It has a linear structure. | It has a linear structure. |
| The C—O bond distance is 1.128A°. | It has equal bond distance for both C—O bonds. |
|  |  |

7 **Give the uses of silicones.**

- Silicones are used for low temperature lubrication.
- Silicones are used for making water proofing clothes.
- Silicones are used as insulating material in electric motor.

8 **Describe the structure of diborane**



- In diborane two $BH_2$ units are linked by two bridged hydrogens. Therefore, it has 8 B-H bonds. However, diborane has only 12 valence electrons and are not sufficient to form normal covalent bonds.
- The four terminal B-H bonds **(two centre – two electron bond)** are normal covalent bonds.
- The remaining four electrons have to be used for the bridged bonds. i.e. two threecentred B-H-B bonds use two electrons each. **Hence, these bonds are three centre –two electron bonds (3c-2e)**
- The bridging hydrogen atoms are in a plane. In diborane, the boron is $sp^3$hybridised.

9 **Write a short note on hydroboration.**

Diborane adds on alkenes and alkynes in ether solvent at room temperature. This reaction is called hydroboration.

$$B_2H_6 \quad + \quad 6RCH = CHR \quad \rightarrow \quad 2B(RCH - CH_2R)_3$$

Diborane Trialkyl borane

10 **Give one example for each of the following:**

| No | GROUP NAME | GROUP NUMBER | FAMILY | EXAMPLE |
|---|---|---|---|---|
| (i) | Icosagens | 13 | Boron family | Aluminium |
| (ii) | Tetragens | 14 | Carbon family | Silicon |
| (iii) | Pnictogens | 15 | Nitrogen family | Phosphorous |
| (iv) | Chalcogens | 16 | Oxygen family | Sulphur |

11 **Write a note on metallic nature of p-block elements.**

- The tendency of an element to form a cation by losing electrons is known as metallic character.
- This character depends on the ionization energy.
- Generally on descending a group the ionization energy decreases and hence the metallic character increases.
- In p-block, the elements present in lower left part are metals.

**12 Complete the following reactions:**

| | |
|---|---|
| ***a*** | $B(OH)_3 + NH_3 \rightarrow$ |
| ***b*** | $Na_2B_4O_7 + H_2SO_4 \rightarrow$ |
| ***c*** | $B_2H_6 + 2NaOH + 2H_2O \rightarrow$ |
| ***d*** | $B_2H_6 + CH_3OH \rightarrow$ |
| ***e*** | $BF_3 + H_2O \rightarrow$ |
| ***f*** | $HCOOH + H_2SO_4 \rightarrow$ |
| ***g*** | $SiCl_4 + NH_3 \rightarrow$ |
| ***h*** | $SiCl_4 + C_2H_5OH \rightarrow$ |
| ***i*** | $B + NaOH \rightarrow$ |
| ***j*** | $H_2B_4O_7 \xrightarrow{Red\ Hot}$ |

| | |
|---|---|
| ***a*** | $B(OH)_3 + NH_3 \rightarrow BN + 3H_2O$ |
| ***b*** | $Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow 4H_3BO_3 + Na_2SO_4$ |
| ***c*** | $B_2H_6 + 2NaOH + 2H_2O \rightarrow 2NaBO_2 + 6H_2$ |
| ***d*** | $B_2H_6 + 6CH_3OH \rightarrow 2B(OCH_3)_3 + 6H_2$ |
| ***e*** | $4BF_3 + 3H_2O \rightarrow H_3BO_3 + 3H^+ + 3[BF_4]^-$ |
| ***f*** | $HCOOH + H_2SO_4 \rightarrow CO + H_2O + H_2SO_4$ |
| ***g*** | $2SiCl_4 + NH_3 \rightarrow Cl_3Si\text{-}NH\text{-}SiCl_3$ **(chlorosilazanes)** $+ 2HCl$ |
| ***h*** | $SiCl_4 + 4C_2H_5OH \rightarrow Si(OC_2H_5)_4 + 4HCl$ |
| ***i*** | $2B + 6NaOH \rightarrow 2Na_3BO_3 + 3H_2$ |
| ***j*** | $H_2B_4O_7 \xrightarrow{Red\ Hot} 2B_2O_3 + H_2O$ |

**13 How will you identify borate radical?**

When boric acid or borate salt is heated with ethyl alcohol in presence of conc. $H_2SO_4$ an ester, trialkylborate is formed. The vapour of this ester burns with a green edged flame and this reaction is used to identify the presence of borate.

$$H_3BO_3 + 3C_2H_5OH \xrightarrow{Con.H_2SO_4} B(OC_2H_5)_3 + 3H_2O$$

**14 Write a note on zeolites.**

- Zeolites are three dimensional crystalline solids containing aluminium, silicon and oxygen.
- The general formula is $Na_2O.(Al_2O_3).x(SiO_2).yH_2O$ .
- The Si and Al atoms are tetrahedrally coordinated with each other through sharedoxygen atoms.

**15 How will you convert boric acid to boron nitride?**

$H_3BO_3 + NH_3 \xrightarrow{800K} BN + 3H_2O$

Boric Acid Boron Nitride

16 **A hydride of 2nd period alkali metal (A) on reaction with compound of Boron (B) togive a reducing agent (C). Identify A, B, and C. (JULY-2020)**

$$\underset{(A)}{2LiH} + \underset{(B)}{B_2H_6} \xrightarrow{Ether} \underset{(C)}{2LiBH_4}$$

(A) Lithium Hydride (B) Diborane (C) Lithium Borohydride

17 **A double salt which contains fourth period alkali metal (A) on heating at 500K gives (B). Aqueous solution of (B) gives white precipitate with $BaCl_2$ and gives a redcolour compound with alizarin. Identify A and B.**

$K_2SO_4.Al_2(SO_4)_3.24H_2O \xrightarrow{500K} K_2SO_4.Al_2(SO_4)_3 + 24H_2O$

(A)Potash alum (B) Burnt alum

18 **CO is a reducing agent. Justify with an example.**

Carbon monoxide is a strong reducing agent. It reduce the oxides of the less activemetals to their respective metals and itself gets oxidised to carbon dioxide in the process.

**Eg**: $3CO + Fe_2O_3 \xrightarrow{Heat} 2Fe + 3CO_2$

## II ADDITIONAL QUESTIONS WITH ANSWERS:

1 **Why boron does not form $B^{3+}$ ions?**

Because of its small size and sum of first three ionization enthalpies is high, boron doesnot lose all its valence electrons to form $B^{3+}$ ions.

2 **Why the ionization enthalpy from Aluminium to Thallium is only a marginal difference? (MAR-2020)**

This is due to the presence of inner d and f-electrons which has poor shielding effect compared to s and p-electrons.

3 **What is Inert pair effect? (MAY-2022)**

In heavier post transition metals, the outer s-electrons (ns) have a tendency to remain inert and show reluctance to take part in the bonding is known as inert pair effect.

4 **What happen when boron burns with nitrogen and oxygen (or) air?**

1) $2B + N_2 \rightarrow 2BN$
2) $4B+3O_2 \xrightarrow{900k} 2B_2O_3$

5 **Write any two methods for the preparation of metal borides**

i. $Cr + nB \xrightarrow{1500K} CrB_n$
ii. $2BCl_3 + 2\,W \xrightarrow{1500K, H_2} 2WB + 2\,Cl_2 + 2\,HCl$

6 **Write any three uses of boron.**

- Amorphous boron is used as a rocket fuel igniter.
- Boron is essential for the cell walls of plants.
- Isotope of boron${}^{10}B_5$ is used as a moderator in nuclear reactors.

7 **How borax is prepared from colemanite ore?**

$2Ca_2B_6O_{11} + 3Na_2CO_3 + H_2O \xrightarrow{Heat} 3Na_2B_4O_7 + 3CaCO_3 + Ca(OH)_2$

Colemanite Borax

8 **Why Borax solution is basic in nature?**

Borax solution in hot-water is alkaline as it dissociates into boric acid and sodium hydroxide

$Na_2B_4O_7 + 7H_2O \rightarrow 4H_3BO_3 + 2NaOH$

9 **How borax reacts with acid?**

Borax reacts with acids to form sparingly soluble boric acid

$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 4H_3BO_3 + 2NaCl$

$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow 4H_3BO_3 + Na_2SO_4$

10 **What happen when borax is heated?**

When borax is heated it forms a transparent borax beads.

$Na_2B_4O_7.10H_2O \xrightarrow{Heat} Na_2B_4O_7 \xrightarrow{Heat} 2NaBO_2 + B_2O_3$

Borax Sodium tetraborate Sodium metaborate

11 **What happen when borax is treated with ammonium chloride?**

When borax is treated with ammonium chloride it forms boron nitride

$Na_2B_4O_7 + 2NH_4Cl \rightarrow 2NaCl + 2BN + B_2O_3 + 4H_2O$

12 **How Boric acid is prepared from borax and colemanite?(OR) What happens when a borax solution is acidified? Write a balanced equation forthe reaction.**

$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3$

$Ca_2B_6O_{11} + 11H_2O + 4SO_2 \rightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$

Colemanite Boric acid

13 **What happen when boric acid is heated?**

$4H_3BO_3 \xrightarrow{373K} 4HBO_2 \xrightarrow{413K} H_2B_4O_7 \xrightarrow{Redhot} 2B_2O_3$

Boric Acid Metaboric Acid Tetraboric Acid

14 **Why Boric acid is a weak monobasic acid?**

Boric acid act as a weak acid by accepting a hydroxide ion of water and releasinga proton into the solution

$H_3BO_3 + 2H_2O \rightleftharpoons H_3O^+ + [B(OH)_4]^-$

15 **How sodium metaborate and sodium tetraborate are prepared from boric acid**

$NaOH + H_3BO_3 \rightarrow NaBO_2 + 2H_2O$

Sodium metaborate

$2NaOH + 4H_3BO_3 \rightarrow Na_2B_4O_7 + 7H_2O$

Sodium tetraborate

16 **Explain the structure of boric acid**

Boric acid has a two dimensional layered structure. It consists of $[BO_3]^{3-}$ unit andthese are linked to each other by hydrogen bonds.

**17 Write the uses of boric acid (MAY-22, AUG-22)**

- Boric acid is used in the manufacture of pottery glasses, enamels and pigments.
- It is used as an antiseptic and as an eye lotion.
- It is also used as a food preservative.

**18 What happen when diborane react with water and alkali?**

$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$
Diborane Boric Acid

$B_2H_6 + 2NaOH + 2H_2O \rightarrow 2NaBO_2 + 6H_2$
Diborane Sodium metaborate

**19 What happen when diborane react with metal hydride?**

$B_2H_6 + 2LiH \xrightarrow{Ether} 2LiBH_4$
Diborane Lithium Borohydride

$B_2H_6 + 2NaH \xrightarrow{Diglyme} 2NaBH_4$
Diborane Sodium Borohydride

**20 How to prepare trimethyl borate?**

$B_2H_6 + 6CH_3OH \rightarrow 2B(OCH_3)_3 + 6H_2$
Diborane Methylalcohol Trimethyl Borate

**21 What happen when diborane react with ammonia?**

**(OR)**

**How to prepare borazine or borazole or inorganic benzene?**

$3B_2H_6 + 6NH_3 \xrightarrow{-153K} 3(B_2H_6.2NH_3)$
Diboranediammonate

$3B_2H_6 + 2NH_3 \xrightarrow{High\ Temp} 2B_3N_3H_6$
Diborane Borazole

**22 Why $BF_3$ forms a coordinate covalent bonds with ammonia and water?**

Boron trifluoride is an electron deficient compound and accept electron pairs from ammonia and water to form coordinate covalent bond.

$BF_3 + NH_3 \rightarrow F_3B \leftarrow NH_3$
$BF_3 + H_2O \rightarrow F_3B \leftarrow OH_2$

**23 Explain McAfee process**

Aluminium chloride is obtained by heating a mixture of alumina and coke in a current of chlorine

$2Al_2O_3 + 3C + 6Cl_2 \xrightarrow{Heat} 4AlCl_3 + 3CO_2$

On industrial scale it is prepared by chlorinating aluminium around 1000K

$2Al + 3Cl_2 \xrightarrow{1000K} 2AlCl_3$

**24 Why anhydrous aluminium chloride produces fumes in moist air?**

Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture toliberate HCl gas. Moist HCl appears white in colour.

$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3\,HCl$

**25 What is silicate?**

The mineral which contains silicon and oxygen in tetrahedral $[SiO_4]^{4-}$ units linkedtogether in different patterns are called silicates

**26 Explain the types of silicates**

| No | TYPES OF SILICATES | ION PRESENT | CONNECTIVITY | EXAMPLE |
|---|---|---|---|---|
| 1 | Ortho silicates (or) Neso silicates | $[SiO_4]^{4-}$ | Discrete $[SiO_4]^{4-}$ tetrahedral units. | Phenacite<br>$Be_2SiO_4$ |
| 2 | Pyro silicate (or) Soro silicates | $[Si_2O_7]^{6-}$ | Linking two $[SiO_4]^{4-}$ tetrahedral units by sharing oneoxygen atom at one corner. | Thortveitite<br>$Sc_2Si_2O_7$ |
| 3 | Cyclic silicate (or) Ring silicates | $(SiO_3)_n^{2n-}$ | Linking three or more $[SiO_4]^{4-}$ tetrahedral units.<br>Each silicate unit shares two of its oxygen atoms with other units | Beryl<br>$Be_3Al_2(SiO_3)_6$ |
| 4 | Inosilicates | Silicates which contain 'n' number of silicate units liked by sharing two ormore oxygen atoms are called inosilicates. They are further classified as chain silicates and double chain silicates | | |
| 4(i) | Chain silicates (or) Pyroxenes | $[(SiO_3)_n]^{2n-}$ | Linking 'n' number oftetrahedral $[SiO_4]^{4-}$ units linearly.<br>Each silicate unit shares two of its oxygen atoms with other units. | Spodumene<br>$LiAl(SiO_3)_2$ |
| 4(ii) | Double chain silicates(or) Amphiboles | $[Si_4O_{11}]_n^{6n-}$ | There are two different types of tetrahedral :<br>i) sharing 3 vertices<br>ii) sharing 2 vertices | Asbestos |
| 5 | Sheet (or) Phyllo silicates | $[Si_2O_5]^{2n-}$ | Each $[SiO_4]^{4-}$ tetrahedron unit share three oxygen atoms with others and thus byforming two dimensional sheets | Talc, Mica |
| 6 | Three dimensional silicates (or) Tecto silicates | $[SiO_4]^{4-}$ | Silicates in which all the oxygen atoms of $[SiO_4]^{4-}$ tetrahedral are shared with other tetrahedral to form three-dimensional network are called three dimensional silicate. | Quartz |

**27 Boron shows diagonal relationship with silicon of group 14. Illustrate it.**

- Oxides of boron and silicon are similar in their acidic nature.
- Boron and silicon form covalent hydrides that can be easily hydrolysed.
- Except boron trifluoride, halides of both the elements are readily hydrolysed.

**28 Give the anomalous properties of carbon in group 14.**

- Carbon is a non-metal while other elements are metalloids or metals.
- Unlike other elements of the group, carbon can form multiple bonds.
- Carbon has greater tendency to form catenation than the other elements of the group.

**29 Give the anomalous properties of nitrogen in group 15.**

- Unlike other elements of the group nitrogen can form multiple bonds.
- Unlike other elements of the group nitrogen is a diatomic gas.

**30 Give the anomalous properties of fluorine in group 17.**

**(OR)**

**How fluorine differs from other elements of the group?**

- Fluorine is the most electronegative element.
- Fluorine can form hydrogen bonds.
- Fluorine shows only -1 oxidation state.
  Fluorine is the strongest oxidising agent and most reactive element among the halogens

**31 Many compounds of boron are electron deficient and has unusual type of covalent bonding. Give reason.**

- It is due to its
- Small size, high ionization energy
- Similarity in electronegativity with carbon and hydrogen.

**32 How is potash alum prepared? (JULY-2020)**

- When alum stone is treated with excess of sulphuric acid the aluminium hydroxide is converted into aluminium sulphate.
- A calculated quantity of potassium sulphate is added and the solution is crystallised to generate potash alum.

Alum stone + Sulphuric acid → Potassium sulphate + Aluminium sulphate + water

potassium sulphate+ aluminium sulphate +24$H_2O$ →potash alum

**33 What is burnt alum?**

- Potash alum melts at 365K.
- At 475K potash alum loses water of hydration and swells up.
- The swollen mass is known as burnt alum

Potash alum + heating to 475K → burnt alum + 24 $H_2O$

**34 Write a note on graphite.**

- Graphite is a most stable allotrope of carbon at normal temperature and pressure.
- It is soft and conducts electricity.
- It is composed of flat two dimensional sheets of carbon atoms.
- Each sheet is a hexagonal net of $sp^2$ hybridised carbon atoms.
- C – C bond length is 1.41 $A^o$
- Successive carbon sheets are held together by weak Vanderwaals forces.
- It is used as a lubricant

35 **Write a note on diamond**.

- Diamond is very hard.
- Carbon atoms in diamond are sp3 hybridised.
- C – C bond length is 1.54 Aº
- It has no free electrons for conductivity.
- It is used for sharpening hard tools, cutting glasses, making bores and rock drilling.

36
- **Give an account on fullerenes**.
- Fullerenes are newly synthesised allotropes of carbon.
- These allotropes are discrete molecules such as $C_{32}$,$C_{50}$, $C_{60}$,$C_{70}$,$C_{76}$ etc
- These molecules have cage like structure.
- The $C_{60}$ molecules have a soccer ball like structure and is called bucky balls.
- It has fused ring like structure consists of 20 six membered rings and 12 five membered rings.
- Each carbon atom is sp2 hybridised
- It forms three sigma bonds and a delocalised pi bond giving aromatic character to these molecules'
- The C-C bond distance is 1.44Aº and C=C distance is 1.38Aº.

37 **Write a note on carbon nano tubes**

- Carbon nano tubes have graphite like tubes with fullerene ends.
- Along the axis nano tubes are stronger than steel and conducts electricity.
- They are used in nanoscale electronics, catalysis, polymers and medicine.

38 **How is pure carbon monoxide prepared?**

Pure carbon monoxide is prepared by warming methanoic acid with concentrated sulphuric acid which acts as a dehydrating agent.

$$HCOOH + H_2SO_4 \rightarrow CO + H_2SO_4.H_2O$$

39 **What is water gas equilibrium?**

The equilibrium involved in the reaction between carbondioxide and hydrogen is called water gas equilibrium.

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

40 **Prove that carbon dioxide is acidic in nature.**

The aqueous solution of carbon dioxide is slightly acidic as it forms carbonic acid.

Carbon Dioxide + Water → Carbonic Acid

41 **Carbon dioxide acts as a strong oxidizing agent. Prove it.**

At elevated temperature carbon dioxide acts as a strong oxidizing agent.

Carbon dioxide + Magnesium → Magnesium Oxide + Carbon

42 **What are silicones? Mention the different types of silicones.**

Silicones or poly siloxanes are organo silicon polymers with general empirical formula $R_2SiO$

Types of silicones:

1)Linear silicones a)Silicone rubber b)Silicone resins

2)Cyclic silicones

3)Cross linked silicones

**43 Give the uses of diborane.**

- Diborane is used as a high energy fuel for propellants.
- It is used as a reducing agent.
- It is used in welding torches

**44 Give the uses of boron tri fluoride.**

- Boron tri fluoride is used for preparing $HBF_4$
- It is used as fluorinating agent

**45 Give the uses of aluminium chloride**

- Anhydrous aluminium chloride is used as a catalyst in Friedelcrafts reactions.
- It is used in the manufacture of petrol.
- It is used as a catalyst in the manufacture of dyes, drugs and perfumes.

**46 Give the uses of alum or potash alum.**

- Alum is used for purification of water.
- It is used for water proofing and textiles.
- It is used in dyeing, paper and leather tanning industries.
- It is used as a styptic agent to arrest bleeding.

**47 Give the uses of carbon monoxide**.

- Water gas ($CO+H_2$) and producer gas ($CO + N_2$) are important industrial fuels.
- It is used as a reducing agent

**48 Give the uses of carbon dioxide.**

- It is important for photosynthesis.
- It is used as fire extinguisher and as a propellant gas.
- It is used in the production of carbonated beverages and foam.

**49 Give the uses of Silicon tetrachloride**

- Silicon tetrachloride is used in the production of semiconducting silicon.
- It is used in the synthesis of silica gel and Silicic esters.

**50 $Al^{3+}$ is more stable than $Al^{1+}$ while $Tl^{1+}$ is more stable than $Tl^{3+}$. Why?**

- In group 13 as we move from Boron to Thallium inert pair effect increases.
- $AlCl_3$ is stable as it has less inert pair effect.
- In Thallium the outer 's' electrons remain inert and hence $Tl^{1+}$ is more stable than $Tl^{3+}$

**51 $AlCl_3$ behaves like a lewis acid. Substantiate this statement**

$AlCl_3$ is electron deficient.

- Al forms three bonds with chloride and hence outer shell has six electron.
- It needs two more electrons to complete its octet.
- So readily accept a pair of electrons.
- Hence $AlCl_3$ is a Lewis acid and forms addition compounds with ammonia and phosphate.

# UNIT 6 - SOLID STATE

## I TEXT BOOK QUESTION AND ANSWERS

1. **Define unit cell. (AUG-2021, JULY-22)**
   A basic repeating structural unit of a crystalline solid is called a unit cell.
2. **Give any three characteristics of ionic crystals**.
   - High melting points.
   - Do not conduct electricity in solid state.
   - Conduct electricity in molten state (or) when dissolved in water.

**3. Differentiate crystalline solids and amorphous solids. (JULY-2020, MAY-2022)**

| S.NO | CRYSTALLINE SOLIDS | AMORPHOUS SOLIDS |
|---|---|---|
| **1** | Long range orderly arrangement of constituents | Short range random arrangement of constituents |
| 2 | Definite shape | Irregular shape |
| **3** | Anisotropic in nature | Isotropic in nature |
| **4** | They are true solids | They are pseudo solids (or) super cooled liquids |
| **5** | Definite Heat of fusion | Heat of fusion is not definite |
| **6** | They have sharp melting points | They do not have sharp melting points |
| **7** | Examples: NaCl , diamond etc., | Examples: Rubber, plastics, glass etc |

**4. Classify the following solids**

a. $P_4$ b. Brass c. diamond d. NaCl e. Iodine

| | | |
|---|---|---|
| a | $P_4$ | Covalent solid |
| b | Brass | Metallic solid |
| c | diamond | Covalent solid |
| d | NaCl | Ionic solid |
| e | Iodine | Molecular solid |

**5. Explain briefly seven types of unit cell.**

There are seven primitive crystal systems. They differ in the arrangement of their crystallographic axes and angles.

| S.NO | NAME OF THE UNIT CELL | EDGE LENGTH | ANGLES |
|---|---|---|---|
| 1 | Cubic | $a=b=c$ | $\alpha=\beta=\gamma=90^{o}$ |
| 2 | Rhombohedral | $a=b=c$ | $\alpha=\beta=\gamma\neq90^{o}$ |
| 3 | Hexagonal | $a=b\neq c$ | $\alpha=\beta= 90^{o}, \gamma=120^{o}$ |
| 4 | Tetragonal | $a=b\neq c$ | $\alpha=\beta=\gamma=90^{o}$ |
| 5 | Orthorhombic | $a\neq b\neq c$ | $\alpha=\beta=\gamma=90^{o}$ |
| 6 | Monoclinic | $a\neq b\neq c$ | $\alpha= \gamma =90^{o}, \beta \neq90^{o}$ |
| 7 | Triclinic | $a\neq b\neq c$ | $\alpha\neq\beta\neq\gamma\neq90^{o}$ |

**6. Distinguish between hexagonal close packing and cubic close packing.**

| S.NO | HEXAGONAL CLOSE PACKING | CUBIC CLOSE PACKING |
|---|---|---|
| **1** | “ABA’’ arrangement | “ABC’’ arrangement |
| **2** | The arrangement of spheres in the third layer exactly resembles the first layer. | The arrangement of spheres in the third layer dose not resembles with those of either the first or second layer. |
| **3** | It is based on the hexagonal unit cells with sides of equal length. | It is based on the face centered cubic unit cell. |
| **4** | Tetrahedral voids of the second layer are exactly covered by the sphere of the third layer. | Octahedral voids of the second layer are partially covered by the sphere of the third layer. |

**7. Distinguish tetrahedral and octahedral voids.**

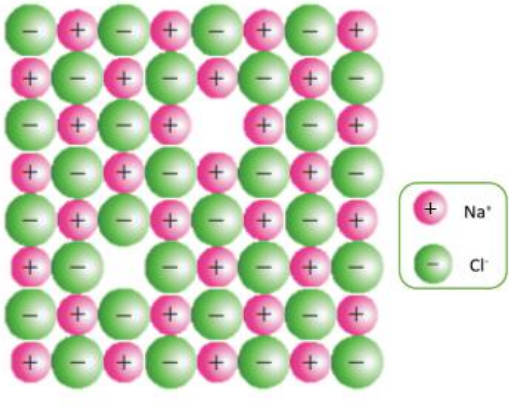
| S.NO | TETRAHEDRAL VOIDS | OCTAHEDRAL VOIDS |
|---|---|---|
| 1 | When a sphere of second layer is above the void in the first layer, tetrahedral void is formed | When a sphere of second layer partially covers the void in the first layer, octahedral void is formed |
| 2 | Number of close packed spheres = n<br>Number of tetrahedral voids = 2n. | Number of close packed spheres = n<br>Number of octahedral voids = n |
| 3 | This constitutes four spheres, three in the lower layer and one in the upper layer | This constitutes six spheres, three in the lower layer and three in the upper layer |
| 4 | When the centers of these four spheres are joined, a tetrahedron is formed. | When the centers of these six spheres are joined, an octahedron is formed. |

**8. What are point defects?**

Point defects are the deviations from ideal arrangement that occurs at some points or atoms in a crystalline substance.

**9. Explain Schottky defect. (SEPT 2020)**

- This defect arises due to the missing of equal number of cations and anions from the crystal lattice.
- Example: **NaCl**.
- The size of the cation and anion are of almost of similar.
- Presence of large number of schottky defects in a crystal lowers its density.



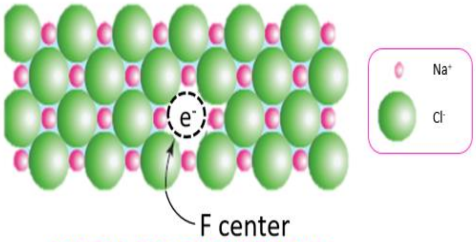
SCHOTTKY DEFECT

**10. Write short note on metal excess and metal deficiency defect with an example. (or) Write a short note on non-stoichiometric defects.**

**Metal excess defect:**

- This defect arises due to the presence of more number of metal ions than the anions.

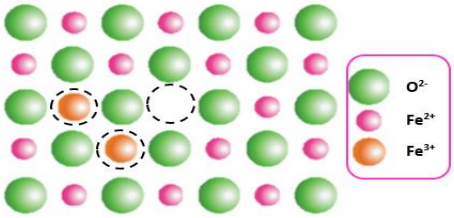
  Ex: **NaCl, KCl**
- The electrical neutrality of the crystal is maintained by the presence of anionic vacancies equal to the excess metal ions.
- The anionic vacancies, which are occupied by unpaired electrons are called **F centers.**



METAL EXCESSS DEFECT

**Metal deficiency defect:**

- Metal deficiency defect arises due to the presence of less number of cations than the anions.
- This defect is observed in a crystal in which the cations have variable oxidation state. Example: **FeO**



METAL DEFICIENCY DEFECT

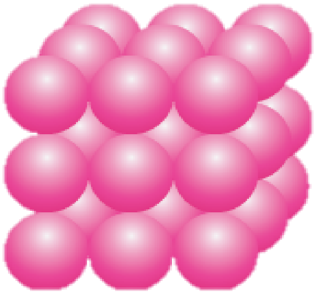
**11. Calculate the number of atoms in an FCC unit cell**

$$\text{Number of atoms in FCC unit cell} = \frac{\mathrm{Nc}}{8} + \frac{\mathrm{Nf}}{2} = \frac{8}{8} + \frac{6}{2} = 1 + 3 = 4$$

**12. Explain AAAA and ABABA and ABCABC type of three dimensional packing with the help of neat diagram.**

i. **AAAA three dimensional packing:**

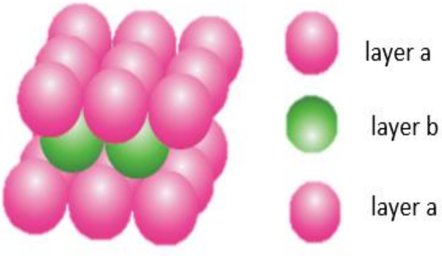
- It occurs in simple cubic arrangement.
- This is obtained by repeating the AAAA type two dimensional arrangements in three dimensions.
- Spheres in one layer sitting directly on the top of those in the previous layer so that all layers are identical.
- All spheres of different layers of crystal are perfectly aligned horizontally and also vertically.
- Each sphere is in contact with 6 neighbouring spheres i.e., four in its own layer, one above and one below and hence the coordination number is 6.



Simple Cubic (SC)

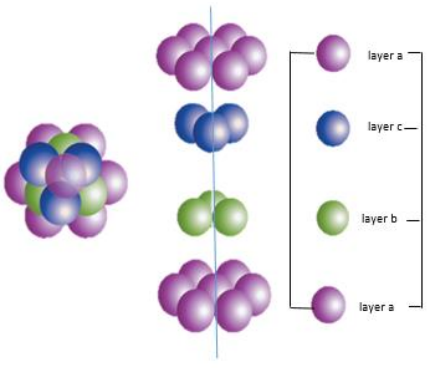
ii **ABABA three dimensional packing:**

- It occurs in body centered cubic arrangement.
- This is obtained by repeating the ABABAB type two dimensional arrangements in three dimensions.
- Spheres in the **first layer (a)** are slightly separated and the **second layer (b)** is formed by arranging the spheres in the depressions between the spheres in **first layer (a)**.
- The third layer is a repeat of the first.
- Each sphere is in contact with 8 neighbouring spheres i.e., four in the above layer and four in the below layer and hence the coordination number is 8.



Body Centered Cubic BCC

### iii ABCABC three dimensional packing:



abc arrangement – ccp structure

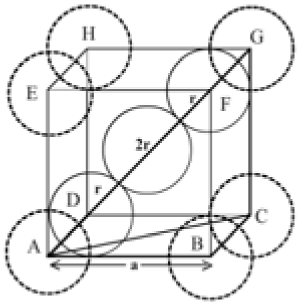
- It occurs in cubic close packed (ccp) structure.
- The **first layer (a)** is formed by arranging the spheres as in the case of two dimensional arrangements.
- The **second layer (b)** is formed by placing the spheres in the depressions of the first layer.
- A **tetrahedral void (x) and octahedral voids(y)** are formed in the first layer.
- The third layer is placed over the second layer in such a way that all the spheres of the third layer fit in octahedral voids.
- This arrangement of the third layer is different from other two layers **(a)** and **(b).** Hence, the third layer is designated **(c).**
- The stacking of layers is continued in abcabc...pattern.
- Each sphere is in contact with 12 neighbouring spheres i.e., six neighbouring spheres in its own layer, three spheres in the layer above and three sphere in the layer below and hence the coordination number of each sphere is 12.

### 13. Why ionic crystals are hard and brittle?

- Ionic crystal is hard due to strong electrostatic force of attraction between cations and anions.
- They are brittle because ionic bonds are non-directional.

### 14. Calculate the percentage efficiency of packing in case of body centered cubic crystal.

In bcc, the spheres are touching along the leading diagonal of the cube as shown in the fig.



In ΔABC

$AC^2 = AB^2 + BC^2$

$AC = \sqrt{AB^2 + BC^2}$

$AC = \sqrt{a^2 + a^2} = \sqrt{2a^2} = \sqrt{2}\,a$

In ΔACG

$AG^2 = AC^2 + CG^2$

$AG = \sqrt{AC^2 + CG^2}$

$AG = \sqrt{(\sqrt{2a})^2 + a^2} = \sqrt{2a^2 + a^2} = \sqrt{3a^2} = \sqrt{3}\,a$

But $\sqrt{3}\,a = 4\,r$: $r = \frac{\sqrt{3}}{4}a$

Volume of the sphere with radius 'r' = $\frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left[\frac{\sqrt{3}}{4}\,a\right]^3 = \frac{\sqrt{3}}{16}\pi\,a^3$

Number of spheres in bcc unit cell = 2

Total volume of all spheres in bcc unit cell = $2 \times \frac{\sqrt{3}}{16}\pi\,a^3 = \frac{\sqrt{3}}{8}\pi\,a^3$

Volume of the cube with edge length a = $a \times a \times a = a^3$

Packing fraction = $\frac{\text{Total volume occupied by all spheres in a unit cell}}{\text{Volume of unit cell}} \times 100$

$= \frac{\frac{\sqrt{3}}{8}\pi\,a^3}{a^3} \times 100 = \frac{\sqrt{3}\pi}{8} \times 100 = \sqrt{3}\pi \times 12.5 = 1.732 \times 3.14 \times 12.5 = 68\%$

**15. What is the two dimensional coordination number of a molecule in square close packed layer?**

The two dimensional coordination number of a molecule in square close packed layer is 4. In this arrangement each sphere is in contact with four of its neighbours.

**16. What is meant by the term "coordination number"? What is the coordination number of atoms in a bcc structure? (AUG-2021, MAY-2022)**

- The neighbouring atoms surrounded by each atom is called coordination number.
- The coordination number of atoms in a bcc structure is 8**.**

**17. An element has bcc structure with a cell edge of 288 pm. The density of the element is 7.2 gcm$^{-3}$. How many atoms are present in 208g of the element?**

**Given**

Edge of bcc (a) = 288pm = $2.88 \times 10^{-8}$ cm: For bcc, n = 2

Density = 7.2 gcm$^{-3}$

Mass of element = 208g

$$M = \frac{a^3\,\rho \times N_A}{n} = \frac{(2.88 \times 10^{-8})^3 \times 7.2 \times 6.023 \times 10^{23}}{2}$$

$$= \frac{1035.9 \times 10^{-24} \times 10^{23}}{2} = 51.795 \text{gmol}^{-1}$$

Number of atoms of an element $= \frac{\text{mass}}{\text{atomic mass}} \times 6.023 \times 10^{23}$

Number of atoms present in 208 g = $\frac{208}{51.795} \times 6.023 \times 10^{23}$ = **$2.418 \times 10^{24}$ atoms**

**18. Aluminium crystallizes in a cubic close packed structure. Its metallic radius is 125pm. Calculate the edge length of unit cell.**

**Given:** r = 125pm.

For ccp $r = \frac{a\sqrt{2}}{4} = \frac{a\sqrt{2}}{2\times\sqrt{2\times\sqrt{2}}} = \frac{a}{2\sqrt{2}}$

$a = 2\sqrt{2}\,r$

$= 2 \times 1.414 \times 125$ pm = **353.5 pm**

**19. If NaCl is doped with 10$^{-2}$ mol percentage of strontium chloride, what is the concentration of cation vacancy?**

100 moles of NaCl is doped with $10^{-2}$ moles of $SrCl_2$

Therefore 1 mole of NaCl is doped with $\frac{10^{-2}}{100} = 10^{-4}$ moles of $SrCl_2$

Each $Sr^{2+}$ ion will create 1 cation vacancy in NaCl.

Number of cationic vacancy produced by $10^{-4}$ mol $Sr^{2+}$ ion = $6.023 \times 10^{23} \times 10^{-4}$

$= 6.023 \times 10^{19}$

Number of cation vacancies produced by $SrCl_2$ = **$6.023 \times 10^{19}$ per mol**

**20. KF crystallizes in FCC structure like sodium chloride. Calculate the distance between K$^+$ and F$^-$ in KF. (Given: density of KF is 2.48 $g\ cm^{-3}$)**

Molar mass of KF = 39.1 + 19 = 58.1

$a^3 = \frac{n \times M}{N_A \times \rho} = \frac{4 \times 58.1}{6.023 \times 10^{23} \times 2.48} = 15.56 \times 10^{-23} = 1.56 \times 10^{-24}$

$\sqrt[3]{1.56}$ x $10^{-8}$ = 5.383 x $10^{-8}$ cm = 537.5 pm

Inter ionic distance (d) = $\frac{a}{\sqrt{2}}$ = $\frac{537.5}{1.414}$ pm = **380.13 pm**

**21. An atom crystallizes in fcc crystal lattice and has a density of 10 *gcm*$^{-3}$ with unit cell edge length of 100pm. Calculate the number of atoms present in 1 g of crystal.**

**Given:**

Density =10 $gcm^{-3}$: a = 100 pm = 100 x $10^{-10}$ cm: Mass = 1g

Number of atoms in FCC unit cell = 4

$$M = \frac{a^3 \rho \text{ x } N_A}{n} = \frac{(100 \text{ x } 10^{-10})^3 \text{ x } 10 \text{ x } 6.023 \text{ x } 10^{23}}{4}$$

$$= \frac{(1 \text{ x } 10^{-8})^3 \text{ x } 10 \text{ x } 6.023\text{x } 10^{23}}{4} = \frac{6.023}{4} = 1.505 \text{ gmol}^{-1}$$

Number of atoms of an element = $\frac{\text{mass}}{\text{atomic mass}}$x 6.023 x $10^{23}$

Number of atoms in 1 g of crystal == $\frac{1}{1{,}505}$ x 6.023 x$10^{23}$ = **4 x $10^{23}$ atoms**

**22. Atoms X and Y form bcc crystalline structure. Atom X is present at the corners of the cube and Y is at the centre of the cube. What is the formula of the compound?**

Number of corner atoms (X) = $\frac{N_C}{8} = \frac{8}{8} = 1$

Number of body centre atoms (Y) = $\frac{N_b}{1} = \frac{1}{1} = 1$

Formula of the compound = **XY**

**23. Sodium metal crystallizes in bcc structure with the edge length of the unit cell 4.3 ×$10^{-8}$ *cm*. Calculate the radius of sodium atom.**

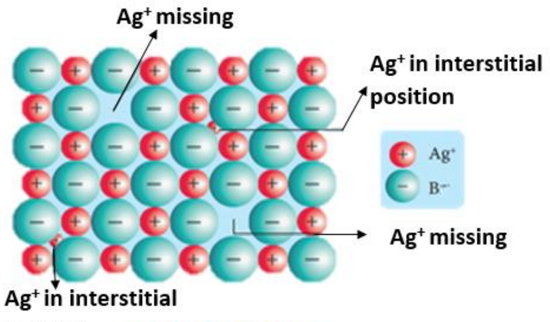
**Given: a = 4.3 ×$10^{-8}$ *cm*.**

For BCC

r = $\frac{\sqrt{3}}{4} a = \frac{1.732 \text{ x } 4.3 \times 10^{-8}}{4}$ =**1.86 ×$10^{-8}$ cm**

**24. Explain Frenkel defect (MARCH-20, JULY-22)**

- Frenkel defect arises due to the dislocation of ions from its crystal lattice.
- The ion which is missing from the lattice point occupies an interstitial position.
- This defect occurs when cation and anion differ in size.
- Unlike Schottky defect, this defect does not affect the density of the crystal. Ex: AgBr



FRENKEL DEFECT

## II ADDITIONAL QUESTIONS:

**1. How solids are classified?**

Solids

Crystalline solids

Amorphous solids
Ex: glass, rubber

(a) Ionic crystals. Ex: NaCl, KCl
(b) Covalent crystals Ex: Diamond, $SiO_2$
(c) Molecular crystals. Ex: Naphthalene, Anthracene, Glucose
(d) Metallic crystals. Ex: Na, Mg, Au, Ag
(e) Atomic solids. Ex: Frozen elements of group 18

**2. What are the characteristics of solids?**

(i) Definite volume and shape.
(ii) Rigid and incompressible
(iii) Strong cohesive forces and short inter atomic, ionic or molecular distances.

**3. Explain isotropy and anisotropy? (SEPT-2020)**

| No | Isotropy | Anisotropy |
|---|---|---|
| 1 | Isotropy means having identical values of physical properties (refractive index, electrical conductance) in all directions | Anisotropy means having different values of physical properties when measured along different directions. |
| 2 | Ex-amorphous solids. | Ex- crystalline solids |

**4. Give a note on covalent solids?**

- Atoms are bound together in a three dimensional network entirely by covalent bonds
- Examples: Diamond, silicon carbide etc.
- Hard and high melting point.
- Poor thermal and electrical conductors

**5. What are molecular crystals? How are they classified?**

- In molecular solids, the constituents are neutral molecules.
- Held together by weak Vanderwaals forces.
- Soft and do not conduct electricity
- Molecular solids are further classified into three types.

| No | Types 0f molecular crystals | Name of the force | Features | Examples |
|---|---|---|---|---|
| 1 | Non-polar molecular solids | London force | Low melting point, and are usually in liquids or gaseous state at room temperature. | Naphthalene, anthracene |
| 2 | Polar molecular solids | Dipole-dipole interaction | They have higher melting points than the non-polar molecular solids. | Solid $CO_2$ , Solid $NH_3$ |
| 3 | Hydrogen bonded molecular solids | Hydrogen bonds | They are generally soft solids under room temperature | Solid ice , glucose, urea |

**6. Explain metallic solids.**

- The lattice points are occupied by positive metal ions and a cloud of electrons pervades the space.
- Hard and have high melting point.
- Excellent electrical and thermal conductivity and possess bright lustre.
- Examples: Metals (Cu, Fe, Zn, Ag, Au) and metal alloys (Cu- Zn)

**7. Classify the following into covalent, molecular, ionic or metallic solids (AUG-2021)**

a. Diamond b. NaCl c. Glucose d. Brass e. Naphthalene f. $SiO_2$

| | | |
|---|---|---|
| a | Diamond | Covalent solid |
| b | NaCl | Ionic solid |
| c | Glucose | Molecular solid |
| d | Brass | Metallic solid |
| e | Naphthalene | Molecular solid |
| f | $SiO_2$ | Covalent solid |

**8. Name the parameters that characterize a unit cell**

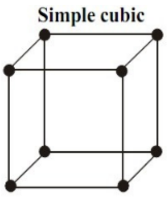
- Three edge lengths ( a, b and c )
- The angle between the edges $\alpha$, $\beta$ and $\gamma$.

**9. What are primitive and non-primitive unit cell?**

- A unit cell that contains only one lattice point is called a primitive unit cell,
- A unit cell that contains additional lattice points, either on a face or within the unit cell is called a non-primitive unit cells.

**10. Sketch i.SC ii. BCC iii. FCC & calculate its number of atoms per unit cell**

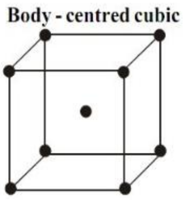
**i. SC**



Number of atoms in SC unit cell $= \frac{\mathrm{Nc}}{8} = \frac{8}{8}$

$= 1$

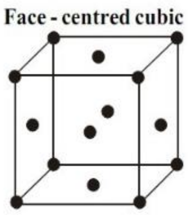
**ii. BCC**



Number of atoms in BCC unit cell $= \frac{\mathrm{Nc}}{8} + \frac{\mathrm{N}_b}{1} = \frac{8}{8} + \frac{1}{1}$

$= 1 + 1 = 2$

**iii. FCC**



Number of atoms in FCC unit cell $= \frac{\mathrm{Nc}}{8} + \frac{\mathrm{Nf}}{2} = \frac{8}{8} + \frac{6}{2}$

$= 1 + 3 = 4$

**11. How inter planar distance are calculated in unit cell? (OR) Explain Bragg's equation**

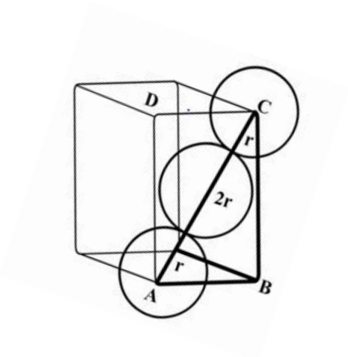
The inter planar distance (d) can be calculated using the Bragg's equation

$2d\sin\theta = n\lambda$

where

$\lambda$ - wavelength of X-ray used for diffraction.
$\theta$ - angle of diffraction
n - order of refraction
d - inter planar distance

**12. Explain the relationship between atomic radius and edge length of FCC unit cell and calculate its packing efficiency**



In ΔABC

$AC^2 = AB^2 + BC^2$

$AC = \sqrt{AB^2 + BC^2}$

$AC = \sqrt{a^2 + a^2} = \sqrt{2a^2} = \sqrt{2}\,a$

From the figure

$AC = 4r$

$4r = a\sqrt{2}$

$r = \frac{a\sqrt{2}}{4}$

Volume of the sphere with radius 'r' = $\frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left[\frac{\sqrt{2}}{4}\,a\right]^3$

$= \frac{4}{3}\pi\frac{2\sqrt{2}}{64}a^3 = \frac{\sqrt{2}}{24}\pi a^3$

Total number of spheres in FCC unit cell = 4

Total volume of all spheres in FCC unit cell = 4 x $\frac{\sqrt{2}}{24}\pi a^3 = \frac{\sqrt{2}}{6}\pi a^3$

Volume of the cube with edge length a = a x a x a = $a^3$

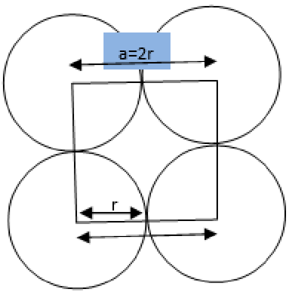
Packing fraction = $\frac{\text{Total volume occupied by all spheres in a unit cell}}{\text{Volume of unit cell}}$ x 100

$= \frac{\frac{\sqrt{2}}{6}\pi a^3}{a^3} \times 100$

$= \frac{\sqrt{2}\pi}{6} \times 100 = \frac{1.414 \times 3.14 \times 100}{6} = \mathbf{74\ \%}$

**13. Calculate the packing efficiency of polonium. (or) Calculate its packing efficiency of simple cubic system**

Polonium crystallizes in simple cubic pattern. So let us consider simple cubic system.
Let us consider a cube with an edge length ‘a’ as shown in fig.
Volume of the cube with edge length a is = a x a x a = $a^3$



Let ‘r’ is the radius of the sphere.
From the figure, a=2r, r=a/2

Volume of the sphere with radius ‘r’ = $\frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left[\frac{a}{2}\right]^3$

$$=\frac{4}{3}\pi\frac{a^3}{8}=\frac{\pi a^3}{6}$$

Total number of spheres in SC unit cell= 1

Total volume of all spheres in SC unit cell = $\frac{\pi a^3}{6}$ x 1= $\frac{\pi a^3}{6}$

Packing fraction = $\frac{\text{Total volume occupied by all spheres in a unit cell}}{\text{Volume of unit cell}}$ x 100

$$=\frac{\frac{\pi a^3}{6}}{a^3}\times 100=\frac{100\pi}{6}=\frac{100\times 3.14}{6}=\mathbf{52.33\%}$$

**14. What is packing efficiency? (AUG-2022)**

The percentage of total volume occupied by these constituent spheres gives the packing efficiency of an arrangement

Packing fraction = $\frac{\text{Total volume occupied by all spheres in a unit cell}}{\text{Volume of unit cell}}$ x 100

**15. Mention the packing efficiency and vacant space in SC, BCC and FCC unit cell**

| UNIT CELL | PACKING EFFICIENCY | VACANT SPACE |
|---|---|---|
| **SC** | 52.33% | 47.67% |
| **BCC** | 68% | 32% |
| **FCC** | 72% | 26% |

**16 How structure of an ionic compound is determined?**

The structure of an ionic compound is determined by radius ratio $\left(\frac{r_{C^+}}{r_{A^-}}\right)$

| $\left(\frac{r_{C^+}}{r_{A^-}}\right)$ | Coordination number | Structure | Example |
|---|---|---|---|
| 0.155 – 0.225 | 3 | Trigonal planar | $B_2O_3$ |
| 0.225 – 0.414 | 4 | Tetrahedral | ZnS |
| 0.414 – 0.732 | 6 | Octahedral | NaCl |
| 0.732 – 1.0 | 8 | Cubic | CsCl |

**17. Radius ratio of an ionic solid is found to be 0.415. Where the cations are occupied?**

Cations occupies the octahedral voids.

{Hint: radius ratio <0.4 – tetrahedral voids
radius ratio >0.4 – octahedral voids}

**18. If the radius ratio of the compound is between0.155- 0.225, find out the coordination number and structure of the compound. (JULY -2020)**

Coordination number = 3

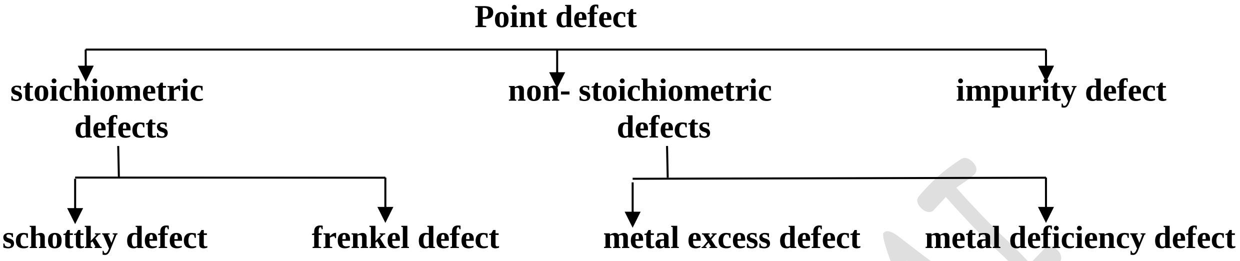
Structure =Trigonal planar

**19. If the number of close packed sphere is 6, calculate number of octahedral voids and tetrahedral voids. (MARCH -2020)**

Number of tetrahedral voids = 12

Number of octahedral voids = 6

**20. How point defects are classified?**



**21. How electrical neutrality is maintained in stoichiometric ionic crystals?**

In stoichiometric ionic crystals, a vacancy of one ion must always be associated with either by the absence of another oppositely charged ion (or) the presence of same charged ion in the interstitial position so as to maintain the electrical neutrality.

**22. Explain impurity defect**

- Due to the presence of impurity ions in ionic solids causes vacancies in the crystal lattice of the host.
- For example, addition of $CdCl_2$ to silver chloride yields solid solutions where the divalent cation $Cd^{2+}$ occupies the position of $Ag^+$.
- This disturbs the electrical neutrality of the crystal.
- In order to maintain the same, proportional number of $Ag^+$ ions leave the lattice This produces a cation vacancy in the lattice, such kind of crystal defects are called impurity defects.

**23. What happens when ZnO is heated?**

- ZnO is colourless at room temperature.
- When it is heated, it becomes yellow in colour.
- On heating, it loses oxygen and thereby forming free $Zn^{2+}$ ions.
- The excess $Zn^{2+}$ ions move to interstitial sites and the electrons also occupy the interstitial positions.

**24. Why Frenkel defect is not found in alkali halides?**

Larger size of alkali metal ions does not allow them to fit in interstitial sites.

**25. Schottky defect lowers the density of the ionic solid. Why?**

The total number of ions in a crystal with this defect is less than the theoretical value of ions. Thus the density of the solid crystal is less than expected.

**26. What are F centers?**

Anionic vacancies occupied by unpaired electrons is called F centers.

**27. When NaCl crystals are heated in the presence of sodium vapour, excess of $Na^+$ ions are observed. Justify your answer.**

- When **NaCl** crystals are heated in the presence of sodium vapour, $Na^+$ ions are formed and are deposited on the surface of the crystal.
- Chloride ions ($Cl^-$) diffuse to the surface from the lattice point and combines with $Na^+$
- The electron lost by the sodium vapour diffuse into the crystal lattice and occupies the vacancy created by the $Cl^-$ ions.
- Such anionic vacancies which are occupied by unpaired electrons are called **F centers.**
- Hence, the formula of NaCl which contains excess $Na^+$ ions can be written as $\mathbf{Na_{1+x}Cl}$

**28. How density of the unit cell in a crystal is calculated?**

Density of the unit cell $\rho = \frac{massof\ the\ unit\ cell}{volume\ of\ the\ unit\ cell}$

**29. Give the relationship between atomic radius (r), edge length (a) and packing efficiency of the unit cell of a cubic crystal.**

| UNIT CELL | NO:OF ATOMS | COORD NO | INTER ATOMIC DISTANCE (d) | ATOMIC RADIUS (r) | PACKING EFFICIENCY |
|---|---|---|---|---|---|
| SIMPLE CUBIC | 1 | 6 | d = a | $r = \frac{a}{2}$ | 52.33% |
| BODY CENTERED CUBIC | 2 | 8 | $d = \frac{\sqrt{3}}{2}a = 0.866\ a$ | $r = \frac{\sqrt{3}}{4}a = 0.433\ a$ | 68% |
| FACE CENTERED CUBIC | 4 | 12 | $d = \frac{a}{\sqrt{2}} = 0.7076\ a$ | $r = \frac{a}{2\sqrt{2}} = 0.3536\ a$ | 74% |

## III EVALUATE YOURSELF:

**1. An element has a face centered cubic unit cell with a length of 352.4 pm along an edge. The density of the element is 8.9 gcm-3. How many atoms are present in 100 g of an element?**

**Given:** Density =8.9 $gcm^{-3}$: a = 352.4 pm = $3.524 \times 10^{-8}$cm, Mass = 100g, n = 4

$$M = \frac{a^3\ \rho \text{ x } N_A}{n} = \frac{(3.524\text{x } 10^{-8})^3 \text{ x } 8.9 \text{ x } 6.023 \text{ x } 10^{23}}{4}$$

$$= \frac{2345.9\text{x } 10^{-1}}{4} = 586.5\text{x}10^{-1} = 58.65\ \text{gmol}^{-1}$$

Number of atoms of an element = $\frac{\text{mass}}{\text{atomic mass}}$ x $6.023 \times 10^{23}$

Number of atoms in 100g of an element = $\frac{100}{58.65}$ x $6.023 \times 10^{23}$ = $\mathbf{10.27 \times 10^{23}}$ **atoms**

2. **Determine the density of CsCl which crystallizes in a bcc type structure with an edge length 412.1 pm.**

   **Given:** M=133 + 35.5 =168.5 $gmol^{-1}$, a= 412.1 pm= 4.121 x $10^{-8}$ cm, n=2

$$\rho = \frac{\mathrm{M\ x\ n}}{\mathrm{a^3\ \ x\ N_A}} = \frac{168.5\ \mathrm{x}\ 2}{(4.121\mathrm{x}\ 10^{-8})^3 \mathrm{x}\ 6.023\ \mathrm{x}\ 10^{23}} = \frac{337}{42.15} = 7.99$$

   Density of CsCl crystal = **8 $gcm^{-3}$**

3. **A face centered cubic solid of an element (atomic mass 60) has a cube edge of 4 $A^0$. Calculate its density.**

   **Given:** M=60 $gmol^{-1}$ a = 4 $A^0$= 4 x $10^{-8}$ cm, n=4

$$\rho = \frac{\mathrm{M\ x\ n}}{\mathrm{a^3\ \ x\ N_A}} = \frac{60\ \mathrm{x}\ 4}{(4\ \mathrm{x}\ 10^{-8})^3 \mathrm{x}\ 6.023\ \mathrm{x}\ 10^{23}} = \frac{240}{38.54} = \mathbf{6.227 gcm^{-3}}$$

   Density of an element = **6.227$gcm^{-3}$**

**<u>IV EXAMPLE:</u>**

**Barium has a body centered cubic unit cell with a length of 508pm along an edge. What is the density of barium in g $cm^{-3}$?**

**Given:** M=137.3 $gmol^{-1}$, a= 508 pm= 5.08 x $10^{-8}$ cm, n=2

$$\rho = \frac{\mathrm{M\ x\ n}}{\mathrm{a^3\ \ x\ N_A}} = \frac{137.3\mathrm{x}\ 2}{(5.08\mathrm{x}\ 10^{-8})^3 \mathrm{x}\ 6.023\ \mathrm{x}\ 10^{23}} = \frac{274.6}{78.96} = 3.477$$

Density of CsCl crystal = **3.5 $gcm^{-3}$**

# UNIT-7 CHEMICAL KINETICS

## I. ANSWER THE FOLLOWING QUESTIONS

1. **Define average rate and instantaneous rate.**

| Average rate | Instantaneous rate |
|---|---|
| It is the rate between the intervals of time | It is the rate at a particular time.<br>Average rate becomes instantaneous rate when $\Delta t \to 0$ |

2. **Define rate law and rate constant.**

**Rate Law**

$aA + bB \longrightarrow$ products

rate $\propto [A]^x [B]^y$

rate = $k [A]^x [B]^y$

Rate is given in terms of molar concentration of reactants raised to the power which may or may not equal to stoichiometric coefficient.

**Rate constant**

Rate constant is same as rate of reaction when concentration of all the reactants is unity.

3. **Derive integrated rate law for a zero order reaction A $\longrightarrow$ product. (AUG-21, AUG-22)**

Rate is independent of the concentration of reactant is called zero order reaction.

Consider a general zero order reaction. **A $\longrightarrow$ Product**

At t = 0 concentration of reactant = $[A_0]$

At time t, concentration of reactant left = $[A]$

rate = $k[A]^0$

$$-\frac{d[A]}{dt} = k \; : -d[A] = k\,dt$$

Integrate between limits of $[A_0]$ at t = 0 and $[A]$ at time 't'.

$$-\int_{[A_0]}^{[A]} d[A] = k\int_0^t dt$$

$$-\left([A]\right)_{[A_0]}^{[A]} = k(t)_0^t \; : [A_0] - [A]/t = k$$

$$\boxed{k = \frac{[A]_0 - [A]}{t}}$$

4. **Define half life of a reaction. Show that for a first order reaction half life is independent of initial concentration.**

Time required for the reactant concentration to reach one half its of initial value is called half life of a reaction.

**First order reaction half-life**

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

when $t = t_{1/2}$ then $[A] = \dfrac{[A_0]}{2}$

$$k = \frac{2.303}{t_{1/2}} \log \frac{[A_0]}{\frac{[A_0]}{2}}$$

$$t_{1/2} = \frac{2.303}{k} \log 2$$

$$t_{1/2} = \frac{2.303}{k} \times 0.3010$$

$$\boxed{t_{1/2} = \frac{0.693}{k}}$$

No concentration terms involved, so half life is independent on initial concentration of reactant.

**5. What is an elementary reaction? Give the differences between order and molecularity of a reaction. (AUG-22)**

Each and every single step in a reaction mechanism is called an elementary reaction.

| No | Order of a reaction | Molecularity of a reaction |
|---|---|---|
| 1. | It is the sum of the powers of concentration terms involved in the experimentally determined rate law. | It is the total number of reactant species that are involved in an elementary step. |
| 2. | It can be zero (or) fraction (or) Integer | It is always whole number, cannot be zero or fraction. |
| 3. | It is assigned for a overall reaction | It is assigned for each elementary step of mechanism. |

**6. Explain the rate determining step with an example.**

Consider a reaction $\boxed{2H_2O_2 \xrightarrow{I^-} 2H_2O + O_2}$

This reaction takes place in two steps

Step – 1 $\quad H_2O_{2(aq)} + I^-_{(aq)} \xrightarrow[RDS]{slow} H_2O(l) + OI^-_{(aq)}$

Step – 2 $\quad H_2O_{2(aq)} + OI^-_{(aq)} \longrightarrow H_2O(l) + I^-_{(aq)} + O_{2(g)}$

Overall reaction $\quad 2H_2O_{2(aq)} \longrightarrow 2H_2O(l) + O_{2(g)}$

Step – 1 is a slow step and rate determining step. In this step $H_2O_2$ and $I^-$ are involved, hence it is bimolecular reaction.

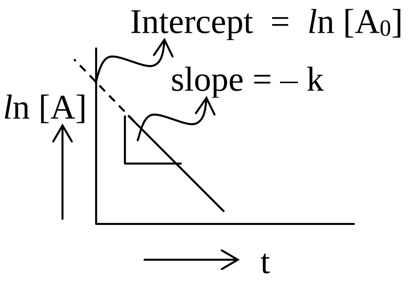
**7. Describe the graphical representation of first order reaction.**

$$k = \frac{1}{t} ln \frac{[A_0]}{[A]}$$

$kt = ln\,[A_0] - ln[A]$

$ln\,[A] = -kt + ln\,[A_0]$

$y = -mx + C$



Plot of ln [A] Vs t gives straight line with negative slope.
Slope equal to – k and intercept equals to ln[A].

**8. Write the rate law for the following reactions.**
**(a) A reaction that is 3/2 order in x and zero order in y.**
**(b) A reaction that is second order in NO and first order in $Br_2$.**

(a) rate = $k\,[X]^{3/2}\,[Y]^0$
rate = $k\,[X]^{3/2}$
(b) rate = $k\,[NO]^2\,[Br_2]^1$

**9. Explain the effect of catalyst on reaction rate with an example.**

1. Energy of activation is lowered.
2. greater no of molecules cross the energy barrier and change over to products.
3. rate of reaction increases.

Example : $2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$
$MnO_2$ acts as catalyst.

**10. The rate law for a reaction of A, B and L has been found to be rate = k $[A]^2$ [B] $[L]^{3/2}$. How would the rate of reaction change when**

**(i) Concentration of [L] is quadrupled**
**(ii) Concentration of both [A] and [B] are doubled**
**(iii) Concentration of [A] is halved**
**(iv) Concentration of [A] is reduced to (1/3) and concentration of [L] is quadrupled.**

| | | | |
|---|---|---|---|
| **(i)** | rate = $k\,[A]^2\,[B]\,[L]^{3/2} \longrightarrow (1)$<br>x rate = $k\,[A]^2\,[B]\,[4L]^{3/2} \longrightarrow (2)$<br>$\frac{(2)}{(1)} \Rightarrow \frac{x\ \cancel{rate}}{\cancel{rate}} = \frac{\cancel{k}\,\cancel{[A]^2}\,\cancel{[B]}[4\cancel{L}]^{3/2}}{\cancel{k}\,\cancel{[A]^2}\,\cancel{[B]}\,\cancel{[L]}^{3/2}}$<br>$x = 4^{3/2}$<br>$x = (4)^{3\times\frac{1}{2}}$<br>$x = 8$ $x = (64)^{\frac{1}{2}}$<br>Rate increase by 8 times | **(ii)** | (ii) x rate = $k\,[2A]^2\,[2B]\,[L]^{3/2} \longrightarrow (3)$<br>$\frac{(3)}{(1)} \Rightarrow \frac{x\ \cancel{rate}}{\cancel{rate}} = \frac{\cancel{k}[2\cancel{A}]^2[2\cancel{B}]\,\cancel{[L]^{3/2}}}{\cancel{k}\,\cancel{[A]^2}\,\cancel{[B]}\,\cancel{[L]^{3/2}}}$<br>$x = (2)^2\,(2)$<br>$x = 8$<br>Rate increase by 8 times |
| **(iii)** | x rate = $k\left[\frac{A}{2}\right]^2 [B][L]^{3/2} \longrightarrow (4)$<br>$\frac{(4)}{(1)} \Rightarrow \frac{x\ \cancel{rate}}{\cancel{rate}} = \frac{\cancel{k}\left[\frac{\cancel{A}}{2}\right]^2[\cancel{B}][\cancel{L]^{3/2}}}{\cancel{k}[\cancel{A}]^2[\cancel{B}][\cancel{L]^{3/2}}}$<br>$x = \left(\frac{1}{2}\right)^2$<br>$x = \frac{1}{4}$<br>Rate decrease by $\frac{1}{4}$ times | **(iv)** | x rate = $k\left[\frac{A}{3}\right]^2 [B][4L]^{3/2} \longrightarrow (5)$<br>$\frac{(5)}{(1)} \Rightarrow \frac{x\ \cancel{rate}}{\cancel{rate}} = \frac{\cancel{k}\left[\frac{\cancel{A}}{3}\right]^2[\cancel{B}][\cancel{4L]^{3/2}}}{\cancel{k}[\cancel{A}]^2[\cancel{B}][\cancel{L]^{3/2}}}$<br>$x = \left(\frac{1}{3}\right)^2 (4)^{3/2}$<br>$x = \left(\frac{1}{9}\right)(8)$<br>Rate decrease by $\frac{8}{9}$ times |

11. **The rate of formation of a dimer in a second order reaction is 7.5 × $10^{-3}$ mol $L^{-1}$ $s^{-1}$ at 0.05 mol $L^{-1}$ monomer concentration. Calculate the rate constant.**

rate = k [monomer]$^2$

$$7.5\times10^{-3} = k\times(0.05)^2$$

$$k = \frac{7.5\times10^{-3}}{(0.05)^2} = \frac{7.5\times10^{-3}}{(5\times10^{-2})^2} = \frac{7.5\times10^{-3}}{25\times10^{-4}}$$

$$= \frac{7.5\times10^{1}}{25} = \frac{75}{25} = 3\ \text{molL}^{-1}\text{s}^{-1}$$

12. **For a reaction X + Y + Z $\longrightarrow$ products the rate law is given by rate = k $[X]^{3/2}$ $[Y]^{1/2}$ . What is the overall order of the reaction and what is the order of the reaction with respect to z.**

X + Y + Z $\longrightarrow$ product

rate = k $[X]^{3/2}$ $[Y]^{1/2}$

order w.r.to Z = 0

overall order = $\frac{3}{2}+\frac{1}{2}=2$

13. **Explain briefly the collision theory of bimolecular reactions. (or) Derive** $k = pz\ e^{\frac{-Ea}{RT}}$

Consider a bimolecular reaction between $A_2$ and $B_2$ proceeds through collision between them which is proportional to number of collision per second

Rate α Collision rate

Collision rate α $[A_2]$ $[B_2]$

Collision rate = Z $[A_2]$ $[B_2]$ Z is the collision Frequency

Collision rate in gas phase reaction is calculated from kinetic theory of gas and its value is $10^9$ collision per seconds at 298K and 1 atm pressure.

All these collisions are not effective and in order for reaction to takes place, the colliding molecules must possess activation energy.

Fraction of effective collision (f) is given by $f = e^{-\frac{E_a}{RT}}$

In addition to activation energy, orientation factor(p) also necessary for reaction to take place.

rate = p × f × collision rate

rate = p × $e^{-\frac{E_a}{RT}}$ × Z $[A_2]$ $[B_2]$ $\longrightarrow$ (1)

As per rate law

rate = k $[A_2]$ $[B_2]$ $\longrightarrow$ (2)

comparing (1) and (2)

$$\boxed{k = pze^{-\frac{E_a}{RT}}}$$

14. **Write Arrhenius equation and explains the terms involved. (MAY-22)**

Arrhenius equation $k = Ae^{-\frac{E_a}{RT}}$

k is rate constant, A is Frequency factor

$E_a$ is Activation energy( $Jmol^{-1}$), T is Temperature in Kelvin

R is gas constant (8.314 $JK^{-1}$ $mol^{-1}$)

15. **The decomposition of $Cl_2O_7$ at 500 K in the gas phase to $Cl_2$ and $O_2$ is a first order reaction. After 1 minute at 500K, the pressure of $Cl_2O_7$ falls from 0.08 to 0.04 atm. Calculate the rate constant in $s^{-1}$.**

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$k = \frac{2.303}{60}\log\frac{0.08}{0.04} \quad = \frac{2.303}{60}\log 2 \quad = \frac{2.303}{60}\times 0.3010 \quad = \frac{0.6932}{60} \quad = 0.011553\ s^{-1}$$

$$\boxed{k\ =\ 1.153\times 10^{-2}s^{-1}}$$

16. **Give two examples for zero order reaction**.

(i) $H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$ (ii) $N_2O(g) \rightleftarrows N_2(g) + \frac{1}{2}O_2(g)$

17. **Explain pseudo first order reaction with an example.**

A second order reaction can be altered to a first order reaction by taking one of the reactants in large excess, such reaction is called pseudo first order reaction.

Example : Acid hydrolysis of ester

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

18. **Identify the order for the following reactions**

**(i) Rusting of Iron**

**(ii) Radioactive disintegration of $_{92}U^{238}$**

**(iii) 2A + 3B $\longrightarrow$ products ; rate = $[A]^{1/2}\ [B]^2$**

(i) First order

(ii) First order

(iii) $\frac{1}{2} + 2 \ = \frac{1+4}{2} = \frac{5}{2}$

19. **A gas phase reaction has energy of activation 200 kJ $mol^{-1}$. If the frequency factor of the reaction is $1.6 \times 10^{13}\ s^{-1}$. Calculate the rate constant at 600 K. ($e^{-40.09} = 3.8 \times 10^{-18}$)**

$E_a$ = 200 kJ $mol^{-1}$

A = $1.6 \times 10^{13}\ s^{-1}$

T = 600 K and R = 8.314 J $K^{-1}$ $mol^{-1}$

k = ?

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$= \log 1.6\times 10^{13} - \frac{2000\cancel{0}\cancel{0}}{2.303\times 8.314\times 6\cancel{0}\cancel{0}} \quad = \log 1.6\times 10^{13} - \frac{2000}{2.303\times 8.314\times 6}$$

$$= \log 1.6\times 10^{13} - \frac{2000}{114.88}$$

$$= \log 1.6\times 10^{13} - 17.409 = \log 1.6 + 13 - 17.409$$

$$= 0.2041 + 13 - 17.409 = 13.2041 - 17.409$$

log k = – 4.2049

= – 4 – 0.2049 + 1 – 1

= – 5 + 0.7951

$= = \bar{5}.7951$

$k = \text{Anti}\log\ \bar{5}.7951$

$$\boxed{k = 6.238\times 10^{-5}s^{-1}}$$

**20.** **For the reaction 2x + y $\longrightarrow$ L. Find the rate law from the following data.**

| [x]<br>(min) | [y]<br>(min) | rate<br>($M\ s^{-1}$) |
|---|---|---|
| **0.2** | **0.02** | **0.15** |
| **0.4** | **0.02** | **0.30** |
| **0.4** | **0.08** | **1.20** |

rate = $k\ [X]^a\ [Y]^b$

$0.15 = k\ (0.2)^a\ (0.02)^b \longrightarrow (1)$

$0.30 = k\ (0.4)^a\ (0.02)^b \longrightarrow (2)$

$1.20 = k\ (0.4)^a\ (0.08)^b \longrightarrow (3)$

$$\frac{(2)}{(1)} \Rightarrow \frac{0.30}{0.15} = \frac{\cancel{k}(0.4)^a\,\cancel{(0.02)^b}}{\cancel{k}(0.2)^a\,\cancel{(0.02)^b}}$$

$$2 = 2^a$$

order w.r.to X = 1

$$\frac{(3)}{(2)} \Rightarrow \frac{1.20}{0.30} = \frac{\cancel{k(0.4)^a}\,(0.08)^b}{\cancel{k(0.4)^a}\,(0.02)^b}$$

$$4 = 4^b$$

$$b = 1$$

order w.r.to Y = 1

rate law is rate = $k\ [X]^1\ [Y]^1$

**21.** **How do concentrations of the reactant influence the rate of reaction?**

Rate of reaction increases with increases of concentration of reactant.

rate $\alpha$ [Reactant]

As reactant concentration is more, which leads to more collision of reactant molecules which increases the rate of reaction.

**22.** **How do nature of the reactant influence rate of reaction. (or)**
**Titration between potassium permanganate and oxalic acid is carried out at 60°C where as titration between potassium permanganate and ferrous ammonium sulphate at room temperature. Give reason.**

Chemical reaction involves bond breaking and bond formation. The net energy involved in this process depends on nature of reactants and hence rate differs for different reactants.

For example, titration between $KMnO_4$ vs FAS takes place at room temperature whereas titration between $KMnO_4$ vs Oxalic acid is heated to 60°C. This is because oxidation of oxalate ion by $KMnO_4$ is slow compared to reaction between $KMnO_4$ and $Fe^{2+}$.

**23.** **The rate constant for a first order reaction is $1.54 \times 10^{-3}\ s^{-1}$. Calculate its half life time. (JUN-20)**

$k = 1.54 \times 10^{-3}\ s^{-1}$

$t_{1/2} = ?$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.54 \times 10^{-3}} = \frac{0.693 \times 10^3}{1.54} = \frac{693}{1.54}$$

$$\boxed{t_{1/2} = 450\ \text{sec}}$$

**24. The half life of the homogeneous gaseous reaction $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$ which obeys first order kinetics is 8.0 minutes. How long will it take for the concentration of $SO_2Cl_2$ to be reduced to 1% of the initial value?**

$t_{1/2} = 8$ min        t = ?

$[A_0] = 100$

[A] = 1% of initial value

$$[A] = \frac{1}{100} \times 100 = 1$$

$$k = \frac{0.693}{t_{1/2}}$$

$$\boxed{k = \frac{0.693}{8}\ \text{min}^{-1}}$$

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$\frac{0.693}{8} = \frac{2.303}{t}\log\frac{100}{1}$$

$$\frac{0.693}{8} = \frac{2.303}{t} \times 2$$

$$\frac{0.693}{8} = \frac{4.606}{t}$$

$$t = \frac{4.606 \times 8}{0.693} = \frac{36.848}{0.693}$$

$$\boxed{t = 53.17\ \text{min}}$$

**25. The time for half change in a first order decomposition of a substance A is 60 seconds. Calculate the rate constant. How much of A will be left after 180 seconds.**

(i) $t_{1/2} = 60\,\text{sec}$        k = ?

(ii) t = 180 sec        [A] = ?

$[A_0] = 100$

(i) $t_{1/2} = \frac{0.693}{k}$

$$k = \frac{0.693}{t_{t_{1/2}}} = \frac{0.693}{60} = 0.01155\ \text{sec}^{-1}$$

(ii) $k = \frac{0.693}{t_{t_{1/2}}}\log\frac{[A_0]}{[A]}$

$$0.01155 = \frac{2.303}{180}\log\frac{[A_0]}{[A]}$$

$$\log\frac{100}{[A]} = \frac{0.01155 \times 180}{2.303} : \log\frac{100}{[A]} = \frac{2.079}{2.303}$$

$$\log\frac{100}{[A]} = 0.9027$$

$$\frac{100}{[A]} = \text{Anti}\log 0.9027$$

$$[A] = \frac{100}{7.993} \ : \ \frac{100}{[A]} = 7.993$$

$[A] = 12.5\%$

**26. A zero order reaction is 20% complete in 20 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?**

(i) $[A_0] = 100$ $\quad$ $[A] = 80$

$t = 20$ min $\quad$ $k = ?$

(ii) $t = ?$ $\quad$ $[A] = 20$

(i) $k = \frac{[A_0]-[A]}{t} = \frac{100-80}{20} = \frac{20}{20}$

$$\boxed{k = 1 \text{ mol L}^{-1}\text{min}^{-1}}$$

(ii) $k = \frac{[A_0]-[A]}{t}$

$$1 = \frac{100-20}{t}$$

$$\boxed{t = 80 \text{ min}}$$

**27. The activation energy of a reaction is 225 k cal mol$^{-1}$ and the value of rate constant at 40°C is 1.8 × 10$^{-5}$ s$^{-1}$. Calculate the frequency factor A.**

$E_a = 225 \text{ k cal.mol}^{-1} = 225000 \text{ cal . mol}^{-1}$

$k = 1.8 \times 10^{-5} \text{ s}^{-1}$

$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$

$T = 40°C = 40 + 273 = 313 \text{ K}$

$A = ?$

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\log 1.8 \times 10^{-5} = \log A - \frac{22500}{2.303 \times 1.987 \times 313}$$

$$\log 1.8 \times 10^{-5} = \log A - \frac{22500}{1432}$$

$\log 1.8 \times 10^{-5} = \log A - 15.7089$

$\log 1.8 \times 10^{-5} = \log A - 15.7089$

$\log 1.8 - 5 = \log A - 15.7089$

$0.2553 - 5 = \log A - 15.7089$

$\log A = 15.7089 + 0.2553 - 5$

$\log A = 10.9642$

$A = \text{Antilog } 10.9642$

$$\boxed{A = 9.208 \times 10^{10} \text{ collisons s}^{-1}}$$

**28 A first order reaction is 40% complete in 50 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?**

(i) $t = 50$ min $\quad$ $[A_0] = 100$ $\quad$ $[A] = 60$ $\quad$ $k = ?$

(ii) $[A] = 20$ $\quad$ $t = ?$

$$\text{(i)}\quad k = \frac{2.303}{t}\log\frac{[A_0]}{[A]} = \frac{2.303}{50}\log\frac{100}{60} = \frac{2.303}{50}\log 1.667 = \frac{2.303}{50}\times 0.2219 = \boxed{0.01022\ \text{min}^{-1}}$$

$$\text{(ii)}\quad k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$0.01022 = \frac{2.303}{t}\log\frac{100}{20}$$

$$0.01022 = \frac{2.303}{t}\log 5$$

$$0.01022 = \frac{2.303}{t}\times 0.6990$$

$$t = \frac{2.303}{k}\times 0.6990 = \frac{1.61}{0.01022} \qquad \boxed{t\ =\ 157.51\ \text{min}}$$

## II. EXAMPLES

### Example-1 (Page 211)

**Consider the oxidation of nitric oxide to form $NO_2$**

**$2NO(g) + O_2(g) \longrightarrow 2NO_2\ (g)$**

**(a) Express the rate of the reaction in terms of changes in the concentration of NO, $O_2$ and $NO_2$.**

**(b) At a particular instant, when $[O_2]$ is decreasing at 0.2 mol $L^{-1}$ $s^{-1}$ at what rate is $[NO_2]$ increasing at that instant?**

$$\text{(a)}\quad -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$$

$$\text{(b)}\quad -\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$$

$$0.2 = \frac{1}{2}\frac{d[NO_2]}{dt}$$

$$\frac{d[NO_2]}{dt} = 0.2\times 2 = 0.4\ \text{mol}\cdot L^{-1}s^{-1}$$

### Example-2 (Page 211)

**What is the order with respect to each of the reactant and overall order of the following reaction?**

**(a)** $5Br^{-}(aq) + BrO_3^{-}(aq) + 6H^{+}(aq) \longrightarrow$ **$3Br_2(l)$ + $3H_2O(l)$**

**The experimental rate law is**

**Rate = k $[Br^{-}]$ $[BrO_3]$ $[H^{+}]^2$**

**(b)** $CH_3CHO(g) \xrightarrow{\Delta} CH_4(g) + CO(g)$

**The experimental rate law is**

$$\text{Rate} = k[CH_3CHO]^{3/2}$$

(a) Order w.r.t. $Br^{-}$ is 1

Order w.r.t. $BrO_3^{-}$ is 1

Order w.r.t. $H^{+}$ is 2

Overall order is 1 + 1 + 2 = 4

(b) order = 3/2

**Example-3 (Page 211)**

**The rate of the reaction x + 2y → product is $4 \times 10^{-3}$ mol $L^{-1}$ $s^{-1}$, if [x] = [y] = 0.2 M and rate constant at 400 K is $2 \times 10^{-2} s^{-1}$, What is the overall order of the reaction. [Sep 2020]**

rate = k $[X]^a [Y]^b$

$4 \times 10^{-3} = 2 \times 10^{-2} \times (0.2)^a (0.2)^b$

$$\frac{4\times10^{-3}}{2\times10^{-2}} = (0.2)^{a+b}$$

$$2\times10^{-1} = (0.2)^{a+b}$$

$$0.2 = (0.2)^{a+b}$$

Comparing the powers a + b = 1

Overall order = a + b = 1

**Example-4 (Page 216)**

**A first order reaction takes 8 hours for 90% completion. Calculate the time required for 80% completion. (log 5 = 0.6989 ; log 10 = 1)**

t = 8 hr

$[A_0] = 100$

[A] = 10

t = ? for [A] = 20 (80% completion)

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]} = \frac{2.303}{8}\log\frac{100}{10} = \frac{2.303}{8}\log 10$$

$$\boxed{k = \frac{2.303}{8}\ hr^{-1}}$$

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$\frac{2.303}{8} = \frac{2.303}{t}\log\frac{100}{20}$$

$$\frac{2.303}{8} = \frac{2.303}{t}\log 5$$

$$\frac{2.303}{8} = \frac{2.303}{t}\times 0.6989$$

$$\frac{2.303}{8} = \frac{1.6096}{t}$$

$$t = \frac{1.6096}{2.303} = \frac{12.876}{2.303}$$

t= 5.59 hr

**Example-6 (Page 217)**

**Show that in case of first order reaction, the time required for 99.9% completion is nearly ten times the time required for half completion of the reaction.**

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$t_{99.9\%} = \frac{2.303}{k}\log\frac{100}{0.1}$$

$$t_{99.9\%} = \frac{2.303}{k}\log 1000$$

$$t_{99.9\%} = \frac{2.303}{k}\times 3$$

$$\boxed{t_{99.9\%} = \frac{6.909}{k}} \longrightarrow (1)$$

$$\boxed{t_{50\%} = \frac{0.693}{k}} \longrightarrow (2)$$

From $\frac{(1)}{(2)}$, $\frac{t_{99.9\%}}{t_{50\%}} = \frac{6.909}{k}\times\frac{k}{0.693}$

$$\frac{t_{99.9\%}}{t_{50\%}} = 10$$

$$\boxed{t_{99.9\%} = 10\ t_{50\%}}$$

Hence proved.

**Example-7 (Page 221)**

**The rate constant of a reaction of a reaction at 400 and 200 K are 0.04 and 0.02 $s^{-1}$ respectively. Calculate the value of activation energy.**

$T_1 = 200$ K $k_1 = 0.02\ s^{-1}$

$T_2 = 400$ K $k_1 = 0.04\ s^{-1}$

$R = 8.314\ JK^{-1}\,mol^{-1}$

$E_a = ?$

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log\frac{0.04}{0.02} = \frac{E_a}{2.303\times 8.314}\left(\frac{400-200}{400\times 200}\right)$$

$$\log 2 = \frac{E_a}{2.303\times 8.314}\times\frac{2\cancel{0}\cancel{0}}{800\cancel{0}\cancel{0}}$$

$$0.3010 = \frac{E_a}{2.303\times 8.314}\times\frac{2}{800}$$

$$0.3010 = \frac{E_a}{2.303\times 8.314}\times\frac{1}{400}$$

$$E_a = 2.303\times 8.314\times 400\times 0.3010$$

$$\boxed{E_a = 2.305\ \text{J mol}^{-1}}$$

**Example-8 (Page 221)**

**Rate constant k of a reaction varies with temperature T according to the following Arrhenius equation**

$$\mathbf{\log k = \log A \frac{E_a}{2.303R}\left(\frac{1}{T}\right)}$$

**Where $E_a$ is the activation energy. When a graph is plotted for log k Vs $\frac{1}{T}$ a straight line with a slope of –4000 K is obtained. Calculate the activation energy**

Slope = –4000 K

$E_a$ = ?

$$\text{slope} = -\frac{E_a}{2.303R}$$

$$\cancel{-}4000\text{K} = \cancel{-}\frac{E_a}{2.303 \times 8.314\ \text{JK}^{-1}\text{mol}^{-1}}$$

$$E_a = 2.303 \times 8.314\ \text{J}\cancel{\text{K}^{-1}}\text{mol}^{-1} \times 4000\cancel{\text{K}}$$

$$\boxed{E_a = 76589\ \text{J mol}^{-1}}$$

## III EVALUATE YOURSELF

### Evaluate Yourself-1 (Page 211)

**(1) Write the rate expression for the following reactions, assuming them as elementary reactions.**

**(i) $3A + 5B_2 \longrightarrow 4CD$ (ii) $X_2 + Y_2 \longrightarrow 2XY$**

(i) $\frac{-d[A]}{3dt} = \frac{-d[B_2]}{5dt} = \frac{d[CD]}{4dt}$

**(ii)** $\frac{-d[X_2]}{dt} = \frac{-d[Y_2]}{dt} = \frac{d[XY]}{2dt}$

**(2) Consider the decomposition of $N_2O_5(g)$ to form $NO_2(g)$ and $O_2(g)$. At a particular instant $N_2O_5$ disappears at a rate of $2.5 \times 10^{-2}$ mol dm$^{-3}$ s$^{-1}$. At what rate are $NO_2$ and $O_2$ formed? What is the rate of the reaction?**

(1) (i) rate = k $[A]^3$ $[B_2]^5$

(ii) rate = k $[X_2]^1$ $[Y_2]^1$

(2) $2N_2O_5 \longrightarrow 4NO_2 + O_2$

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt}$$

$$\frac{1}{2} \times 2.5 \times 10^{-2} = \frac{1}{4}\frac{d[NO_2]}{dt}$$

$$\frac{d[NO_2]}{dt} = \frac{4}{2} \times 2.5 \times 10^{-2} = 2 \times 2.5 \times 10^{-2} = 5 \times 10^{-2}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{d[O_2]}{dt}$$

$$\frac{1}{2} \times 2.5 \times 10^{-2} = \frac{d[O_2]}{dt}$$

$$\frac{d[O_2]}{dt} = 1.25 \times 10^{-2}\ \text{mol L}^{-1}\text{s}^{-1}$$

## Evaluate Yourself-2 (Page 212)

**(1) For a reaction, X + Y $\longrightarrow$ product ; quadrupling [x], increases the rate by a factor of 8. Quadrupling both [x] and [y], increases the rate by a factor 16. Find the order of the reaction with respect to x and y. What is the overall order of the reaction?**

**(2) Find the individual and overall order of the following reaction using the given date**

$$2NO_{(g)} + Cl_{2(g)} \longrightarrow 2NOCl_{(g)}.$$

| **Expt.** | **[NO]** | **[$Cl_2$]** | **Initial rate** |
|---|---|---|---|
| **1.** | **0.1** | **0.1** | **$7.8 \times 10^{-5}$** |
| **2.** | **0.2** | **0.1** | **$3.12 \times 10^{-4}$** |
| **3.** | **0.2** | **0.3** | **$9.36 \times 10^{-4}$** |

(1) rate = k $[X]^a [Y]^b \longrightarrow$ (1)

8 rate = k $[4X]^a [Y]^b \longrightarrow$ (2)

16 rate = k $[4X]^a [Y]^b \longrightarrow$ (3)

$$\frac{(2)}{(1)} \Rightarrow \frac{8\,\cancel{rate}}{\cancel{rate}} = \frac{\cancel{k}[4\cancel{X}]^a[\cancel{Y}]^b}{\cancel{k}[\cancel{X}]^a[\cancel{Y}]^b}$$

$$8 = 4^a$$
$$2^3 = 2^{2a}$$
$$3 = 2a$$
$$a = 3/2$$

order w.r.to X = 3/2

$$\frac{(3)}{(2)} \Rightarrow \frac{16\,\cancel{rate}}{\cancel{8rate}} = \frac{\cancel{k}[\cancel{4X}]^a[4\cancel{Y}]^b}{\cancel{k}[\cancel{4X}]^a[\cancel{Y}]^b}$$

$$2 = 4^b$$
$$b = 1/2$$

order w.r.to Y = 1/2

(2) rate = $k[NO]^x[Cl_2]^y$

$$7.8 \times 10^{-5} = k(0.1)^x(0.1)^y \longrightarrow (1)$$

$$3.12 \times 10^{-4} = k(0.2)^x(0.1)^y \longrightarrow (2)$$

$$9.36 \times 10^{-4} = k(0.2)^x(0.3)^y \longrightarrow (3)$$

$$\frac{(2)}{(1)} \Rightarrow \frac{3.12 \times 10^{-4}}{7.8 \times 10^{-5}} = \frac{\cancel{k}(0.2)^x(\cancel{0.1})^y}{\cancel{k}(0.1)^x(\cancel{0.1})^y}$$

$$4 = 2^x$$
$$x = 2$$

order w.r.to NO = 2

$$\frac{(3)}{(2)} \Rightarrow \frac{9.36 \times 10^{-4}}{3.12 \times 10^{-4}} = \frac{\cancel{k}\,\cancel{(0.2)^x}\ (0.3)^y}{\cancel{k}\,\cancel{(0.2)^x}\ (0.1)^y}$$

$$3 = \left(\frac{0.3}{0.1}\right)^y$$

$$3^1 = (3)^y$$

Equating the powers

$y = 1$

order w.r.to $Cl_2 = 1$

rate = k $[NO]^2 [Cl_2]^1$

overall order = 2 +1 = 3

## Evaluate Yourself-3 (Page 217)

**(1) In a first order reaction A → products 60% of the given sample of A decomposes in 40 min. What is the half life of the reaction?**

t = 40 min

$[A_0] = 100$

$[A] = 40$

$t_{1/2} = ?$

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]} = \frac{2.303}{40}\log\frac{100}{40} = \frac{2.303}{40}\log 2.5 = \frac{2.303}{40}\times 0.3979 = \frac{0.9163}{40}$$

$$\boxed{k = 0.0229\ \text{min}^{-1}}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0229}$$

$t_{1/2} = 3.026$ min

$$\boxed{t_{1/2} = 3\,\text{min}}$$

## IV ADDITIONAL QUESTIONS WITH ANSWERS

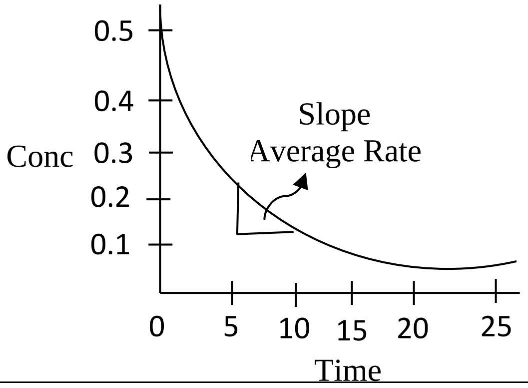
1. **Define rate of a reaction.**
Rate is defined as change in concentration of reactant or product with respect to time.

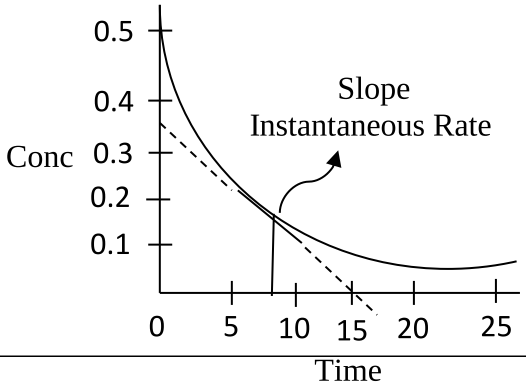
2. **Give the unit of rate of reaction for (i) aqueous reaction (ii) Gaseous reaction**
(i) mol $L^{-1}$ $s^{-1}$ (ii) atm $s^{-1}$

3. **How to determine rate of a reaction**

Draw a plot of concentration vs time graph. The slope of the curve between the interval of time gives the average rate.

Instantaneous rate is the rate at a particular time which is calculated by drawing a tangent at that point on the concentration vs time graph. The slope of the tangent gives the instantaneous rate.





**4. Differentiate rate and rate constant. (AUG-21)**

| No | Rate of a reaction | Rate constant of a reaction |
|---|---|---|
| 1. | It represents the speed at which the reactants are converted into products at any instant. | It is a proportionality constant |
| 2. | It is measured as decrease in the concentration of the reactants or increase in the concentration of products. | It is equal to the rate of reaction, when the concentration of each of the reactants in unity. |
| 3. | It depends on the initial on the concentrations of reactants. | It does not depend on the initial concentration of reactants. |

**5. Define molecularity.**

It is the total number of reactant species that are involved in an elementary step.

**6. Define order of a reaction.**

$aA + bB \longrightarrow \text{products}$

rate = $k\,[A]^x\,[B]^y$

overall order = $x + y$

It is the sum of the powers of concentration terms involved in the experimentally determined rate law.

**7. Derive an expression of half life of a zero order reaction.**

$$k = \frac{[A_0]-[A]}{t}$$

$t = t_{1/2}$ then $[A] = \frac{[A_0]}{2}$

$$k = \frac{[A_0]-\frac{[A_0]}{2}}{t_{1/2}}$$

$$t_{1/2} = \frac{2[A_0]-[A_0]}{2k} \quad \boxed{t_{1/2} = \frac{[A_0]}{2k}}$$

**8. Give general expression for half life of n^th^ order reaction.**

Half life of n^th^ order reaction is $t_{1/2} = \frac{2^{n-1}-1}{(n-1)k[A_0]^{n-1}}$

**9. Draw a plot of concentration vs time for zero order reaction.**

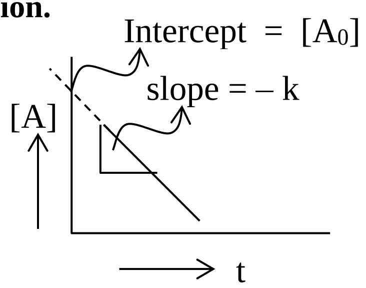
$$k = \frac{[A_0]-[A]}{t}$$

$$[A] = -kt + [A_0]$$

$$y = -mx + C$$

Plot of [A] Vs t gives straight line with negative slope.

Slope equal to –k and intercept equals to $[A_0]$.



**10. Give examples of first order reaction. (MAY-22)**

(i) $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$

(ii) $SO_2Cl_2(l) \longrightarrow SO_2(g) + Cl_2(g)$

(iii) $H_2O_2(aq) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g)$

(iv) All radioactive decay

(v) Isomerisation of cyclopropane to propene

11. **Give units of rate constant of**
**(a) first order reaction** **(b) zero order reaction**
(a) $\text{sec}^{-1}$ (b) $\text{mol L}^{-1}\,\text{s}^{-1}$

12. **What is collision frequency?**
Number of collisions per second per unit volume is called collision frequency.

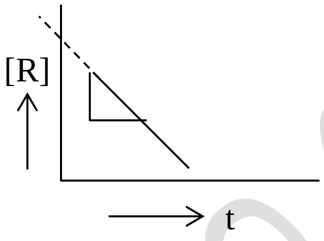
13. **Why molecularity can never be more than 3?**
Probability of simultaneous collision of more than three reactants is rare.
So molecularity can never be more than three.

14. **Define activation energy?**
In order to react, the colliding molecules must possess a minimum energy called activation energy.

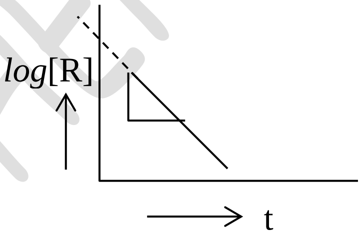
15. **What is the usefulness of Arrhenius equation.**
With the help of Arrhenius equation, we can calculate activation energy of the reaction provided rate constants at two different temperatures are given.

16. **Mention the factors affecting rate of reaction.**
1. Nature and state of reactant 2. Concentration of reactant.
3. Surface area of reactant. 4. Temperature of reaction.
5. Presence of catalyst.

17. **What does the slope represent in the following graphs.**



$\boxed{\text{slope} = -k}$



$\boxed{\text{slope} = -\dfrac{k}{2.303}}$

18. **Which of the following reaction is fast. Give reason.**
**(i)** $2Na_{(s)} + I_{2(s)} \longrightarrow 2NaI_{(s)}$
**(ii)** $2Na_{(s)} + I_{2(g)} \longrightarrow 2NaI_{(s)}$
Second reaction is fast because the state of reactant is gas. Gaseous reaction is faster than solid state reactants.

19. **Which of the two reacts faster? Why?**
**(i) Powdered $CaCO_3$ with dil. HC*l***
**(ii) Lump of $CaCO_3$ as marble with dil. HC*l***
First reaction is faster because powdered form of reactant has more surface area.

20. **Derive integrated rate law for a first order reaction A $\longrightarrow$ product. (MAR-20)**
Rate is directly proportional to the concentration of one reactant is called first order reaction.
Consider a general first order reaction **A** $\longrightarrow$ **Product**
At t = 0 concentration of reactant = $[A_0]$

At time t, concentration of reactant left = [A]

rate = $k[A]^1$

$$-\frac{d[A]}{dt} = k[A]$$

$$-\frac{d[A]}{[A]} = k\ dt$$

Integrate between limits of $[A_0]$ at t = 0 and [A] at time 't'.

$$-\int_{[A_0]}^{[A]} \frac{d[A]}{[A]} = k\int_0^t dt$$

$$-\left(ln\ [A]\right)_{[A_0]}^{[A]} = k(t)_0^t$$

$$-ln\ [A] - (-ln\ [A_0]) = k\ (t - 0)$$

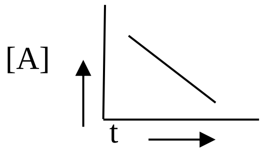
$$-ln\ [A] + ln\ [A_0] = kt$$

$$\ln\left(\frac{[A_0]}{[A]}\right) = kt$$

$$k = \frac{1}{t} ln \frac{[A_0]}{[A]}$$

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

**21. For the general reaction A ⟶ B .Plot of concentration of A Vs time is given in the graph below. Answer the following questions on the basis of this graph.**



(i) what is the order of the reaction?
(ii) what is the slope of the curve ?
(iii) what is the unit of rate constant ?

(i) Zero order reaction.
(ii) m = - k
(iii) mol $L^{-1}$ $S^{-1}$

**22. What is the effect of surface area of the reactant on the rate of the reaction ?**

- For a given mass of a reactant ,when the particle size decreases surface area increases.
- Increase in surface area of the reactant leads to more collisions per litre per second, hence the rate of the reaction is increased.

**23. Derive Arrhenius equation to calculate activation energy from the rate constant $k_1$ and $k_2$ at temperature $T_1$ and $T_2$ ?**

$$k = Ae^{-\frac{E_a}{RT}} \quad \text{-----------------------------------------(1)}$$

Taking logarithm on both side of the equation (1)

$$\ln k = \ln A + \ln e^{-\left(\frac{E_a}{RT}\right)}$$

$$\ln k = \ln A - \left(\frac{E_a}{RT}\right) \qquad (\therefore \ \ln e = 1)$$

$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \qquad ....(2)$$

$$y = c + m\,x$$

If the rate constant for a reaction at two different temperatures is known, we can calculate the activation energy as follows.

At temperature $T = T_1$ ; the rate constant $k = k_1$

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \text{-------------------(3)}$$

At temperature $T = T_2$ ; the rate constant $k = k_2$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \qquad \text{-----------------(4)}$$

Equation (4) – Equation (3)

$$\ln k_2 - \ln k_1 = -\left[\frac{E_a}{RT_2} - \frac{E_a}{RT_1}\right]$$

$$\ln\left[\frac{k_2}{k_1}\right] = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$2.303 \log\left[\frac{k_2}{k_1}\right] = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

This equation can be used to calculate $E_a$ from rate constants $k_1$ and $k_2$ at temperatures $T_1$ and $T_2$ .

# UNIT – 8 IONIC EQUILIBRIUM

## I. TEXT BOOK QUESTIONS AND ANSWERS

### 1. What are Lewis acids and bases? Give two examples for each. (MAR-2020, AUG-2022)

| S. No | Lewis Acids | Lewis Bases |
|---|---|---|
| 1 | Species that accepts an electron pair | Species that donates an electron pair |
| 2 | Ex: $BF_3$, $AlCl_3$ | Ex: $NH_3$, $H_2O$ |

### 2. Discuss the Lowry-Bronsted concept of acids and bases.

- An acid is a proton donar.

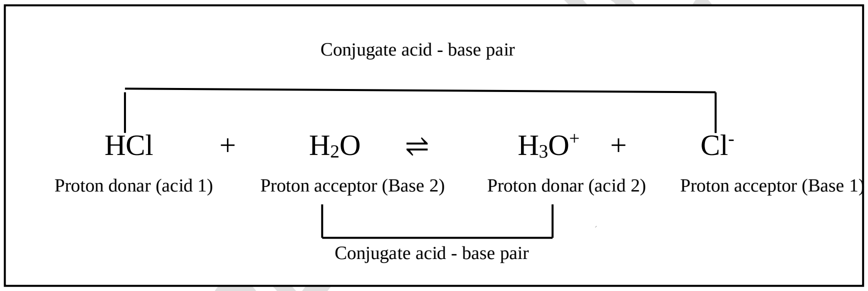
$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

- A base is a proton acceptor.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

- The species that remains after the donation of a proton is a base ($Base_1$) and is called the conjugate base of the Bronsted acid ($Acid_1$).
- The species that remains after the acceptance of a proton is an acid ($Acid_2$) and is called the conjugate acid of the Bronsted base ($Base_2$).
- Lowry – Bronsted (acid – base) reaction is represented as

$$Acid_1 + Base_2 \rightleftharpoons Acid_2 + Base_1$$

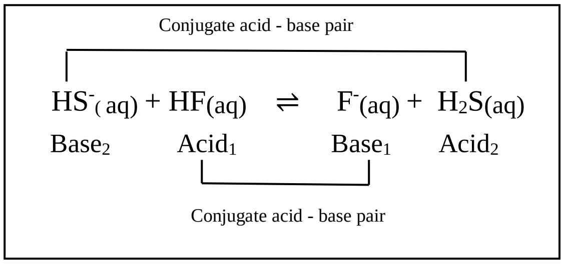


- In other words, chemical species that differ only by a proton are called conjugate acid – base pairs.
- **Limitations of Lowry-Bronsted Theory**

  Substance like $BF_3$, $AlCl_3$ do not have a proton but they are acids.

### 3. Identify the conjugate acid base pair for the following reaction in aqueous solution (JULY-2020)

i) $\mathbf{HS^-_{(aq)} + HF \rightleftharpoons F^-_{(aq)} + H_2S_{(aq)}}$



**ii) $HPO_4^{2-} + SO_3^{2-} \rightleftharpoons PO_4^{3-} + HSO_3^-$**

Conjugate acid - base pair

$HPO_4^{2-} + SO_3^{2-} \rightleftharpoons PO_4^{3-} + HSO_3^-$

$Acid_1$ $Base_2$ $Base_1$ $Acid_2$

Conjugate acid - base pair

**iii) $NH_4^+ + CO_3^{2-} \rightleftharpoons NH_3 + HCO_3^-$**

Conjugate acid - base pair

$NH_4^+ + CO_3^{2-} \rightleftharpoons NH_3 + HCO_3^-$

$Acid_1$ $Base_2$ $Base_1$ $Acid_2$

Conjugate acid - base pair

**4. Account for the acidic nature of $HClO_4$ in terms of Bronsted – Lowry theory, identify its conjugate base.**

$$HClO_4 + H_2O \rightleftharpoons H_3O^+ + ClO_4^-$$

- The conjugate base of $HClO_4$ is $ClO_4^-$.
- When oxidation number of an element in an oxy acid increases then its acidic nature increases.
- The oxidation number of chlorine in $HClO_4$ is 7, which weakens the bond between O-H bond and increases the acidity.

**5. When aqueous ammonia is added to $CuSO_4$ solution, the solution turns deep blue due to the formation of tetramminecopper (II) complex, $[Cu(H_2O)_4]^{2+}_{(aq)} + 4NH_{3\,(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)}$, among $H_2O$ and $NH_3$ which is stronger Lewis base.**

- In complexes, central metal ion act as a lewis acid which has a tendency to accept lone pair of electron from lewis base (ie) ligands.
- In the presence of a strong lewis base, the lewis acid (ie) the central metal ion undergoes ligand exchange reaction with weak lewis base.
- In the above equation, $NH_3$ replaces $H_2O$ molecule to form the deep blue complex, so $NH_3$ is the strong lewis base.

**6. The concentration of hydroxide ion in a water sample is found to be $2.5 \times 10^{-6}$ M. Identify the nature of the solution.**

**GIVEN**: $[OH^-] = 2.5 \times 10^{-6}$ M

$pOH = -\log\,[OH^-]$

$= -\log\,[2.5 \times 10^{-6}]$

$= 6 - \log 2.5 = 6 - 0.3979 = 5.6021$

$pH = 14 - pOH$

$pH = 14 - 5.6021 = 8.3979.$

**pH = 8.3979. Since the pH is greater than 7, the solution is basic**.

**7. A lab assistant prepared a solution by adding a calculated quantity of HCl gas at 25 $C^0$ to get a solution with $[H_3O^+] = 4 \times 10^{-5}$ M. Is the solution neutral (or) acidic (or) basic?**

**GIVEN**: $[H_3O^+] = 4 \text{ x } 10^{-5} M$

$$pH = -\log \ [H_3O^+]$$
$$= -\log [4 \text{ x } 10^{-5}]$$
$$= 5 - \log 4 = 5 - 0.6021 = 4.3979$$

**pH= 4.3979. Since the pH is lesser than 7, the solution is acidic**

**8. Calculate the pH of 0.04 M $HNO_3$**

**GIVEN**: $[H^+] = 0.04M$

$$pH = -\log[H^+] = -\log 0.04$$
$$= -\log [4 \text{ x } 10^{-2}]$$
$$= 2 - \log 4 = 2 - 0.6021 = 1.3979$$

**pH= 1.3979**

**9. Define Solubility Product.**

The solubility product of a compound is defined as the product of the molar concentration of the constituent ions, each raised to the power of its stoichiometric co – efficient in a balanced equilibrium equation.

$$X_mY_n \rightleftharpoons mX^{n+} + nY^{m-}$$

$$\boxed{K_{sp} = [X^{n+}]^m \times [Y^{m-}]^n}$$

**10. Define Ionic product of water. Give its value at room temperature. (SEPT-2020)**

- The product of concentration of hydrogen ion and hydroxyl ion of pure water is known as ionic product of water ($K_W$).

$$\boxed{K_W = [H_3O^+] [OH^-]}$$

$$K_W = 1 \times 10^{-7} \times 1 \times 10^{-7}$$

$$K_W = 1 \times 10^{-14} mol^2 dm^{-6}$$

$K_W$ = Ionic product of water

- At room temperature, the value of $K_w$ is $1 \times 10^{-14} mol^2 dm^{-6}$

.

**11. Explain Common Ion effect with an example. (JULY-2020, MAY-2022)**

- When the salt of the weak acid is added to the acid, the dissociation of the weak acid decreases. This is known as common ion effect.
- Ex. When sodium acetate is added to acetic acid, the dissociation of acetic acid decreases. Here $CH_3COO^-$ is the common ion present.

**12. Derive an expression for Oswald's Dilution law (JULY-20202, AUG-2021)**

Ostwald's dilution law relates the dissociation constant of the weak acid ($K_a$) with its degree of dissociation ($\alpha$) and the concentration (C).

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{Total number of moles}}$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

| Content | $CH_3COOH$ | $CH_3COO^-$ | $H^+$ |
|---|---|---|---|
| Initial number of moles | 1 | -- | -- |
| Number of moles Ionized | α | -- | -- |
| Number of moles remaining | 1 − α | α | α |
| Equilibrium concentration | C ( 1 − α ) | C α | C α |

$$K_a = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]} = \frac{C\alpha \text{ x } C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

When 1 >> α, the denominator can be neglected.

$$K_a = C\,\alpha^2$$

$$\boxed{\boldsymbol{\alpha = \sqrt{\frac{K_a}{C}}}}$$

**13. Define pH (MAY-2022)**

pH is defined as the negative logarithm of base 10 of the molar concentration of the hydronium ions present in the solutions.

$$\mathbf{pH = -log_{10}\ [H_3O^+]}$$

**14. Calculate the pH of 1.5 x $10^{-3}$M solution of Ba $(OH)_2$**

**Ba $(OH)_2 \rightarrow Ba^{2+} + 2\,OH^-$**

$$\text{Concentration of hydroxide ion} = 2[OH^-] = 2 \text{ x } 1.5 \text{ x } 10^{-3}M = 3 \text{ x } 10^{-3}M$$

$$pOH = -\log\,[OH^-]$$

$$= -\log(3 \text{ x } 10^{-3}) = 3 - \log 3 = 3 - 0.4771 = 2.5229$$

$$pH = 14 - pOH$$

$$pH = 14 - 2.5229 = 11.4771$$

$$\mathbf{pH = 11.4771}$$

**15. 50ml of 0.05M $HNO_3$ is added to 50ml of 0.025M KOH. Calculate the pH of the resultant solution.**

$$V_1M_1 - V_2M_2 = V_3M_3$$

$$(0.05 \text{ x } 50) - (0.025 \text{ x } 50) = 100M_3$$

$$2.5 - 1.25 = 100M_3$$

$$1.25 = 100M_3$$

$$M_3 = \frac{1.25}{100} = 1.25 \text{ x } 10^{-2}$$
$$pH = -\log[H^+] = -\log 1.25 \text{ x } 10^{-2}$$

$$= 2 - \log 1.25 = 2 - 0.0969 = 1.9031$$
$$\mathbf{pH = 1.9031}$$

**16. The Ka value for HCN is $10^{-9}$. What is the pH of 0.4 M HCN solution?**

HCN is a weak acid.

$$[H^+] = \sqrt{K_a\ C} = \sqrt{4 \text{ x } 10^{-1} \text{ x } 10^{-9}} = \sqrt{4 \text{ x } 10^{-10}} = 2 \text{ x } 10^{-5}$$

$$pH = -\log[H^+] = -\log 2 \text{ x } 10^{-5}$$

$$= 5 - \log 2 = 5 - 0.3010 = 4.6990$$

$$\mathbf{pH = 4.6990}$$

**17. Calculate the extent of hydrolysis and the pH of 0.1 M ammonium acetate. Given that $K_a = K_b = 1.8 \text{ x } 10^{-5}$**

$$h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{1 \text{ x } 10^{-14}}{1.8 \text{ x } 10^{-5} \text{ x } 1.8 \text{ x } 10^{-5}}} = \sqrt{\frac{1 \text{ x } 10^{-14}}{1.8 \text{ x } 1.8 \text{ x } 10^{-10}}}$$

$$h = \sqrt{0.3086 \text{ x } 10^{-4}} = 0.5555 \text{ x } 10^{-2} = 5.555 \text{ x } 10^{-3}$$

$$\mathbf{h = 5.555 \text{ x} 10^{-3}}$$

$$pH = 7 + \frac{1}{2} p\,K_a - \frac{1}{2} p\,K_b$$

If $K_a = K_b$, then, $pK_a = pK_b$

pH = 7

**pH = 7**

**18. Derive an expression for the hydrolysis constant and degree of hydrolysis of salt of strong acid and weak base**

Consider the reaction between strong acid and weak base

$$HCl_{(aq)} + NH_4OH_{(aq)} \rightleftharpoons NH_4Cl_{(aq)} + H_2O_{(l)}$$

The salt completely dissociates to give respective ions.

$$NH_4Cl_{(s)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

$NH_4^+$ is a strong conjugate acid of the weak base $NH_4OH$ and it has a tendency to react with $OH^-$ from water to produce unionised $NH_4OH$ shown below.

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightarrow NH_4OH_{(aq)} + H^+{}_{(aq)}$$

Here, $[H^+] > [OH^-]$ so the solution is acidic and the pH is less than 7.

**Hydrolysis constant ($K_h$):**

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightarrow NH_4OH_{(aq)} + H^+{}_{(aq)}$$

$$\begin{matrix} C(1-h) & & C\,h & & C\,h \end{matrix}$$

$$K_b = \frac{[NH_4{}^+][OH^-]}{[NH_4OH]} ----(1) \qquad K_h = \frac{[NH_4OH]\,[H^+]}{[NH_4{}^+]} ----(2)$$

Equ (1) x (2)

$K_b \text{ x } K_h = K_w$

$$\boxed{\mathbf{K_h = \frac{K_w}{K_b}}}$$

**Degree of hydrolysis: (h)**

$$K_h = \frac{C\,h \text{ x } C\,h}{C(1-h)} = C\,h^2$$

$$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_b C}}$$

$$\boxed{\mathbf{h = \sqrt{\frac{K_w}{K_b C}}}}$$

**Concentration of hydrogen ion: $[\mathbf{H^+}]$**

$$[H^+] = C\,h = C\sqrt{\frac{K_w}{K_b C}} = \sqrt{\frac{C\,K_w}{K_b}}$$

$$\boxed{[\mathbf{H^+}] = \sqrt{\frac{\mathbf{C\,K_w}}{\mathbf{K_b}}}}$$

**pH of the solution:**

$$pH = -\log[H^+] = -\log\left[\frac{C\,K_w}{K_b}\right]^{\frac{1}{2}} = -\frac{1}{2}\log C - \frac{1}{2}\log K_w + \frac{1}{2}\log K_b$$

$$pH = \frac{1}{2}pK_w - \frac{1}{2}\log C - \frac{1}{2}pK_b$$

$$\boxed{\mathbf{pH = 7 - \frac{1}{2}\log C - \frac{1}{2}pK_b}}$$

**19. Solubility product of $Ag_2CrO_4$ is 1 x $10^{-12}$. What is the solubility of $Ag_2CrO_4$ in 0.01M $AgNO_3$ solution?**

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

$$\begin{matrix} (S) & (2S) & (S) \end{matrix}$$

$$AgNO_3 \rightarrow Ag^+ + NO_3^-$$

$$\begin{matrix} 0.01M & 0.01\ M & 0.01\ M \end{matrix}$$

| | |
|---|---|
| Initial concentration of $Ag^+$ ion | 2 |
| Concentration of $Ag^+$ ion at equilibrium | 2S |
| Change in concentration of $Ag^+$ ion after addition of $AgNO_3$ | 2S +0.01 |

$[Ag^+] = 2S + 0.01$; $(2S << 0.01)$; $[Ag^+] \cong 0.01$

$[Ag^+] = 0.01 = 1 \times 10^{-2}$; $[CrO_4^{2-}] = S$; $K_{sp} = 1 \times 10^{-12}$

$K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$

$1 \times 10^{-12} = (1 \times 10^{-2})^2 \times S$

$S = \frac{1 \times 10^{-12}}{1 \times 10^{-4}} = 1 \times 10^{-8} M$

$\mathbf{S = 1 \times 10^{-8} M}$

**20. Write the expression for the solubility product of $Ca_3(PO_4)_2$**

$Ca_3(PO_4)_2 \rightleftharpoons 3\,Ca^{2+} + 2\,PO_4^{3-}$

S 3 S 2 S

$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2$

$K_{sp} = [3S]^3 [2S]^2$

$K_{sp} = [27S^3] [4S^2] = 108\, S^5$

$\mathbf{K_{sp} = 108\, S^5}$

**21. A saturated solution, prepared by dissolving $CaF_2$ (s) in water, has $[Ca^{2+}] = 3.3 \times 10^{-4}$ M .What is the Ksp of $CaF_2$?**

$CaF_2 \rightleftharpoons Ca^{2+} + 2\,F^-$

$[F^-] = 2[Ca^{2+}] = 2 \times 3.3 \times 10^{-4} = 6.6 \times 10^{-4}$ M

$K_{sp} = [Ca^{2+}] [F^-]^2$

$K_{sp} = 3.3 \times 10^{-4} \times (6.6 \times 10^{-4})^2 = 143.748 \times 10^{-12} = 1.44 \times 10^{-10}$

$\mathbf{K_{sp} = 1.44 \times 10^{-10}}$

**22. Ksp of AgCl is $1.8 \times 10^{-10}$. Calculate molar solubility in 1 M $AgNO_3$**

$AgCl \rightleftharpoons Ag^+ + Cl^-$

S S

$AgNO_3 \longrightarrow Ag^+ + NO_3^-$

**1M 1M 1M**

| | |
|---|---|
| Initial concentration of $Ag^+$ ion | 1 |
| Concentration of $Ag^+$ ion at equilibrium | S |
| Change in concentration of $Ag^+$ ion after addition of $AgNO_3$ | S +1 |

$[Ag^+] = S + 1$; $(S << 1)$; $[Ag^+] \cong 1$

$[Ag^+] = 1$; $[Cl^-] = S$; $K_{sp} = 1.8 \times 10^{-10}$

$K_{sp} = [Ag^+] [Cl^-]$

$1.8 \times 10^{-10} = 1 \times S$

$\mathbf{S = 1.8 \times 10^{-10} M}$

**23. A particular saturated solution of silver chromate $Ag_2CrO_4$ has $[Ag^+] = 5 \times 10^{-5}$ and $[CrO_4^{2-}] = 4.4 \times 10^{-4}$ M. What is the value of Ksp for $Ag_2CrO_4$?**

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

$[Ag^+] = 5 \times 10^{-5}$ M; $[CrO_4^{2-}] = 4.4 \times 10^{-4}$ M

$K_{sp} = [Ag^+]^2 [CrO_4^{2-}] = (5 \times 10^{-5})^2 (4.4 \times 10^{-4}) = 1.1 \times 10^{-12}$

$\mathbf{K_{sp} = 1.1 \times 10^{-12}}$

**24. Write the expression for the solubility product of $Hg_2Cl_2$ .**

$$\underset{S}{Hg_2Cl_2} \rightleftharpoons \underset{S}{Hg_2^{2+}} + \underset{2S}{2Cl^-}$$

$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = S(2S)^2 = 4S^3$

$\mathbf{K_{sp} = 4S^3}$

**25. Ksp of $Ag_2CrO_4$ is $1.1 \times 10^{-12}$. What is solubility of $Ag_2CrO_4$ in 0.1M $K_2CrO_4$.**

$$\underset{S}{Ag_2CrO_4} \rightleftharpoons \underset{2S}{2Ag^+} + \underset{S}{CrO_4^{2-}}$$

$$\underset{0.1M}{K_2CrO_4} \rightarrow \underset{2 \times 0.1M}{2K^+} + \underset{0.1M}{CrO_4^{2-}}$$

| | |
|---|---|
| Initial concentration of $CrO_4^{2-}$ ion | 1 |
| Concentration of $CrO_4^{2-}$ ion at equilibrium | S |
| Change in concentration of $CrO_4^{2-}$ ion after addition of $K_2CrO_4$. | S +0.1 |

$[CrO_4^{2-}] = S + 0.1$; $(S << 0.1)$; $[CrO_4^{2-}] \cong 0.1$

$[Ag^+] = 2S$; $[CrO_4^{2-}] = 0.1$; $K_{sp} = 1.1 \times 10^{-12}$

$K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$

$1.1 \times 10^{-12} = (2S)^2 (0.1)$

$1.1 \times 10^{-12} = 4S^2 \times 0.1$

$S^2 = \frac{1.1 \times 10^{-12}}{4 \times 0.1} = 2.75 \times 10^{-12}$

$S = \sqrt{2.75 \times 10^{-12}} = 1.658 \times 10^{-6}$

$\mathbf{S = 1.658 \times 10^{-6} M}$

**26. Will a precipitate be formed when 0.150 L of 0.1M $Pb(NO_3)_2$ and 0.100L of 0.2 M NaCl are mixed? Ksp ($PbCl_2$) =$1.2 \times 10^{-5}$**

The concentration of $Pb^{2+}$ and $Cl^-$ in the mixture is different from the concentration of individual solutions. The total volume (0.150 + 0.100 = 0.250L) changes on mixing.

$$\begin{array}{ccccc} Pb(NO_3)_2 & \rightleftharpoons & Pb^{2+} & + & 2NO_3^- \\ 0.1M & & 0.1M & & 0.2M \end{array}$$

Number of moles of $Pb^{2+}$ = molarity x volume of solution in litres = 0.1 x 0.15 = 0.015

Molarity of $Pb^{2+}$ in the mixture = $\frac{\text{Number of moles}}{\text{Volume}}$

$[Pb^{2+}]_{mix} = \frac{0.015}{0.25} = 0.06M$

$$\begin{array}{ccccc} NaCl & \rightleftharpoons & Na^+ & + & Cl^- \\ 0.2M & & 0.2M & & 0.2M \end{array}$$

Number of moles of $Cl^-$ = molarity x volume of solution in litres = 0.1 x 0.2 = 0.02

Molarity of $Cl^-$ in the mixture = $\frac{\text{Number of moles}}{\text{Volume}}$

$[Cl^-]_{mix} = \frac{0.02}{0.25} = 0.08M$

Ionic Product = $[Pb^{2+}]\,[Cl^-]^2 = (0.06)\,(0.08)^2 = 3.84 \times 10^{-4}$

Solubility product = $1.2 \times 10^{-5}$

**Ionic Product > Solubility product**

**$PbCl_2$ is precipitated**.

**27. Ksp of Al $(OH)_3$ is $1 \times 10^{-15}$M. At what pH does $1.0 \times 10^{-3}$ M. $Al^{3+}$ precipitate on the addition of buffer of $NH_4$ Cl and $NH_4OH$ solution?**

$Al(OH)_3 \rightleftharpoons Al^{3+} + 3(OH^-)$

$K_{sp} = [Al^{3+}]\,[OH^-]^3$

Al $(OH)_3$ precipitates when $[Al^{3+}]\,[OH^-]^3 > K_{sp}$

$[Al^{3+}]\,[OH^-]^3 > 1 \times 10^{-15}$

$(1 \times 10^{-3})\,[OH^-]^3 > 1 \times 10^{-15}$

$[OH^-]^3 > 1 \times 10^{-12}$

$[OH^-] > 1 \times 10^{-4}$

$[OH^-] = 1 \times 10^{-4}M$

$pOH = -\log\,[OH^-] = -\log(1 \times 10^{-4})$

$= 4 - \log 1 = 4$

$pH = 14 - pOH = 14 - 4 = 10$

**$Al(OH)_3$ precipitates at a pH above 10**

## II EVALUATE YOURSELF:

1. **Classify the following as acids (or) base using Arrhenius concept.**
   **i) $HNO_3$ ii) $Ba(OH)_2$ iii) $H_3PO_4$ iv) $CH_3COOH$**

| | |
|---|---|
| $HNO_3$ | Acid |
| $Ba(OH)_2$ | Base |
| $H_3PO_4$ | Acid |
| $CH_3COOH$ | Acid |

2. **Write the balanced equation for the dissociation of the following in water and identify the conjugate acid-base pairs.**

i) $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

Conjugate acid - base pair

$$\underset{\text{Acid}_1}{NH_4^+} + \underset{\text{Base}_2}{H_2O} \rightleftharpoons \underset{\text{Base}_1}{NH_3} + \underset{\text{Acid}_2}{H_3O^+}$$

Conjugate acid - base pair

ii) $H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+$

Conjugate acid - base pair

$$\underset{\text{Acid}_1}{H_2SO_4} + \underset{\text{Base}_2}{H_2O} \rightleftharpoons \underset{\text{Base}_1}{HSO_4^-} + \underset{\text{Acid}_2}{H_3O^+}$$

Conjugate acid - base pair

iii) $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

Conjugate acid - base pair

$$\underset{\text{Acid}_1}{CH_3COOH} + \underset{\text{Base}_2}{H_2O} \rightleftharpoons \underset{\text{Base}_1}{CH_3COO^-} + \underset{\text{Acid}_2}{H_3O^+}$$

Conjugate acid - base pair

**3. Identify the Lewis acid and Lewis base in the following reactions.**

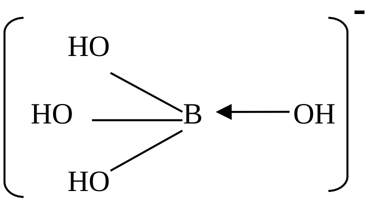
**i) $CaO + CO_2 \rightarrow CaCO_3$**

**ii) $CH_3{-}O{-}{-}CH_3 + AlCl_3 \rightarrow (CH_3)_2O{\rightarrow}AlCl_3$**

| | Compound | Lewis Acid | Lewis Base |
|---|---|---|---|
| 1 | $CaCO_3$ | $CO_2$ | CaO |
| 2. | $(CH_3)_2O{\rightarrow}AlCl_3$ | $AlCl_3$ | $(CH_3)_2O$ |

**4. $H_3BO_3$ accepts hydroxide ion from water as shown below**
**$H_3BO_{3\,(aq)} + H_2O_{(l)} \rightarrow [B(OH)_4]^- + H^+$. Predict the nature of $H_3BO_3$ using Lewis concept.**

$H_3BO_3$ is a Lewis acid. It accepts an electron pair from $H_2O$ as follows.



**5. At a particular temperature, the $K_w$ of a neutral solution was equal to $4 \times 10^{-14}$. Calculate the concentration of $[H_3O^+]$ and $[OH^-]$**

Since the solution is neutral, $[H_3O^+] = [OH^-]$. Let their concentration be x

$$K_w = [H_3O^+]\,[OH^-]$$
$$4 \times 10^{-14} = (x).\,(x)$$
$$x^2 = 4 \times 10^{-14}$$
$$x = \sqrt{4 \times 10^{-14}} = 2 \times 10^{-7}$$
$$\mathbf{[H_3O^+] = [OH^-] = 2 \times 10^{-7}}$$

**6. a) Calculate the pH of $10^{-8}$ M $H_2SO_4$**

**Given:** $[H^+]$= 2 x Concentration of $H_2SO_4$ = $2 \times 10^{-8}$M

$[H_3O^+] = 10^{-7}$ (from water) + $2 \times 10^{-8}$ (from $H_2SO_4$)
$= 10 \times 10^{-8} + 2 \times 10^{-8} = (10 + 2) \times 2 \times 10^{-8}$
$= 12 \times 10^{-8}$ M
pH = $-\log(12 \times 10^{-8}) = 8 - \log 12 = 8 - 1.0792 = 6.9208$
**pH= 6.9208**

**b) Calculate the concentration of hydrogen ion in moles per litre of a solution whose pH is 5.4.**

**Given:** pH = 5.4.

$[H_3O^+]$ = antilog (-pH)
= antilog (-5.4)
= antilog (-5.4 +6 -6)
= antilog (-6 +0.6)
= $3.981 \times 10^{-6}$
**$[H_3O^+] = 3.981 \times 10^{-6}$M**

**c) Calculate the pH of an aqueous solution obtained by mixing 50ml of 0.2 M HCl with 50ml 0.1M NaOH.**

$$V_1M_1 - V_2M_2 = V_3M_3$$

$$(50 \text{ x } 0.2) - (50 \text{ x } 0.1) = 100M_3$$

$10 - 5 = 100M_3$
$5 = 100M_3$

$$M_3 = \frac{5}{100} = 5 \text{ x } 10^{-2}$$

$$\text{pH} = -\log[H^+] = -\log(5 \text{ x } 10^{-2})$$

$= 2 - \log 5 = 2 - 0.6990 = 1.3010$

$$\mathbf{pH = 1.3010}$$

7. **$K_b$ for $NH_4OH$ is 1.8 x $10^{-5}$. Calculate the percentage of ionization of 0.06M ammonium hydroxide solution.**

**Given:** $K_b$= 1.8 x $10^{-5}$, C = 0.06M

$$\alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{1.8 \text{ x } 10^{-5}}{0.06}}$$

$$= \sqrt{\frac{1.8 \text{ x } 10^{-5}}{6 \text{ x } 10^{-2}}} = \sqrt{0.3 \text{ x } 10^{-3}}$$

$$= \sqrt{3 \text{ x } 10^{-4}} = \sqrt{3} \text{ x } 10^{-2} = 1.732 \text{ x } 10^{-2}$$

$$\textbf{Degree of ionisation } (\boldsymbol{\alpha}) = \mathbf{1.732 \text{ x } 10^{-2}}$$

Percentage of ionization = 1.732 x $10^{-2}$ x 100 = 1.732%

**Percentage of ionization = 1.732%**

**8. a) Explain the buffer action in a basic buffer containing equimolar ammonium hydroxide and ammonium chloride.**

Consider the buffer action in a solution containing $NH_4OH$ and $NH_4Cl$. The dissociation of buffer components occur below.

$$NH_4OH_{(aq)} \rightleftharpoons NH_4{}^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$NH_4Cl_{(s)} \xrightarrow{H_2O(l)} NH_4{}^+{}_{(aq)} + Cl^-{}_{(aq)}$$

If a base is added to this mixture, it will be consumed by the conjugate acid $NH_4^+$ to form the undissociated weak base i.e. the increases in the concentration of $OH^-$ does not reduce the pH significantly.

$$NH_4{}^+{}_{(aq)} + OH^-{}_{(aq)} \rightarrow NH_4OH_{(aq)}$$

If an acid is added, it will be neutralised by $OH^-$, and the ammonium hydroxide is dissociated to maintain the equilibrium. Hence the pH is not significantly altered.

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

$$NH_4OH_{(aq)} \overset{H_2O(l)}{\Longleftrightarrow} NH_4{}^+_{(aq)} + OH^-_{(aq)}$$

---

$$H^+_{(aq)} + NH_4OH_{(aq)} \rightarrow NH_4{}^+_{(aq)} + H_2O_{(l)}$$

**b) Calculate the pH of the buffer solution consisting of 0.4M $CH_3COOH$ and 0.4M $CH_3COONa$. What is the change in the pH after adding 0.01 mol of HCl to 500ml of the above solution? Assume that the addition of HCl causes negligible change in the volume. Given $K_a = 1.8 \times 10^{-5}$**

**pH of the buffer solution:**

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ $\quad$ $CH_3COONa \rightarrow CH_3COO^- + Na^+$

$0.4 \quad \alpha \quad \alpha$ $\quad$ $0.4 - \alpha \quad \alpha \quad \alpha$

$$K_a = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]}$$

$$[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]} = \frac{K_a(0.4 - \alpha)}{(0.4 + \alpha)}$$

$\alpha << 0.4$, therefore $[0.4 - \alpha = 0.4]$ and $[0.4 - \alpha = 0.4]$

$$[H^+] = \frac{K_a(0.4)}{(0.4)} = K_a$$

$$[H^+] = 1.8 \times 10^{-5}$$

$$pH = -\log[H^+] = -\log 1.8 \times 10^{-5}$$
$$= 5 - \log 1.8 = 5 - 0.2553 = 4.7447$$

$\mathbf{pH = 4.7447}$

**Calculation pH after adding 0.01 mol of HCl to 500ml of buffer.**

$$\text{Added } [H^+] = \frac{0.01 \text{ mol}}{500 \text{ ml}} = 0.02M$$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ $\quad$ $CH_3COONa \rightarrow CH_3COO^- + Na^+$

$0.4 - \alpha \quad \alpha \quad \alpha$ $\quad$ $0.4 \quad \alpha \quad \alpha$

$CH_3COO^- + HCl \rightarrow CH_3COOH + Cl^-$

$0.02 \quad 0.02 \quad 0.02 \quad 0.02$

0.02 mol HCl is added with 0.02 mol acetate ion and produce 0.02 mol acetic acid. Therefore

$$[CH_3COOH] = (0.4 - \alpha) + (0.02) = 0.42 - \alpha = 0.42$$

$$[CH_3COO^-] = (0.4 + \alpha) - (0.02) = 0.38 - \alpha = 0.38$$

$$[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$$

$$[\mathrm{H^+}] = \frac{(1.8 \text{ x } 10^{-5})(0.42)}{(0.38)} = 1.99 \text{ x}10^{-5}$$

$$\mathrm{pH} = -\log[1.99 \text{ x}10^{-5}]$$

$$= 5 - \log 1.99 = 5 - 0.2989 = 4.7011$$

$$\mathbf{pH = 4.7011}$$

**The addition of strong acid 0.01 mol HCl decreased the pH only slightly ie., from 4.7447 to 4.7011. So the buffer action is verified.**

**9. a) How can you prepare a buffer solution of pH 9. You are provided with 0.1M $NH_4OH$ solution and ammonium chloride crystals. $(\mathbf{pK_b = 4.7})$**

$$\mathrm{pOH} = \mathrm{pK_b} + \log\frac{[\text{salt}]}{[\text{base}]}$$

$$\mathrm{pH} + \mathrm{pOH} = 14$$

$$9 + \mathrm{pOH} = 14$$

$$\mathrm{pOH} = 14 - 9 = 5$$

$$5 = 4.7 + \log\frac{[\mathrm{NH_4Cl}]}{[\mathrm{NH_4OH}]}$$

$$0.3 = \log\frac{[\mathrm{NH_4Cl}]}{0.1}$$

$$\frac{[\mathrm{NH_4Cl}]}{0.1} = \text{antilog of } (0.3)$$

$$[\mathrm{NH_4Cl}] = 0.1\mathrm{M} \text{ x } 1.995 = 0.2\mathrm{M}$$

Amount of $NH_4Cl$ required to prepare 1 litre of 0.2M solution

= Strength x molar mass of $NH_4Cl$ = 0.2 x 53.5 = 10.70g

**Amount of $NH_4Cl$ required to prepare 1 litre of 0.2M solution= 10.70g**

**b) What volume of 0.6M sodium formate solution is required to prepare a buffer solution of pH 4.0 by mixing it with 100ml of 0.8M formic acid ($pK_a$ = 3.75)**

$$\mathrm{pH} = \mathrm{pK_a} + \log\frac{[\text{sodium formate}]}{[\text{formic acid}]}$$

$$[\text{sodium formate}] = 0.6 \text{ x } V$$

$$[\text{formic acid}] = 0.8 \text{ x } 100 = 80$$

$$4 = 3.75 + \log\frac{[0.6\ V]}{[80]}$$

$$4 - 3.75 = \log\frac{[0.6\ V]}{[80]}$$

$$\text{antilog of } 0.25 = \frac{[0.6\ V]}{[80]}$$

$$0.6V = 1.778 \text{ x } 80 = 142.24$$

$$V = \frac{142.24}{0.6} = 237.08$$

$$\textbf{Volume required} = \mathbf{237.08\ mL}$$

**10. Calculate the i) hydrolysis constant ii) degree of hydrolysis and iii) pH of 0.05M sodium carbonate ($pK_a$= 10.26)**

$pK_a = 10.26$
$pK_a = -\log K_a$
$K_a = \text{antilog}(-pK_a) = \text{antilog}(-10.26)$
$= \text{antilog}(-10.26 + 11 - 11)$
$= \text{antilog}(-11 + 0.74) = 5.495 \times 10^{-11}$

**i) hydrolysis constant ($K_h$)**

$$K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{5.5 \times 10^{-11}} = 1.8 \times 10^{-4}$$

**hydrolysis constant ($K_h$) = $\mathbf{1.8 \times 10^{-4}}$**

**ii) degree of hydrolysis (h)**

$$h = \sqrt{\frac{K_w}{K_a C}} = \sqrt{\frac{1 \times 10^{-14}}{5.5 \times 10^{-11} \times 0.05}} = \sqrt{\frac{1 \times 10^{-3}}{0.275}} = \sqrt{3.63 \times 10^{-3}} = \sqrt{36.3 \times 10^{-4}} = 6.025 \times 10^{-2}$$

**degree of hydrolysis (h) = $\mathbf{6.025 \times 10^{-2}}$**

**iii) pH of the solution:**

$$pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C = 7 + \frac{10.26}{2} + \frac{\log 0.05}{2} = 7 + 5.13 - 0.6505 = 11.4795$$

**pH= $\mathbf{11.4795}$**

## III TEXT BOOK EXAMPLES:

**Example: 1 (page no 8)**

**Calculate the concentration of $OH^-$ in a fruit juice which contains 2 x $10^{-3}$M, $H_3O^+$ ion. Identify the nature of solution.**

**Given:** $[H_3O^+] = 2 \times 10^{-3}$M

$K_w = [H_3O^+][OH^-]$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1 \times 10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12}\ \text{M}$$

$2 \times 10^{-3} >> 5 \times 10^{-12}$ i.e. $[H_3O^+] >> [OH^-]$, **hence the juice is acidic in nature.**

**Example: 2 (page no 11)**

**Calculate the pH of 0.001M HCl solution.**

$pH = -\log [H_3O^+] = -\log(0.001)$
$= -\log 10^{-3} = 3$
$\mathbf{pH = 3}$

**Example: 3 (page no 11)**

**Calculate the pH of 10 $^{-7}$M HCl solution**

**Given:** Concentration of HCl = $10^{-7}$

$[H_3O^+] = 10^{-7}$ (from water) + $10^{-7}$ (from HCl)

$= 10^{-7} + 10^{-7} = (1 + 1) \times 10^{-7} = 2 \times 10^{-7}$

$$\mathrm{pH} = -\log\ [H_3O^+] = -\log\ (2 \times 10^{-7}) = 7 - \log 2 = 7 - 0.3010 = 6.699 = 6.70$$

**pH = 6.70**

**Example: 4 (page no 14)**

**A solution of 0.10M of a weak electrolyte is found to be dissociated to the extent of 1.20% at 25ºC. Find the dissociation constant of the acid**

**Given:** $\alpha = 1.20\% = \frac{1.20}{100} = 1.2 \times 10^{-2}$

$$K_a = \alpha^2 C = (1.2 \times 10^{-2})^2\ (0.1) = 1.44 \times 10^{-4} \times 10^{-1} = 1.44 \times 10^{-5}$$

**Example: 5 (page no 15)**

**Calculate the pH of 0.1M $CH_3COOH$ solution. Dissociation constant of acetic acid is $1.8 \times 10^{-5}$**

**Given:** $K_a = 1.8 \times 10^{-5}$, C = 0.1M

For weak acids, $[H^+] = \sqrt{K_a \times C}$

$[H^+] = \sqrt{1.8 \times 10^{-5} \times 0.1} = \sqrt{1.8 \times 10^{-6}}$

$= 1.34 \times 10^{-3}$ M

pH= -log $(1.34 \times 10^{-3})$

= 3 – log 1.34

= 3- 0.1271 = 2.8729

**pH = 2.8729**

**Example: 6 (page no 19)**

**Find the pH of the buffer solution containing 0.20 mole per litre sodium acetate and 0.18 mole per litre acetic acid. $K_a = 1.8 \times 10^{-5}$ (AUG-2021)**

**Given:** $K_a = 1.8 \times 10^{-5}$, [acid] = 0.18 mole per litre, [salt] = 0.20 mole per litre

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{salt}]}{[\mathrm{acid}]}$$

$$= 4.7447 + \log\frac{0.20}{0.18}$$

$$= 4.7447 + \log\frac{10}{9}$$

$$= 4.7447 + \log 10 - \log 9 = 4.7447 + 1 - 0.9542$$

$$= 4.7905$$

**pH= 4.7905**

**Example:7 (page no 20)**

**What is the pH of an aqueous solution obtained by mixing 6 gram of acetic acid and 8.2 gram of sodium acetate and making the volume equal to 500ml. ($K_a = 1.8 \times 10^{-5}$)**

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{sodium acetate}]}{[\text{acetic acid}]}$$

$$\mathrm{p}K_a = 4.7447$$

$$\text{Number of moles of sodium acetate} = \frac{\text{mass}}{\text{molar mass}} = \frac{8.2}{82} = 0.1\text{mole}$$

$$[\text{sodium acetate}] = \frac{\text{number of moles}}{\text{volume of soluition}} = \frac{0.1}{0.5} = 0.2\text{M}$$

$$\text{Number of moles of acetic acid} = \frac{\text{mass}}{\text{molar mass}} = \frac{6}{60} = 0.1\text{mole}$$

$$[\text{acetic acid}] = \frac{\text{number of moles}}{\text{volume of soluition}} = \frac{0.1}{0.5} = 0.2\text{M}$$

$$\begin{aligned} \text{pH} &= 4.7447 + \log\frac{0.2}{0.2} \\ &= 4.7447 \end{aligned}$$

**pH= 4.7447**

**Example: 8 (page no 24)**

**Calculate the i) hydrolysis constant ii) degree of hydrolysis and iii) pH of 0.1M sodium acetate ($pK_a$ of acetic acid= 4.74) (SEPT-2020)**

$pK_a$= 4.74

$pK_a$= -log $K_a$

$K_a$= antilog (-$pK_a$) = antilog (-4.74)

= antilog (-4.74 +5 -5)
= antilog (-5 + 0.26) = 1.8 x $10^{-5}$

**i) hydrolysis constant ($K_h$)**

$$K_h = \frac{K_w}{K_a} = \frac{1\ x 10^{-14}}{1.8\ x\ x 10^{-5}} = 5.6x\ 10^{-10}$$

**hydrolysis constant ($K_h$) = $\mathbf{5.6x\ 10^{-10}}$**

**ii) degree of hydrolysis (h)**

$$h = \sqrt{\frac{K_w}{K_a C}} = \sqrt{\frac{1\ x\ 10^{-14}}{1.8\ x\ 10^{-5}\ x\ 0.1}} = \sqrt{\frac{1\ x\ 10^{-8}}{1.8}} = \sqrt{0.5555x\ 10^{-8}} = 0.75\ x\ 10^{-4}$$

**degree of hydrolysis (h) = $\mathbf{7.5\ x\ 10^{-5}}$**

**iii) pH of the solution:**

$$\text{pH} = 7 + \frac{1}{2}\text{p}\,K_a + \frac{1}{2}\log C = 7 + \frac{4.74}{2} + \frac{\log 0.1}{2} = 7 + 2.37 - 0.5 = 8.87$$

**pH= $\mathbf{8.87}$**

**Example: 9 (page no 25)**

**Find out whether lead chloride gets precipitated or not when 1mL of 0.1M lead nitrate and 0.5mL of 0.2M NaCl solution are mixed? $K_{sp}$ of $PbCl_2$= 1.2 x $10^{-5}$**

The concentration of $Pb^{2+}$ and $Cl^-$ in the mixture is different from the concentration of individual solutions. The total volume (1 + 0.5 = 1.5mL) changes on mixing.

$$Pb(NO_3)_2 \rightleftharpoons Pb^{2+} + 2NO_3^-$$
$$0.1M \quad\quad 0.1M \quad 0.2M$$

Number of moles of $Pb^{2+}$ = molarity x volume of solution in litres = $0.1 \times 1 \times 10^{-3} = 10^{-4}$

Molarity of $Pb^{2+}$ in the mixture = $\frac{\text{Number of moles}}{\text{Volume}}$

$$[Pb^{2+}]_{mix} = \frac{10^{-4}}{1.5 \times 10^{-3}} = 6.7 \times 10^{-2}\ M$$

$$NaCl \rightleftharpoons Na^+ + Cl^-$$
$$0.2M \quad 0.2M \quad 0.2M$$

Number of moles of $Cl^-$ = molarity x volume of solution in litres = $0.2 \times 0.5 \times 10^{-3} = 10^{-4}$

Molarity of $Cl^-$ in the mixture = $\frac{\text{Number of moles}}{\text{Volume}}$

$$[Cl^-]_{mix} = \frac{10^{-4}}{1.5 \times 10^{-3}} = 6.7 \times 10^{-2}\ M$$

Ionic Product = $[Pb^{2+}][Cl^-]^2 = (6.7 \times 10^{-2})(6.7 \times 10^{-2})^2 = 3.01 \times 10^{-4}$

Solubility product = $1.2 \times 10^{-5}$

**Ionic Product > Solubility product**

**$PbCl_2$ is precipitated**.

**Example: 10 (page no 26)**
**Establish a relationship between the solubility product and molar solubility for the following**

**a) $BaSO_4$**

$$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = (S)(S) = S^2$$

$$\mathbf{K_{sp} = S^2}$$

**b) $Ag_2CrO_4$**

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (2S)^2(S) = 4S^3$$

$$\mathbf{K_{sp} = 4S^3}$$

## IV ADDITIONAL QUESTIONS AND ANSWERS:

**1. Discuss Arrhenius concept of acids and bases with suitable example. Give its limitations. (MAY-2022)**

- An acid is a substance that dissociates to give hydrogen ion in water. Ex: HCl, $H_2SO_4$
- A base is a substance that dissociates to give hydroxyl ion in water. Ex: NaOH, KOH

**Limitations:**

- It does not explain the behavior of acids and bases in non - aqueous solvents like acetone, tetrahydrofuran etc...
- It does not account the basicity of the substance like ammonia which do not possess hydroxyl group.

**2. Distinguish Lewis acids and Lewis bases.**

| **Lewis acids** | **Lewis bases** |
|---|---|
| Electron deficient molecules.<br>Ex: $BF_3$, $AlCl_3$ | Molecules with one or more lone pairs of electrons.<br>Ex: $NH_3$, $H_2O$ |
| All metal ions or atoms. Ex: $Fe^{2+}$, $Fe^{3+}$, $Cr^{3+}$ | All anions. Ex: $F^-$,$Cl^-$, $CN^-$ |
| Molecules with polar double bond. Ex: $SO_2$, $CO_2$ | Molecules with carbon – carbon double bond Ex: $CH_2{=}CH_2$, $CH \equiv CH$ |
| Molecules in which the central atom can expand its octet due to the availability of empty d-orbitals. Ex: $SiF_4$, $SF_4$ | All metal oxides. Ex: CaO, MgO |
| Carbonium ion. Ex: $(CH_3)_3C^+$ | Carbanion. Ex: $CH_3^-$ |

**3. Classify the following into Lewis acid and Lewis base? (SEPT 2020)**

**i) $BF_3$ ii) $CO_2$ iii) MgO iv) $CH_3^-$**

| | |
|---|---|
| **i) $BF_3$** | **Lewis acid** |
| **ii) $CO_2$** | **Lewis acid** |
| **iii) MgO** | **Lewis base** |
| **iv) $CH_3^-$** | **Lewis base** |

**4. Conjugate base of a strong acid is a weak base. Justify your answer**

Consider the dissociation of HCl in aqueous solution.

$$\underset{\text{Acid}_1}{HCl} + \underset{\text{Base}_2}{H_2O} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^+} + \underset{\text{Base}_1}{Cl^-}$$

Due to complete dissociation, the equilibrium lies almost to the right i.e., the $Cl^-$ ion has only a negligible tendency to accept proton from $H_3O^+$. It means that conjugate base of a strong acid is a weak base.

**5. Aqueous solution of HCl is acidic and solution of NaOH is basic. Why?**

The following equilibrium exist in aqueous solution of HCl.

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

HCl molecules also produces $H_3O^+$ by donating proton to water and so $[H_3O^+] > [OH^-]$.
Hence, aqueous solution of HCl is acidic. Similarly, in basic solutions, $[OH^-] > [H_3O^+]$.
Hence, aqueous solution of NaOH is basic.

**6. Derive the relation between pH and pOH.**

A relation between pH and pOH can be established using their following definitions

$\mathrm{pH} = -\log_{10}\ [\mathrm{H_3O^+}]$ ---------------------(1)

$\mathrm{pOH} = -\log_{10}[\mathrm{OH^-}]$ ----------------------(2)

Adding equation (1) and (2)

$$\begin{aligned}\mathrm{pH} + \mathrm{pOH} &= -\log_{10}\ [\mathrm{H_3O^+}] - \log_{10}[\mathrm{OH^-}] \\ &= -\{\ \log_{10}\ [\mathrm{H_3O^+}] + \log_{10}[\mathrm{OH^-}]\ \}\end{aligned}$$

$$\mathrm{pH} + \mathrm{pOH} = -\log_{10}\ [\mathrm{H_3O^+}][\mathrm{OH^-}]$$

we know that $[\mathrm{H_3O^+}][\mathrm{OH^-}] = K_w$

$$\mathrm{pH} + \mathrm{pOH} = -\log_{10} K_w$$

$$\mathrm{pH} + \mathrm{pOH} = pK_w$$

At $25^0$C, $K_w = 1 \text{ x } 10^{-14}$

$$pK_w = -log_{10}10^{-14} = 14\log_{10}10 = 14$$

At $25^0$C, $\mathrm{pH} + \mathrm{pOH} = 14$

**7. Write the pH value for the following. (MAR-2020)**

| **pH** | **Substances** | **pH** | **Substances** |
|---|---|---|---|
| 0 | Battery acid | 8 | Sea water |
| 1 | Stomach a | **9** | **Baking soda** |
| **2** | **vinegar** | 10 | Indigestion tablet |
| 3 | Orange juice | 11 | Ammonia solution |
| 4 | Tomato | **12** | **Soapy water** |
| **5** | **Black coffee** | 13 | Bleach |
| 6 | Urine | 14 | Drain cleaner |
| 7 | Water | | |

**8. Express the concentration of $H_3O^+$ and $OH^-$ present in a solution, when concentration of acid and base is less than $10^{-6}$.**

If the concentration of acid and base is less than $10^{-6}$, then the concentration of $H_3O^+$ produced due to the auto ionisation of water cannot be neglected.

$[H_3O^+] = 10^{-7}$ (from water) + $[H_3O^+]$ (from the acid)

$[OH^-] = 10^{-7}$ (from water) + $[OH^-]$ (from the base)

**9. From Ostwald dilution law, how the concentration of $H^+$( $H_3O^+$) can be calculated from $K_a$ value.**

$$[\mathrm{H^+}] = \alpha\,\mathrm{C}$$

$$[\mathrm{H^+}] = \sqrt{\frac{\mathrm{K}_a}{\mathrm{C}}} \text{ x } \mathrm{C} = \sqrt{\mathrm{K}_a\ \mathrm{C}}$$

$$[\mathbf{H^+}] = \sqrt{\mathbf{K}_a\ \mathbf{C}}$$

**10. What are buffer solution? What are its types? (AUG-2022)**

- Buffer solution is a mixture of a weak acid and its conjugate base (or) a weak base and its conjugate acid.
- It resists drastic changes in its pH upon addition of a small amount of acids or bases.
- There are two types of buffer solutions.
  1. Acidic buffer solution: a solution containing weak acid and its salt. Ex: solution containing acetic acid and sodium acetate.
  2. Basic buffer solution: a solution containing weak base and its salt. Ex: solution containing ammonium hydroxide and ammonium chloride.

**11. Define buffer action. (JULY-2020)**

Buffer action is defined as the ability of the buffer solution to resist the changes in pH value when a small amount of an acid or a base is added to it.

.

**12. Explain the buffer action in an acidic buffer containing equimolar acetic acid and sodium acetate.**

Consider the buffer action in a solution containing $CH_3COOH$ and $CH_3COONa$. The dissociation of buffer components occur below.

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

$$CH_3COONa_{(s)} \xrightarrow{H_2O(l)} Na^+_{(aq)} + CH_3COO^-_{(aq)}$$

If an acid is added to this mixture, it will be consumed by the conjugate base $CH_3COO^-$ to form the undissociated weak acid i.e. the increases in the concentration of $H^+$ does not reduce the pH significantly.

$$H^+_{(aq)} + CH_3COO^-_{(aq)} \rightarrow CH_3COOH_{(aq)}$$

If a base is added, it will be neutralised by $H^+$, and the acetic acid is dissociated to maintain the equilibrium. Hence the pH is not significantly altered.

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

$$CH_3COOH_{(aq)} \overset{H_2O(l)}{\Longleftrightarrow} H^+_{(aq)} + CH_3COO^-_{(aq)}$$

---

$$OH^-_{(aq)} + CH_3COOH_{(aq)} \rightarrow CH_3COO^-_{(aq)} + H_2O_{(l)}$$

**13. What is buffer capacity?**

It is defined as the number of gram equivalents of acid or base added to 1 litre of the buffer solution to change its pH by unity.

$$\boxed{\boldsymbol{\beta = \frac{dB}{d(pH)}}}$$

**14. Derive Henderson – Hasselbalch equation to calculate pH of acidic buffer. (MARCH-2020)**

The concentration of hydronium ion in an acidic buffer solution depends on the ratio of the concentration of the weak acid to the concentration of its conjugate base present in the solution.

$$[H_3O^+] = K_{a} \ \frac{[acid]}{[salt]}$$

Due to common ion effect and very less extent of dissociation, the concentration of weak acid is nearly equal to the initial concentration of unionized acid. Similarly, the concentration of the conjugate base is nearly equal to the initial concentration of added salt.

$$[H_3O^+] = K_{a} \ \frac{[acid]}{[salt]}$$

Taking logarithm on both sides of the equation

$$\log [H_3O^+] = \log K_{a} \ + \ \log \frac{[acid]}{[salt]}$$

Reverse the sign on both sides,

$$-\log [H_3O^+] = -\log K_{a} \ - \log \frac{[acid]}{[salt]}$$

$$pH \ = pK_a \ - \log \frac{[acid]}{[salt]}$$

$$\boxed{\mathbf{pH \ = pK_a \ + \log \frac{[salt]}{[acid]}}}$$

**15 What is salt hydrolysis?**

Salts completely dissociates in aqueous solution to give their constituent ions. The ions so produced are hydrated by water. In certain cases, cations, anions or both react with water and the reaction is called salt hydrolysis.

**16. Derive an expression for the hydrolysis constant and degree of hydrolysis of salt of weak acid and strong base**

Consider the reaction between weak acid and strong base

$$CH_3COOH_{(aq)} + NaOH_{(aq)} \rightleftharpoons CH_3COONa_{(aq)} + H_2O_{(l)}$$

The salt completely dissociates to give respective ions.

$$CH_3COONa_{(s)} \rightarrow Na^+_{(aq)} + CH_3COO^-_{(aq)}$$

$CH_3COO^-$ is a strong conjugate base of the weak acid $CH_3COOH$ and it has a tendency to react with $H^+$ from water to produce unionised $CH_3COOH$ shown below.

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightarrow CH_3COOH_{(aq)} + OH^-_{(aq)}$$

Here, $[OH^-] > [H^+]$ so the solution is basic and the pH is greater than 7.

**Hydrolysis constant ($K_h$):**

$$\underset{C\,(1-h)}{CH_3COO^-_{(aq)}} + H_2O_{(l)} \rightarrow \underset{C\,h}{CH_3COOH_{(aq)}} + \underset{C\,h}{OH^-_{(aq)}}$$

$$K_a = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]} \;----(1) \qquad K_h = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]}----(2)$$

Equation (1) x (2)

$$K_a \text{ x } K_h = K_w$$

$$\boxed{\mathbf{K_h = \frac{K_w}{K_a}}}$$

**Degree of hydrolysis: (h)**

$$K_h = \frac{C\,h \text{ x } C\,h}{C(1-h)} = Ch^2$$

$$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a C}}$$

$$\boxed{\mathbf{h = \sqrt{\frac{K_w}{K_a C}}}}$$

**Concentration of hydroxide ion:** $[OH^-]$

$$[OH^-] = C\,h = C\sqrt{\frac{K_w}{K_a C}} = \sqrt{\frac{C\,K_w}{K_a}}$$

$$\boxed{\mathbf{[OH^-] = \sqrt{\frac{C\,K_w}{K_a}}}}$$

**pH of the solution:**

$$pH = 14 - pOH = 14 + \log[OH^-] = 14 + \log\left[\frac{C\,K_w}{K_a}\right]^{\frac{1}{2}} = 14 + \frac{1}{2}\log C + \frac{1}{2}\log K_w - \frac{1}{2}\log K_a$$

$$= 14 - 7 + \frac{1}{2}\log C - \frac{1}{2}\log K_a = 7 + \frac{1}{2}\log C + \frac{1}{2}pK_a$$

$$\boxed{\mathbf{pH = 7 + \frac{1}{2}\log C + \frac{1}{2}pK_a}}$$

**17. Derive an expression for the hydrolysis constant and degree of hydrolysis of salt of weak acid and weak base**

Consider the reaction between weak acid and weak base

$$CH_3COOH_{(aq)} + NH_4OH_{(aq)} \rightleftharpoons CH_3COO\,NH_{4\,(aq)} + H_2O_{(l)}$$

The salt completely dissociates to give respective ions.

$$CH_3COO\,NH_{4\,(s)} \rightarrow NH_4^+{}_{(aq)} + CH_3COO^-{}_{(aq)}$$

In this case, both the cation and anion have the tendency to react with water.

$$CH_3COO^-{}_{(aq)} + H_2O_{(l)} \rightarrow CH_3COOH_{(aq)} + OH^-{}_{(aq)}$$
$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightarrow NH_4OH_{(aq)} + H^+{}_{(aq)}$$

The nature of the solution depends on the strength of acid or base. If $K_a > K_b$, the solution is acidic and pH < 7, if $K_a < K_b$ , the solution is basic and pH >7,if $K_a = K_b$, then the solution is neutral.

**Hydrolysis constant ($K_h$):**

$$\underset{C(1-h)}{CH_3COO^-{}_{(aq)}} + H_2O_{(l)} \rightarrow \underset{Ch}{CH_3COOH_{(aq)}} + \underset{Ch}{OH^-{}_{(aq)}}$$

$$\underset{C(1-h)}{NH_4^+{}_{(aq)}} + H_2O_{(l)} \rightarrow \underset{Ch}{NH_4OH_{(aq)}} + \underset{Ch}{H^+{}_{(aq)}}$$

$$K_a = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]} ----(1) \qquad K_h = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]} ----(2)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} ----(3)$$

Equations (1) x (2) x (3)

$K_a \text{ x } K_b \text{ x } K_h = K_w$

$$\boxed{\mathbf{K_h = \frac{K_w}{K_aK_b}}}$$

**Degree of hydrolysis: (h)**

$$\underset{C(1-h)}{CH_3COO^-{}_{(aq)}} + \underset{C(1-h)}{NH_4^+{}_{(aq)}} + H_2O_{(l)} \rightarrow \underset{Ch}{CH_3COOH_{(aq)}} + \underset{Ch}{NH_4OH_{(aq)}}$$

$$K_h = \frac{Ch \text{ x } Ch}{C^2(1-h)^2} = h^2$$

$$h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_aK_b}}$$

$$\boxed{\mathbf{h = \sqrt{\frac{K_w}{K_aK_b}}}}$$

**Concentration of hydrogen ion:** $[H^+]$

$$[H^+] = K_a h = K_a\sqrt{\frac{K_w}{K_a K_b}} = \sqrt{\frac{K_w\ \ K_a}{K_b}}$$

$$\boxed{[\mathbf{H}^+] = \sqrt{\frac{\mathbf{K_w\ \ K_a}}{\mathbf{K_b}}}}$$

**pH of the solution:**

$$\mathrm{pH} = -\log[H^+] = -\log\left[\frac{K_w\ \ K_a}{K_b}\right]^{\frac{1}{2}} = -\frac{1}{2}\log\ K_w - \frac{1}{2}\log K_a + \frac{1}{2}\log K_b$$

$$= \mathrm{p}K_w + \frac{1}{2}\ \mathrm{p}\ K_a - \frac{1}{2}\mathrm{p}\ K_b$$

$$\boxed{\mathbf{pH = 7 + \frac{1}{2}\,p\ K_a - \frac{1}{2}\,p\ K_b}}$$

**18. How is solubility product is used to decide the precipitation of ions?**

| | | |
|---|---|---|
| Ionic product > $K_{sp}$ | Precipitation occurs. | Solution is super saturated |
| Ionic product < $K_{sp}$ | No precipitation | Solution is unsaturated |
| Ionic product = $K_{sp}$ | Equilibrium exist | Solution is saturated |

**19. What is molar solubility?**

The maximum number of moles of solute that can be dissolved in one litre of the solution.

# UNIT 14 BIOMOLECULES

## I. Text Book Questions:

**1. What type of linkages hold together monomers of DNA?**

- Monomers of DNA are linked together by phospho diester bond between 5’OH group of one nucleotide and 3’OH group on another nucleotide.

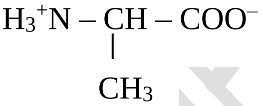
**2. Give the difference between primary and secondary structure of proteins.**

| S.no | Primary | Secondary |
|---|---|---|
| 1 | It is the relative arrangement of amino acids in the polypeptide chain | The amino acids in the polypeptide chain forms highly regular shapes through the hydrogen bond between carbonyl oxygen and amine hydrogen. |
| 2 | It is essential as even small changes can alter the overall structure and function of a protein. | $\propto$ - Helix and $\beta$ – strands or sheets are two most common sub –structures formed by proteins. |

**3. Name the Vitamins whose deficiency cause i) rickets ii) scurvy(JULY-20)**

i) Rickets -Vitamin D
ii) Scurvy -Vitamin C

**4. Write the Zwitter ion structure of alanine.**



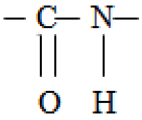
$$H_3^+N - \underset{\displaystyle CH_3}{\underset{|}{CH}} - COO^-$$

**5. Give any three difference between DNA and RNA.**

| S.No | DNA | RNA |
|---|---|---|
| 1 | It is mainly present in nucleus, mitochondria and chloroplast | It is mainly present in cytoplasm, nucleolus and ribosomes. |
| 2 | It contains deoxyribose sugar | It contains ribose sugar |
| 3 | Base pair A=T G $\equiv$ C | Base pair A=U C $\equiv$ G |
| 4 | Double stranded molecules | Single stranded molecules |
| 5 | It’s life time is high | It is short lived. |
| 6 | It is stable and not hydrolysed easily by alkalies. | It is unstable and hydrolysed easily by alkalies. |
| 7 | It can replicate itself | It cannot replicate itself.It is formed from DNA |

**6. Write a short note on peptide bond. (AUG-2021)**

The carboxyl group of the first amino acid react with the amino group of the second amino acid to give an amide linkage between these amino acids. This amide linkage is called peptide bond



$$-\underset{\displaystyle O}{\underset{||}{C}}-\underset{\displaystyle H}{\underset{|}{N}}-$$

**7. Give two difference between Hormones and Vitamins.**

| S.no | Hormones | Vitamins |
|---|---|---|
| 1 | Hormone is an organic substance that is secreted by one tissue. It limits the blood stream and induces a biological response in other tissues. | Vitamins are organic compounds that cannot be synthesized by our body and must be obtained through diet. |
| 2 | Endocrine glands, which are special groups of cells, make hormones. | They are essential for the normal growth and maintenance of our health |
| 3 | Eg. Insulin | Eg. Vitamin A,B,C,D,E and K. |

**8. Write a note on denaturation of Proteins. (SEPT-20)**

- Each protein has a unique three dimensional structure formed by such as di sulphide bond, hydrogen bond, hydrophobic and electro static interactions.
- These interactions can be disturbed when the protein is exposed to a higher temperature.
- The process of losing its higher order structure without losing the primary structures is called denaturation.
- When a protein denatures, its biological function is lost.

Eg. Coagulation of egg white by action of heat.

**9. What are reducing and non- reducing sugars?**

**Reducing sugars:**

- These are carbohydrates which contain free aldehyde or ketonic group.
- Reduces Fehling's solution and Tollen's reagent. Eg. Glucose.

**Non - reducing sugars:**

- They do not have free aldehyde group.
- They do not reduce Tollen's reagent and Fehling's solution. Eg. Sucrose

**10. Why carbohydrates are generally optically active.**

- Carbohydrates are optically active as they have one or more chiral carbons.
- Glucose contains four asymmetric carbon. So 16 isomers are possible.

**11. Classify the following into monosaccharides, oligosaccharides and polysaccharides**.

i) Starch - polysaccharides
ii) Fructose - monosaccharides
iii) Sucrose - oligosaccharides (disaccharides)
iv) Lactose - oligosaccharides (disaccharides)
v) Maltose - oligosaccharides (disaccharides)

**12. How are vitamins classified**?

Vitamins are classified into two groups based on their solubility.

i) **Fat soluble Vitamins** – They do not dissolve in water.
   - Vitamin A, D, E and K.

ii) **Water soluble Vitamins** - They are readily soluble in water
   - Vitamins B(B$_1$, B$_2$, B$_3$, B$_5$, B$_6$, B$_7$, B$_9$ and B$_{12}$) and Vitamin C

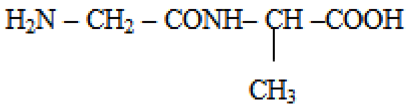
**13. What are hormones? Give examples.**

- Hormone is an organic substance that is secreted by one tissue.
- It limits the blood stream and induces a physiological response in other tissues.
- Endocrine glands, which are special groups of cells make hormones
- It is an intercellular signaling molecule. Eg. Insulin, estrogen

**14. Write the structure of all possible dipeptides which can be obtained from glycine and alanine.**

They form two dipeptides namely glycylalanine and alanylglycine.

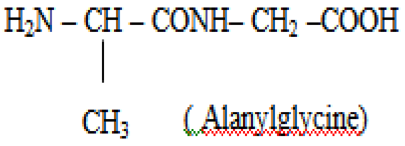
i)



$H_2N - CH_2 - CONH - \underset{\displaystyle CH_3}{\underset{|}{CH}} - COOH$

(Glycylalanine)

ii)



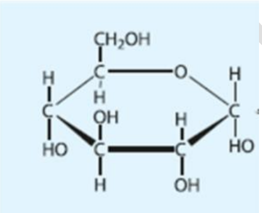
$H_2N - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CONH - CH_2 - COOH$

(Alanylglycine)

**15. Define enzymes.**

- All biochemical reactions occur in the living systems are catalysed by the catalytic proteins called Enzymes.
- Enzymes are biocatalysts that accelerate the reaction rate in the orders of $10^5$ and also make them highly specific. Eg. Sucrase

**16. Write the structure of $\alpha$ – D (+) glucopyranose.**



α-D-glucose
(α–D-Glucopyranose)

**17. What are the different types of RNA which are found in cell? (JUL-2020)**

RNA molecules are classified into three major types.

1. Ribosomal RNA (rRNA)
2. Messenger RNA (mRNA)
3. Transfer RNA (tRNA)

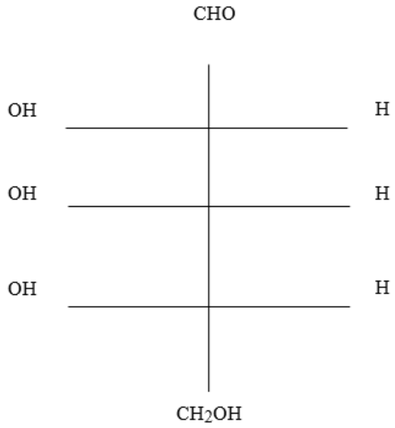
**18. Write a note on formation of $\alpha$-helix.**

- In the $\alpha$-helix sub-structure, the amino acids are arranged in a right handed helical structure.
- They are stabilised by the hydrogen bond between the carbonyl oxygen of one amino acid with amino hydrogen of the fifth residue.
- The side chains of the residues protrude outside of the helix.
- Each turn contains 3.6 residues and is about 5.4A° long.
- The amino acid proline produces a kink in the helical structure and often called as helix breaker due to its rigid cyclic structure.

**19 What are the functions of lipids in living organisms? (SEPT-2020)**

- Lipids are the integral component of cell membrane.
- The main function of triglycerides (lipids) in animals is as an energy reserve.
- They act as protective coating in aquatic organisms.
- Lipids of connective tissues give protection to internal organs.
- Lipids help in the absorption and transport of fat soluble vitamins.
- Essential for activation of enzymes such as lipases.
- Act as emulsifier in fat metabolism.

**20. Is the following sugar, D- sugar or L – sugar?**



L - Sugar

**<u>Additional questions and Answers.</u>**

**1. What are monosaccharides? Give example**.

Monosaccharides are carbohydrates that cannot be hydrolysed further and are also called simple sugars.
General formula $C_n (H_2O)_n$
Eg: glucose, fructose

**2. What are disaccharides? Give exampl**e.

Disaccharides are sugars that yield two molecules of monosaccharides on hydrolysis catalysed by dilute acid or enzyme.
General formula $C_n (H_2O)_{n-1}$.
Eg: Sucrose, Lactose

**3. What are polysaccharide? Give example**.

Polysaccharide consists of large number of monosaccharide units bonded together by glycosidic bonds.Since, they do not have sweet taste polysaccharides are called as non-sugars.
Eg: starch, cellulose

**4. What is mutarotatio**n

- The specific rotation of pure α- and β-(D) glucose are 112° & 18.7°
- When a pure form of any one of these sugars is dissolved in water, slow interconversion of α -D glucose and β -D glucose via open chain form occurs until equilibrium is established giving a constant specific rotation + 53°
- This phenomenon is called **mutarotation**.

### 5. What is epimerization? (MAR-2022)

- Sugar differing in configuration at an asymmetric centre is known as epimers.
- The process by which one epimer is converted into other is called epimerisation and it requires the enzymes epimerase.
- Galactose is converted to glucose by this manner in our body.

### 6. Sucrose is called as invert sugar? Why?

- Sucrose (+66.6°) and glucose (+52.5°) are dextrorotatory compounds while fructose is levo rotatory (-92.4°).
- During hydrolysis of sucrose the optical rotation of the reaction mixture changes from dextro to levo.
- Hence, sucrose is also called as invert sugar.

### 7. Write a short note on the structure of sucrose (or) sucrose is a non-reducing sugar. Justify.

- In sucrose, C1 of α-D-glucose is joined to C2 of β-D-fructose.
- The glycosidic bond thus formed is called α-1, 2 glycosidic bond.
- Since, both the carbonyl carbons (reducing groups) are involved in the glycosidic bonding, sucrose is a non-reducing sugar.

### 8. What is glycosidic linkage? (MAR-2020)

- In disaccharides two monosaccharide's are linked by *oxide linkage* called '*glycosidic linkage*'.
- It is formed by the reaction of the anomeric carbon of one monosaccharide with a hydroxyl group of another monosaccharide.

### 9. Lactose is a reducing sugar? Justify.

- In lactose the β-D–galactose and β-D–glucose are linked by β-1,4 glycosidic bond.
- The aldehyde carbon is not involved in the glycosidic bond
- It retains its reducing property and is called a reducing sugar.

### 10. Maltose acts as a reducing sugar justify.

- Maltose consists two molecules of α -D-glucose units linked by an α-1,4 glycosidic bond between anomeric carbon of one unit and C-4 of the other unit.
- Since one of the glucose has the carbonyl group intact, it also acts as a reducing sugar.

### 11. Write a note on a starch.

- Starch is used for energy storage in plants.
- It is a polymer of glucose in which glucose molecules are linked by α (1,4) glycosidic bonds
- They are separated into two fractions,
  1. water soluble amylose - 20 %
  2. water insoluble amylopectin - 80%

### 12. Write two difference between Amylose and Amylopectin

| S.No | Amylose | Amylopectin |
|---|---|---|
| 1 | Amylose is composed of unbranched chains upto 4000 α -D-glucose molecules joined by α (1, 4) glycosidic bonds. | Amylopetin contains chains upto 10000 α -D-glucose molecules linked by α (1, 4) glycosidic bonds. At branch points, new chains of 24 to 30 glucose molecules are linked by α (1, 6) glycosidic bonds. |
| 2 | Gives blue colour with iodine solution. | Gives purple colour with iodine solution. |
| 3 | Starch contains 20% amylose which is water soluble | Starch contains 80% amylopectin which is water insoluble |

**13. Write the importance of carbohydrates?**

- Carbohydrates, widely distributed in plants and animals, act mainly as energy sources and structural polymers
- Carbohydrate is stored in the body as glycogen and in plant as starch.
- Carbohydrates such as cellulose which is the primary components of plant cell wall, is used to make paper, furniture and cloths.
- Simple sugar glucose serves as an instant source of energy.
- Ribose sugars are one of the components of nucleic acids.
- Modified carbohydrates such as hyaluronate (glycosaminoglycans) act as shock absorber and lubricant.

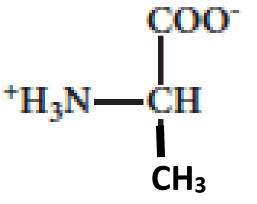
.

**14. What is isoelectric point?**

- At a specific pH the net charge of an amino acid is neutral and this pH is called **isoelectric point**.
- At a pH above the isoelectric point the amino acid will be negatively charged and positively charged at pH values below the isoelectric point.

**15. What are Zwitter ions? (AUG-2022)**

- In aqueous solution the proton from carboxyl group can be transferred to the amino group of an amino acid leaving these groups with opposite charges.
- Despite having both positive and negative charges this molecule is neutral and has amphoteric behaviour.
- These ions are called zwitter ions.



$^{+}H_3N-CH(COO^-)-CH_3$

Zwitter Ion

**16. How are proteins classified? Explain. (MAR-2020)**

Proteins are classified into two major types.

1. Fibrous proteins
2. Globular proteins

**Fibrous proteins**

- Fibrous proteins are linear molecules similar to fibres.
- Generally insoluble in water and are held together by disulphide bridges and weak intermolecular hydrogen bonds.
- The proteins are often used as structural proteins. Example: Keratin, Collagen

**Globular proteins**

- They have an overall spherical shape.
- The polypeptide chain is folded into a spherical shape.
- These proteins are usually soluble in water and have many functions including

Catalysis. Example: myoglobin

**17. Give the importance of proteins.**

- All biochemical reactions occur in the living systems are catalysed by the catalytic proteins called enzymes.
- Proteins such as keratin, collagen act as structural back bones.
- Antibodies help the body to fight various diseases.
- They are used as messengers to coordinate many functions. Insulin and glucagon control the glucose level in the blood.
- They act as receptors that detect presence of certain signal molecules and activate the proper response.
- They are also used to store metals such as iron (Ferritin).

**18. Give the catalytic activity of the following enzymes**
**i) Carbonic anhydrase ii) Sucrase iii) Lactase.**

(i) Carbonic anhydrase - Catalyses the interconversion of carbonic acid to water and carbon dioxide.
(ii) Sucrase - Catalyses the hydrolysis of sucrose to fructose and glucose.
(iii)Lactase enzyme - Hydrolyses the lactose into its constituent monosaccharides, glucose and galactose.

**19. What are the components of nucleic acids?**

The three components of nucleic acids
(i) Nitrogenous base
(ii) Pentose sugar
(iii)Phosphate group

**20. Human cannot use cellulose as food? Why**?

Human cannot use cellulose as food because our digestive system do not contain the necessary enzymes (glycosidases or cellulases) that can hydrolyse the cellulose.

**21. What are nucleoside and nucleotide.**

Sugar + Base → Nucleoside
Nucleoside + Phosphate → Nucleotide

**22. Give the Biological functions of nucleic acids.**

(i) Energy carriers (ATP)
(ii) Components of enzyme cofactors (Eg. FAD)
(iii)Chemical messengers. (Eg. Cyclic AMP)

**23. What are the types of RNA? Write its functions. Explain**.

Types of RNA

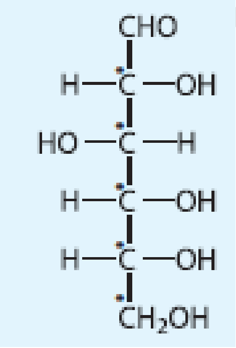
i. **Ribosomal RNA (rRNA)**
   - rRNA is mainly found in cytoplasm and in ribosomes.
   - It contains 60% RNA and 40% protein.
   - Protein synthesis takes place at this site.

ii. **Messenger RNA (mRNA)**
   - It is present in small quantity and very short lived.
   - The synthesis of mRNA from DNA strand is called transcription.
   - It carries genetic information from DNA to the ribosomes for protein synthesis.

iii. **Transfer RNA (tRNA)**
   - Molecules have lowest molecular weight of all nucleic acids.
   - They carry amino acids to the sites of protein synthesis on ribosomes.

**24. Elucidate the structure of glucose.**

1. Elemental analysis and molecular weight determination show that the molecular formula of glucose is $C_6H_{12}O_6$
2. On reduction with concentrated HI and red phosphorus at 373K, glucose gives a mixture of n- hexane and 2–iodohexane indicating that the six carbon atoms are bonded linearly.
3. Glucose reacts with hydroxylamine to form oxime and with HCN to form cyanohydrins.
   The above reactions indicate the presence of carbonyl group in glucose.
4. Glucose gets oxidized to gluconic acid with mild oxidizing agents like bromine water.
   It shows that the carbonyl group is an aldehyde group and it occupies one end of the carbon chain.
5. When oxidised using strong oxidising agent such as conc. nitric acid gives glucaric acid (saccharic acid).It shows that the other end is occupied by a primary alcohol group.
6. Glucose is oxidised to gluconic acid with ammonical silver nitrate (Tollen's reagent) and alkaline copper sulphate (Fehling's solution).Tollen's reagent is reduced to metallic silver and Fehling's solution to cuprous oxide which appears as red precipitate.
   These reactions further confirm the presence of an aldehyde group.
7. Glucose forms penta acetate with acetic anhydride suggesting the presence of five alcohol groups.
8. Glucose is a stable compound and does not undergo dehydration easily.
   - It indicates that not more than one hydroxyl group is bonded to a single carbon atom.
   - Thus the five hydroxyl groups are attached to five different carbon atoms.
   - Sixth carbon is an aldehyde group.
9. The glucose is referred to as D (+) glucose as it has D configuration and is dextrorotatory.



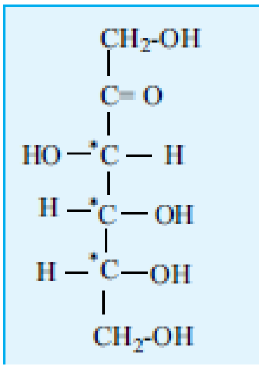
**Structure of D (+) glucose**

**25. What are anomers?**

- In the formation of cyclic structure of glucose, the achiral aldehyde carbon in it is converted to a chiral one leading to the possibility of two isomers.
- These two isomers differ only in the configuration of C1 carbon.
- These isomers are called anomers.
- The two anomeric forms of glucose are called $\alpha$ and β-forms.

**26. Elucidate the structure of fructose**.

1) Elemental analysis and molecular weight determination of fructose show that it has the molecular formula $C_6H_{12}O_6$.
2) On reduction with concentrated HI and red phosphorus, fructose gives a mixture of n- hexane and 2–iodohexane indicating that the six carbon atoms are bonded linearly
3) Fructose reacts with $NH_2OH$ and HCN. It shows the presence of a carbonyl groups in the fructose.
4) Fructose reacts with acetic anhydride in the presence of pyridine to form penta acetate. This reaction indicates the presence of five hydroxyl groups in a fructose molecule.
5) Fructose is not oxidized by bromine water. This rules out the possibility of presence of an aldehyde (-CHO) group.
6) Partial reduction of fructose with sodium amalgam and water produces mixtures of Sorbitol and Mannitol which are epimers at the second carbon. In the above reaction new asymmetric carbon is formed at C-2. This confirms the presence of a keto group.
7) On oxidation with nitric acid, it gives glycolic acid and tartaric acids which contain smaller number of carbon atoms than in fructose. This shows that a keto group is present in C-2. It also shows that 1° alcoholic groups are present at C- 1 and C- 6.



**Structure of D (+) fructose**

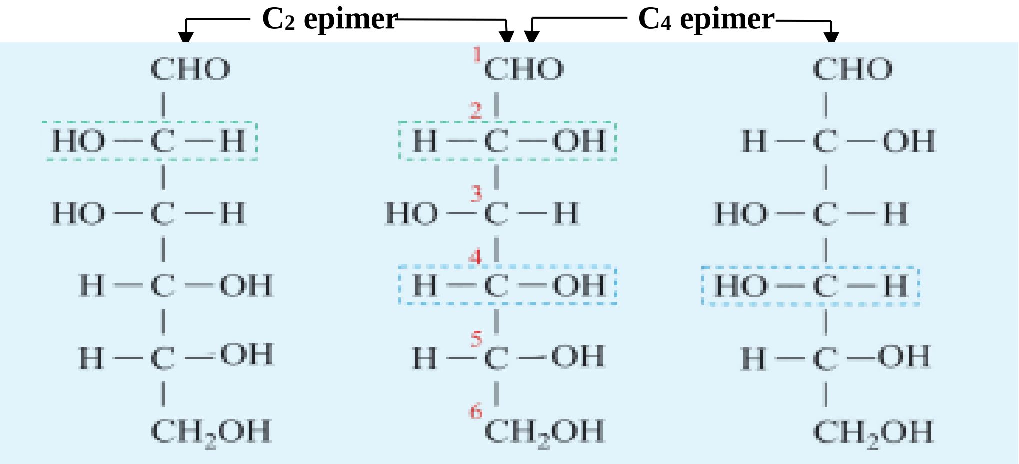
**27. Write a note on DNA finger printing.**

- DNA fingerprinting is also called DNA typing or DNA profiling.
- The DNA finger print is unique for every person.
- It can be extracted from traces of samples from blood, saliva, hair etc…
- By using this method we can detect the individual specific variation in human DNA.

**28 Explain the method of DNA finger printin**g.

- The extracted DNA is cut at specific points along the strand with restriction of enzymes.
- It resulting in the formation of DNA fragments of varying lengths which were analysed by technique called gel electrophoresis.
- This method separates the fragments based on their size.
- The gel containing the DNA fragments is then transferred to a nylon sheet using a technique called blotting.
- Then, the fragments will undergo autoradiography in which they were exposed to DNA probes.
- A piece of X-ray film was then exposed to the fragments, and a dark mark was produced at any point where a radioactive probe had become attached.
- The resultant pattern of marks could then be compared with other samples.
- DNA fingerprinting is based on slight sequence differences between individuals

### 29. Epimers of glucose of $C_2$ and $C_4$ Carbon in epimerisation process



D- Mannose D- Glucose D – Galactose

### 30. How fructose is prepared from Sucrose and Inulin.

**From Surcose**

Surcose by heating with dilute $H_2SO_4$ or with the enzyme invertase

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{(or) Invertase}]{H_2SO_4} C_6H_{12}O_6 + C_6H_{12}O_6$$

Sucrose Glucose Fructose

**I) From Inulin**

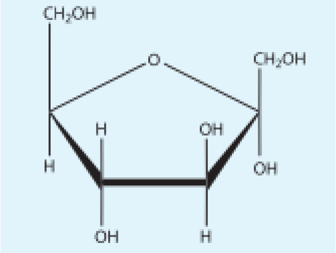
Fructose is prepared commercially by hydrolysis of Inulin in an acidic medium

$$(C_6H_{12}O_5)_n + n\,H_2O \xrightarrow{H^+} n\,C_6H_{12}0_6$$

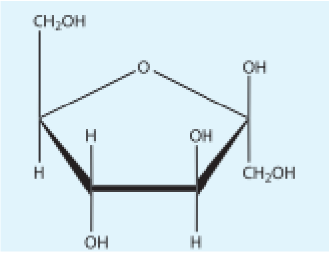
Inulin Fructose

### 31. Draw the cyclic structure of fructose

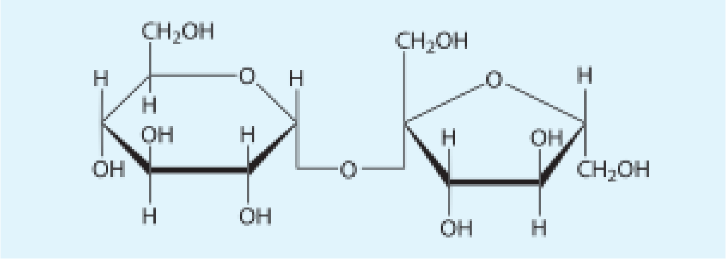
i) α-D – Fructofurnose



ii) β - D - Fructofurnose

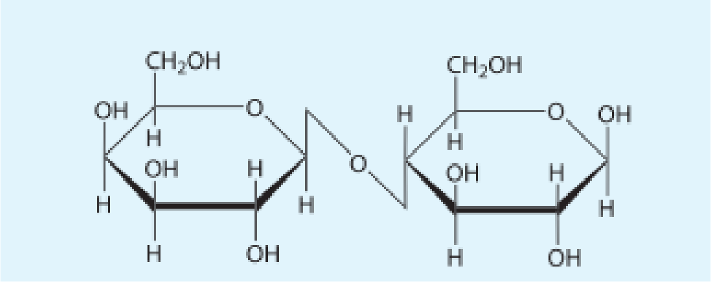


### 32. Draw the structures of disaccharides sucrose, lactose and maltose.



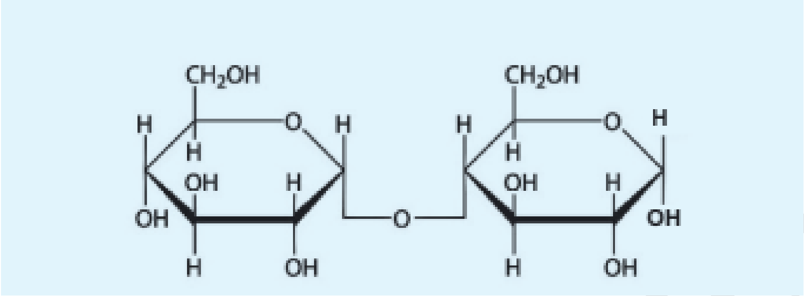
**Surcose**

α-D – Glucopyranosyl - β - D fructofurnoside



**Lactose**

β - D- Galatopyranosyl - β - D- glucopyranose



**Maltose**

α-D – Glucopyranosyl - α-D glucopyranose

**33. Write short notes on classification of polysaccharides**

**Homo polysaccharides**:

It is made up of only one type of monosaccharide unit.

Example: Starch, Cellulose and glycogen

**Hetero polysaccharides**:

It is made up of more than one type of monosaccharide unit.

Example: hyaluronic acid and heparin

**34. Write short notes on Glycogen**

i) Glycogen is the storage of polysaccharide in animals

ii) It is present in liver and muscles of animals

iii) Glycogen on hydrolysis gives glucose molecules

iv) In glycogen every branching occurs in 8-14 glucose units opposed to 24 to 30 units in amylopectin.

v) The excess glucose in animal's body stored as glycogen.

**35. How amino acids are classified? Explain with examples.**

i) Amino acids classified on the nature of their R-groups as acidic, basic and neutral amino acids also they classified as polar and non-polar amino acids.

ii) Amino acids synthesised by humans are called as non-essential amino acids.
Eg: Glycine, Alanine, Proline

iii) Amino acids obtained through diet are called as essential amino acids.
Eg. Phenylalanine, Valine, Lysine.

iii) The amino acids found in cells are called as non-protein amino acids
Eg. Ornithine and Citrulline.

**36. Explain the mechanism “enzyme action”**

i) Enzymes are biocatalysts that catalyse a specific biochemical reaction.
ii) Enzymes activate the reaction by reducing the activation energy by stabilizing the transition state.
iii) A typical reaction enzyme (E) binds with the substrate (s) molecule reversibly to produce an enzyme substrate complex (ES).
iv) During this stage the substrate is converted into product and the enzyme becomes free, and ready to bind to another substrate molecule.

$$\underset{\text{Enzyme}}{E} + \underset{\text{substrate}}{S} \Rightarrow \underset{\text{Enzyme-substrate complex}}{[ES]}$$

$$[ES] \rightarrow E + P$$

**37. Draw the tabulation and explain chemical name, sources, functions and deficiency diseases of Vitamin $B_1$, $B_2$, $B_3$, $B_5$, $B_6$, $B_7$, $B_9$, $B_{12}$ and C (Water soluble)**

| S.NO. | VITAMINS | SOURCES | FUNCTIONS | DEFECIENCY DISEASES |
|---|---|---|---|---|
| 1. | Vitamin $B_1$<br>Thiamine | Yeast, milk, cereals, liver, Green vegetables | Co-enzyme in the form of thiamine Pyro phosphate in glycolysis | Beri – Beri |
| 2. | Vitamin $B_2$<br>Riboflavin | Soya bean, milk, yeast, liver | Co-enzymes in the form of FMN and FAD in redox reaction | Cheilosis |
| 3. | Vitamin $B_3$<br>Niacin | Cereals, green leafy vegetables, liver | Co-enzymes in the form of NAD and NADP redore reaction | Pellagra |
| 4. | Vitamin $B_5$<br>Panthothenic Acid | Mushroom, Avacado, Egg Yolk Sun flower oil | Part of Co-enzyme A in Carbohydrate protein and fat metabolism | Inadequate growth |
| 5. | Vitamin $B_6$<br>(Pyridoxine) | Meat, Cereals, Milk, Whole grains, Egg. | Co-enzymes in amino acid metabolism formation of Heme in Hemoglobin | Convulsions |
| 6. | Vitamin $B_7$<br>Biotin | Liver, Kidney, Milk, Egg Yolk, Vegetables | Co-enzymes in fatty acids biosynthesis | Depression, Hair loss, muscle pain |
| 7. | Vitamin $B_9$<br>(Folic Acid) | Egg, Meat, Beet root, Leafy vegetables, Cereals, yeast | Nucleic acid, synthesis, maturation of red blood cells | Megaloblastic anemia |
| 8. | Vitamin $B_{12}$<br>Cobalamin | Egg, Meat, Fish | Co-enzyme in amino acid metabolism, Red blood cells maturation | Perinicious Anemia |
| 9. | Vitamin C<br>Ascorbic Acid | Citrus fruits, Tomato, Amla, Leafy Vegetable | Coenzymes in antioxidants building of Collagen | Scurvy |

**38. Draw the tabulation and explain chemical names, sources, functions and deficiency diseases of Vitamin A, D, E and K (Fat soluble)**

| S.NO. | VITAMINS | SOURCES | FUNCTIONS | DEFECIENCY DISEASES |
|---|---|---|---|---|
| 1. | Vitamin A<br>Retinol | Liver oil, Fish, Carrot, Milk, Spinach, Papaya and Mango | Vision and Growth | Night blindness,<br>Xerophthalmia,<br>Keratinisation of skin |
| 2. | Vitamin D<br>Cholecalciferol($D_2$)<br>Ergocalciferol ($D_3$) | Fish, Liver oil, milk, egg yolk | Absorption and maintenance of Calcium | Rickets<br>Osteomalacia |
| 3. | Vitamin E<br>Tocopherols | Cotton seed oil, Sun flower oil, Wheat germ oil, Vegetable oils | Antioxidant | Muscular dystrophy and neurological dysfunction |
| 4. | Vitamin K<br>Phylloguinone<br>Menaquinones | Green leafy Vegetables, Soybean oil, Tomato | Blood Clotting | Increased blood clotting time (Haemorrhagic diseases) |

**39. What are Nucleic acids?**

i) The inherent characteristics of each and every species are transmitted from one generation to the next. It has been observed that the particles in nucleus of the cell are responsible for the transmission of these characteristics are called chromosomes.
Chromosomes are made up of proteins and another type of biomolecules called nucleic acids.

**40. Name the two types of pentoses present in Nucleic acids.**

i) Deoxyribonucleicacid DNA –2’deoxy-D-ribose

ii) Ribonucleicacid RNA – D-ribose

**41. How Harmones are classified? Explain it with example.**

i) Endocrine hormones – act on cells distant from the site of their release.

Eg: Insulin and Epinephrine

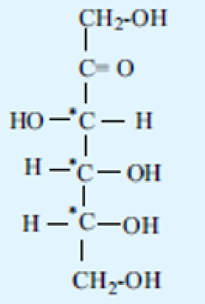
ii) Paracrine hormones – act only on cells close to the cell that released them.

Eg: Interleukin – 1

iii) Autocrine hormones- act on the same cell that released them.

Eg: Interleukin – 2

**42. Draw the structure of D (+) Fructose (AUG-2022)**



# UNIT– 15 CHEMISTRY IN EVERYDAY LIFE

## I Book Back Question:

1. **What are antibiotics?**

   It is a chemical substance produced by one micro-organism that selectively inhibits the growth of another micro-organism. Example: Penicillin

2. **Name one substance which can act as both analgesic and antipyretic.**

   Aspirin

3. **Write a note on synthetic detergents.**

   (i) Synthetic detergents are formulated products containing either sodium salts ofalkyl hydrogen sulphates or sodium salts of long chain alkyl benzene sulphonic acids.

   (ii) They are three types: Anionic, cationic and non-ionic detergents.

   (iii) It can be used even in hard water.

4. **How do antiseptics differ from disinfectants? (SEPT-20)**

| | **Antiseptics** | **Disinfectants** |
|---|---|---|
| 1 | Stop or slow down the growth of micro-organisms | Stop or slow down the growth of micro-organisms |
| 2 | They are not harmful to living tissues | They are harmful to living tissues |
| 3 | Ex : $H_2O_2$ | Ex : Alcohol |

5. **What are food preservatives?**

   These are the chemical substances are capable of inhibiting, retarding or arresting the process of fermentation, acidification or other decomposition of food by growth of micro-organisms. Ex: Acetic acid and Sodium benzoate

6. **What are drugs? How are they classified?**

   (i) A drug is a substance that is used to modify or explore physiological systems or pathological states for the benefits of the recipient.

   (ii) It is used for the purpose of diagnosis, prevention cure or relief of a disease.

   (iii) Classification of drugs based on,

   (a) Chemical structure (b) Pharmacological effect

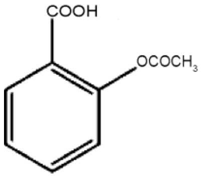
   (c) Target system (d) Site of action

**7. How the tranquilizers work in body?**

(i) They are neurologically active drugs.

(ii) They act on the central nervous system by blocking the neuro transmitterdopamine in the brain. This drug is used for treatment of stress.

**8. Write the structural formula of aspirin.**



**9. Explain the mechanism of cleansing action of soaps and detergents.**

(i) The cleansing action of soap is directly related to the structure of carboxylate ion (palmitate ion) present in soap (Ex: Sodium Palmitate).

(ii) The structure of palmitate exhibit dual polarity (a) Hydrocarbon portion – non polar – soluble in oils and greases. (b) Carboxylate portion – polar – soluble in water.

(iii) When the soap dissolve in the grease, leaving the negatively charged carboxylate and exposed on the grease surface.

(iv) At the same time the negatively charged carboxylate groups are strongly attractedby water thus leading to the formation of micelles and grease is floated away from the solid object.

(v) When the water is rinsed away the grease goes with it. As a result, the cloth gets free from dirt and the droplets are washed away with water.

(vi) The cleansing action of detergents are similar to the cleansing action of soaps.

**10. Which sweetening agent are used to prepare sweets for a diabetic patient?**

(i) Saccharin (ii) Sucralose

**11. What are narcotic and non-narcotic drugs? Give examples.**

Narcotic Drugs: These are the drugs relieve pain and produce sleep. These drugs are addictive. In poisonous dose, these produces coma and ultimately death. Ex: Morphine, Codeine.

Non-Narcotic Drugs: These are the drugs, which reduce the pain without causing impairment of consciousness. Ex: Aspirin, Paracetamol

**12. What are anti fertility drugs? Give examples.**

Anti-fertility drugs are synthetic hormones that suppresses ovulation or fertilisation. Ex: Menstranol, Norethindrone.

**13. Write a note on co-polymer.**

(i) A polymer containing two or more different kinds of monomer units is called aco-polymer.

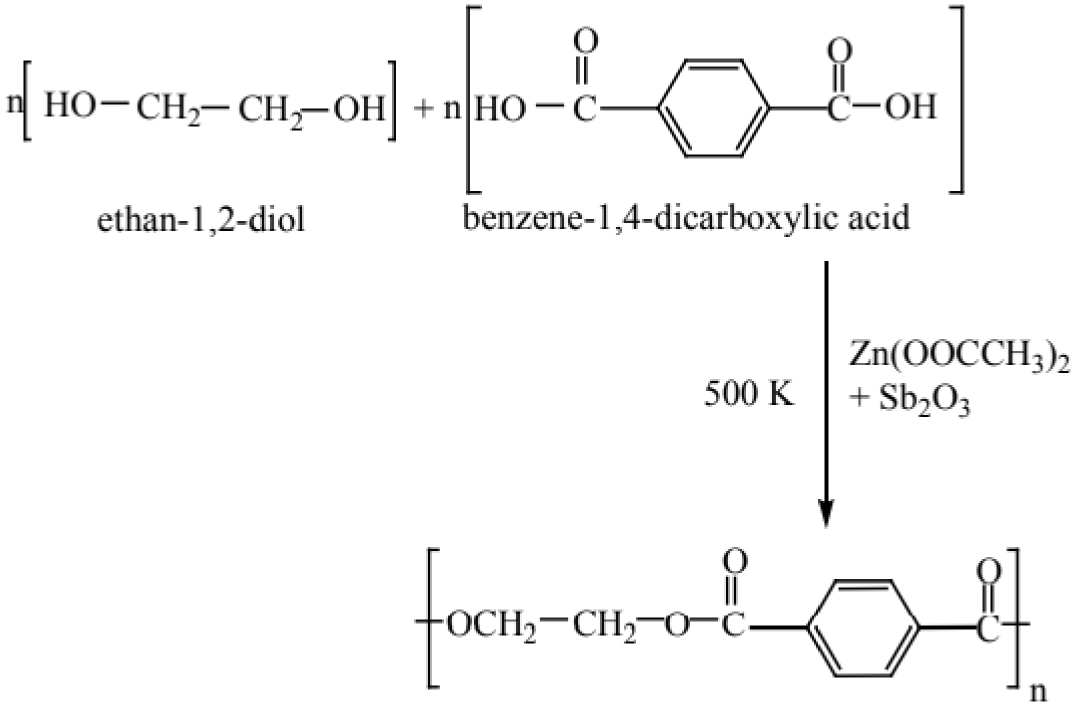
(ii) Examples: (a) Buna-S; (b) Buna-N; (c) Nylon – (6,6)

**14. What are bio-degradable polymers? Give examples**

(i) The materials or polymers that are readily decomposed by micro-organisms in the environment are called bio-degradable polymers.

(ii) Examples: PHB and PHBV

**15. How is terylene prepared?**



Terylene (an Polyester) (or) Dacron (or) PET

**16. Write a note on Vulcanization of rubber. (MAR-20)**

(i) Natural rubber is not so strong or elastic the properties of natural rubber can be modified by the process called vulcanization.

(ii) Natural rubber is mixed with 3 – 5% sulphur and heated at 100 – $150^0$C causes cross linking of the cis – 1,4 – Polyisoprene chains through disulphide (-S-S-) bonds.

(iii) The physical properties of rubber can be altered by controlling the amount of sulphur that is used for vulcanization.

(iv) 1 to 3% sulphur produces soft and stretchy rubbers.

(v) When 3 to 10% sulphur is used the resultant rubber is somewhat harder but flexible.

**17. Classify the following as linear, branched or cross lined polymers.**

**(a) Bakelike (b) Nylon – 6, 6 (c) LDPE (d) HDPE**

(i) Cross lined polymers – Bakelite

(ii) Linear polymers – Nylon – 6,6; LDPE; HDPE

## II Additional Questions:

1. **What is medicine?**

   The drug which interacts with macromolecular targets such as proteins to produce a therapeutic and useful biological response is called medicine.

2. **Define – Chemotherapy.**

   The specific treatment of a disease using medicine is known as chemotherapy.

3. **Define the terms therapeutic index.**

   It is defined as the ratio between the maximum tolerated dose of a drug and the minimum curative dose. Higher the value of therapeutic index, safer is the drug.

4. **What are antagonists & agonists?**

   (i) Antagonists are the drug which block the message by binding to the receptor sideand inhibits to natural function.

   (ii) Agonists are drugs which mimic the natural messenger by switching on thereceptor.

5. **What is meant by anti inflammatory drugs? Give examples.**

   These are the drugs reduces fever by causing the hypothalamus to override aprostaglandin induced increase in temperature. Ex: Ibuprofen

6. **What are antipyretics?**

   It is the chemical substance which lowers the body temperature to normal (reduce thefever). Ex: Paracetamol.

7. **Explain Anaesthetics with examples.**

   (i) These are the chemical substances that induce loss of pain and sensation alongwith loss of reflexes. They are the two types (a) Local anaesthetics (b) General anaesthetics.

   (ii) Local anaesthetics, causes loss of sensation in the area in which it is applied without losing consciousness. Ex: Procaine and Lidocaine.

   (iii) General anaesthetics, cause a controlled and reversible loss of consciousness by affecting central nervous system. Ex: Propofol and Isoflurane.

8. **What are antacids? Give examples.**

   Antacids neutralize the acid in the stomach that causes acidity. Ex: Milk of magnesia, aluminium hydroxide.

9. **What are antihistamines? Give examples.**

   (i) Antihistamines block histamine release from histamine – I receptors.

   (ii) Examples: Cetirizine and Levocetirizine

10. **Write a note on Antimicrobials.**

    (i) Antimicrobials inhibits bacterial cell wall biosynthesis.
    (ii) Example: Penicillin and ampicillin
    (iii) It is used to treat skin infections, dental infections.

11. **What are food additives?**

    (i) The substances which are not naturally a part of the food and added to improvethe quality of food are called additives.
    (ii) Important categories of food additives are aroma compounds, food colours and stabilizers etc.

12. **Mention the advantages of food additives? (MAR-20)**

    (i) Uses of preservatives reduce the product spoilage of food.
    (ii) Addition of vitamins and minerals reduces the mal nutrient.
    (iii) Flavouring agents enhance the aroma of the food.

13. **Explain about antioxidants. (JULY-20)**

    (i) Antioxidants are substances which react the oxidative deteriorations of food.Food containing fats and oils is easily oxidised and then rancid.
    (ii) To prevent the oxidation of fats and oils, chemical BHT, BHA are added as antioxidants.
    (iii) Ex: Sulphur dioxide, Sulphites.

14. **What are sugar substitutes?**

    The compounds that are used like sugars for sweetening, but are metabolised withoutthe influence of insulin are called sugar substituents. Ex: Sorbitol.

15. **What are artificial sweetening agents?**

    Synthetic compounds which imprint a sweet sensation and possess no or negligible nutritional value are called artificial sweeteners. Ex: Saccharin.

16. **Define TFM value.**

    Total fatty matter value is defined as the total amount of fatty matter that can be separated from a sample after splitting with mineral acids. Higher the TFM value in thesoap better is its quality.

17. **What are polymers?**

    They are macromolecules of high molecular masses formed by combination of a large number of simple molecules (called monomer).

**18. Explain the types of polymerisation.**

(i) The process of forming a very large, high molecular mass polymer from small structural unit i.e. monomer is called polymerisation. Polymerisation occurs in the following two ways:

a) Addition polymerisation

b) Condensation polymerization

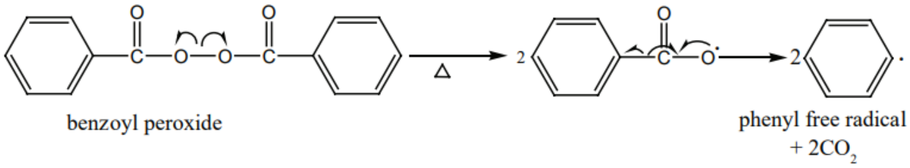
(ii) Addition polymers; monomer units are added to form long chains without the elimination of any by product. Ex: polythene.

(iii) Condensation polymers; monomer units are added to form long chains, with the elimination of some by product. Ex: Nylon – (6,6)

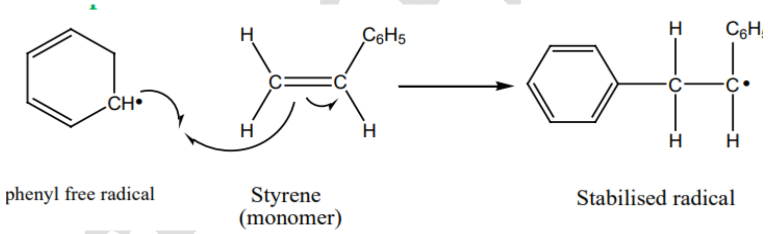
**19. Explain the mechanism of free radical polymerisation.**

When alkenes are heated with free radical initiator such as benzoyl peroxide, they undergo polymerisation reaction

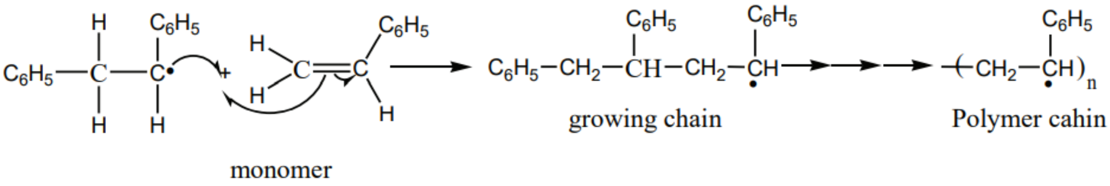
(i) Initiation – Formation of free radical



(ii) Propagation step

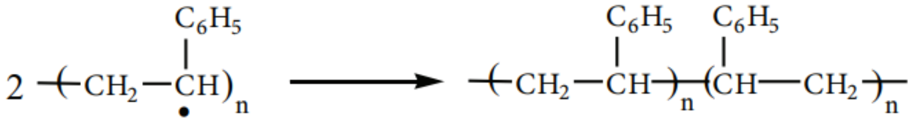


The stabilized radical attacks another monomer molecule to give an elongated radical



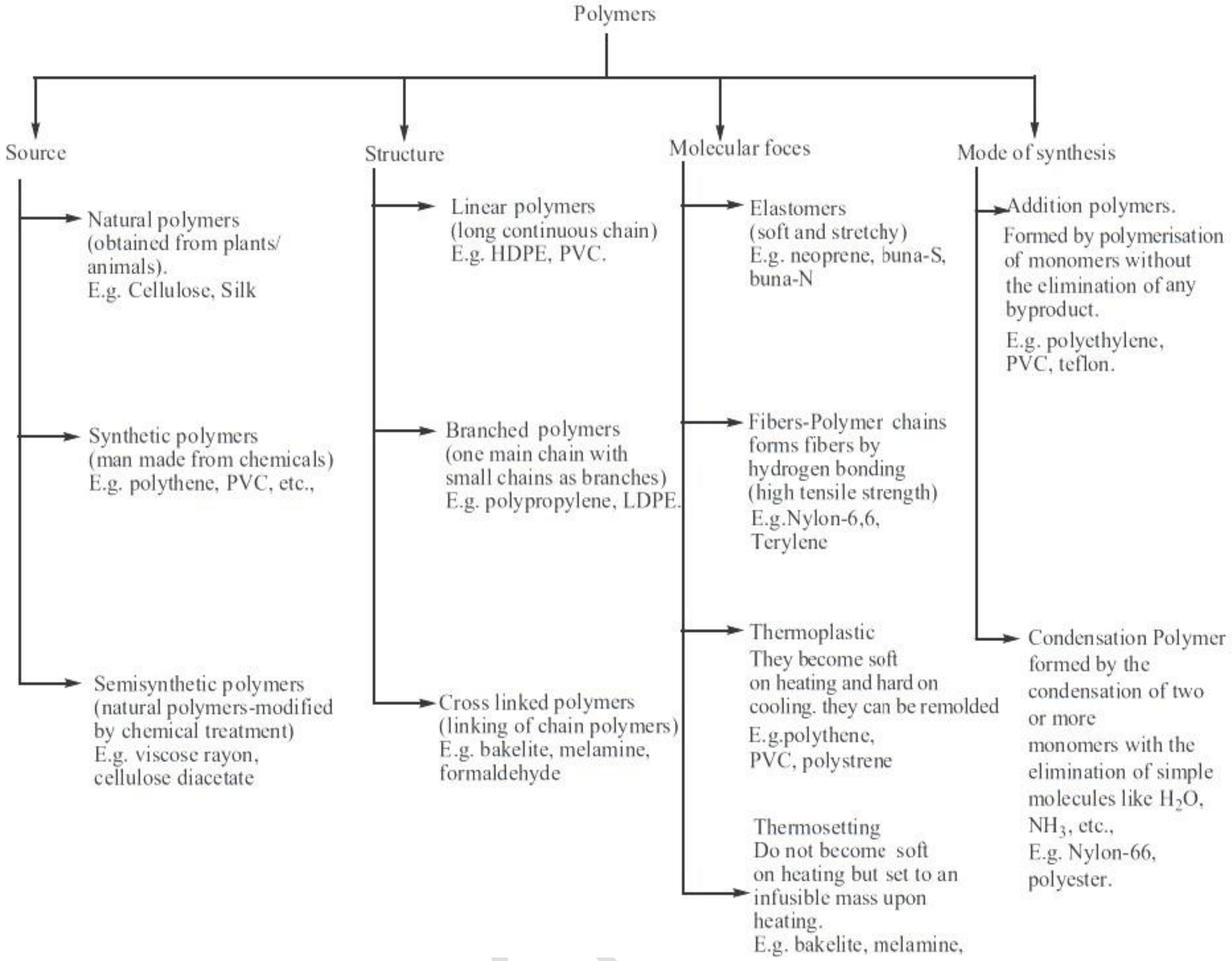
Chain growth will continue with the successive addition of several thousands of monomer units.

(iii) Termination



$$2\ \left(CH_2-\underset{\bullet}{\overset{C_6H_5}{CH}}\right)_n \longrightarrow \left(CH_2-\overset{C_6H_5}{CH}\right)_n\left(\overset{C_6H_5}{CH}-CH_2\right)_n$$

**20. Explain the classification of polymers.**



**21. How will you prepare polythene?**

There are two types of polythenes.

(i) **HDPE:** It is obtained when polymerisation is done in the presence of Ziegler-Nattacatalyst at 333-343K under 6-7 atm pressure

$$n\,CH_2 = CH_2 \xrightarrow[6-7\text{ atm, catalyst}]{333K-343K} -\!\!\left[ CH_2 - CH_2 \right]\!\!-_n$$

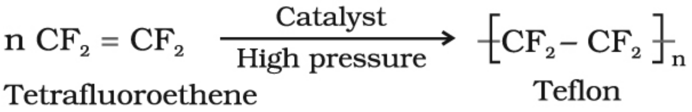
HDPE

(ii) **LDPE:** It is obtained by the polymerisation of ethene under high pressure of 1000-2000 atm at 350-570 K in the presence of an initiator.

$$n\,CH_2 = CH_2 \xrightarrow[\text{peroxide at350}-570\text{ K, }1000-2000\text{ atm}]{\text{Traces of } O_2 \text{ or}} -\!\!\left[ CH_2 - CH_2 \right]\!\!-_n$$

LDPE

**22. Write a note on Teflon**

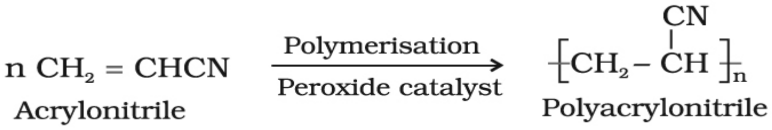


$$n\,CF_2 = CF_2 \xrightarrow[\text{High pressure}]{\text{Catalyst}} \left[ CF_2 - CF_2 \right]_n$$

It is used for coating articles and preparing non-stick utensils.

**23. What is orlon? How will you prepare orlon?**

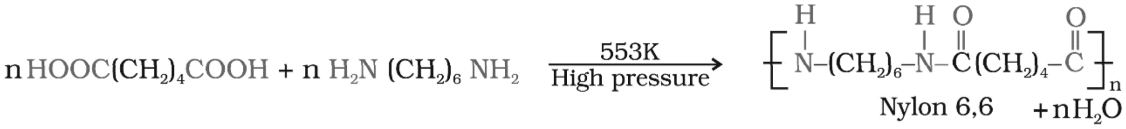
(i) Polyacrylonitrile is called as orlon or PAN



$$n\,CH_2 = CHCN \xrightarrow[\text{Peroxide catalyst}]{\text{Polymerisation}} \left[ CH_2 - \underset{}{\overset{CN}{\overset{|}{CH}}} \right]_n$$

(ii) It is used as a substitute of wool for making blankets.

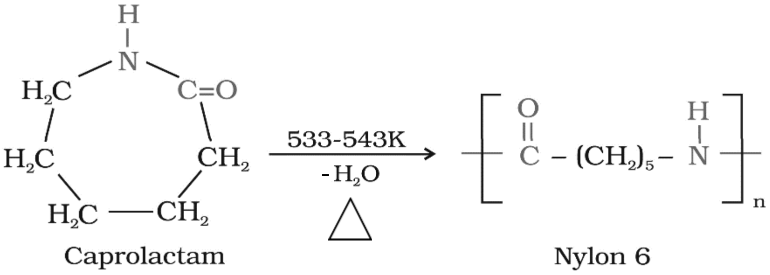
**24. How will you prepare Nylon (6, 6)?**



$$n\,HOOC(CH_2)_4COOH + n\,H_2N(CH_2)_6NH_2 \xrightarrow[\text{High pressure}]{553K} \left[ \overset{H}{\overset{|}{N}} - (CH_2)_6 - \overset{H}{\overset{|}{N}} - \overset{O}{\overset{\|}{C}}(CH_2)_4 - \overset{O}{\overset{\|}{C}} \right]_n + nH_2O$$

**25. How will you convert caprolactam into Nylon – 6?**

It is used in the manufacture of tyre cords, fabrics, etc.



**26. Write a notes on (a) Bakelite, (b) Melamine, (c) Urea formaldehyde polymer**

(a) Bakelite

(i) Phenol reacts with Methanal (HCHO) to form ortho or para hydroxyl methyl phenols which on further reaction with phenol gives linear polymer called Novolac.

(ii) Novolac on further heating with formaldehyde undergo cross linkages to form Bakelite.

(iii) Hard Bakelite are used to prepare combs, pens, etc…

(b) Melamine

(i) Melamine and formaldehyde undergo condensation polymerisation to form melamine formaldehyde resin.

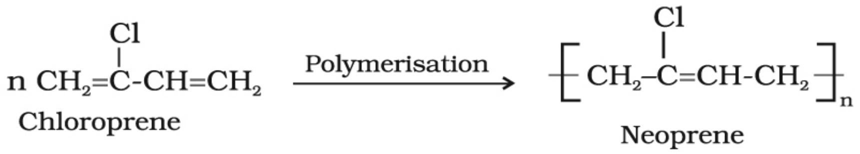
(c) Urea Formaldehyde

It is formed by the condensation polymerisation of the monomers urea and formaldehyde.

**27. What are synthetic rubbers? How will you prepare Neoprene? (SEPT-20)**

(i) Polymerisation of certain organic compounds such as buta-1,3 diene or its derivatives gives rubber like polymer with desirable properties like stretching to agreater extent etc such polymers are called synthetic rubbers.

(ii) Neoprene is used in the manufacture of chemical containers.



$$n\,CH_2{=}\overset{Cl}{\overset{|}{C}}{-}CH{=}CH_2 \xrightarrow{\text{Polymerisation}} \left[ CH_2{-}\overset{Cl}{\overset{|}{C}}{=}CH{-}CH_2 \right]_n$$

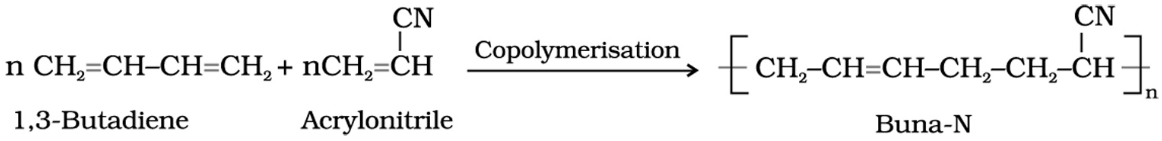
Chloroprene

Neoprene

2-Chloro-buta-1, 3-diene

**28. Write a notes on (i) Buna – N and (ii) Buna – S**

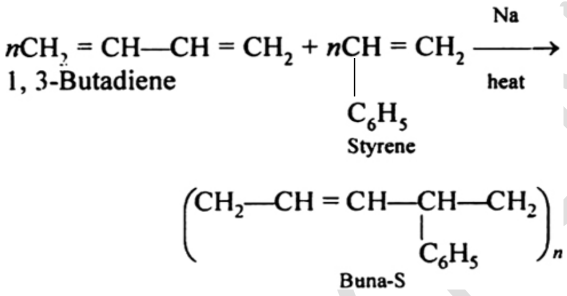
(i) Buna – N: It is used in the manufacture of hoses and tank linings.



$$n\,CH_2{=}CH{-}CH{=}CH_2 + nCH_2{=}\overset{CN}{\overset{|}{CH}} \xrightarrow{\text{Copolymerisation}} \left[ CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\overset{CN}{\overset{|}{CH}} \right]_n$$

1,3-Butadiene Acrylonitrile Buna-N

(ii) Buna – S

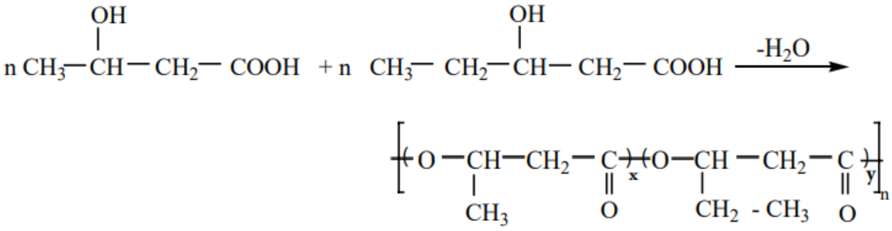


$$nCH_2 = CH{-}CH = CH_2 + n\underset{\underset{C_6H_5}{|}}{CH} = CH_2 \xrightarrow[\text{heat}]{\text{Na}} \left( CH_2{-}CH = CH{-}\underset{\underset{C_6H_5}{|}}{CH}{-}CH_2 \right)_n$$

1, 3-Butadiene Styrene Buna-S

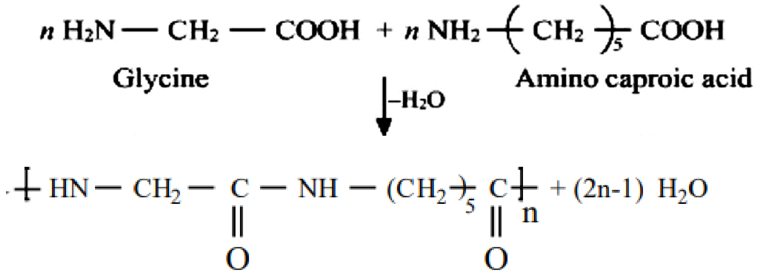
**29. What is PHBV? How will you prepare PHBV?**

Poly (3-hydroxy butyrate – co – 3 – hydroxy valerate) is called as PHBV. It is used in orthopaedic devices.



$$n\,CH_3{-}\overset{OH}{\overset{|}{CH}}{-}CH_2{-}COOH + n\ CH_3{-}CH_2{-}\overset{OH}{\overset{|}{CH}}{-}CH_2{-}COOH \xrightarrow{-H_2O} \left[ \left( O{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_2{-}\underset{\underset{O}{\|}}{C} \right)_x \left( O{-}\underset{\underset{CH_2-CH_3}{|}}{CH}{-}CH_2{-}\underset{\underset{O}{\|}}{C} \right)_y \right]_n$$

**30. How will you prepare Nylon – 2 – Nylon – 6?**



$$n\,H_2N-CH_2-COOH + n\,NH_2\text{-}(CH_2)_5\text{-}COOH \xrightarrow{-H_2O} \left[ HN-CH_2-\underset{\underset{O}{\|}}{C}-NH-(CH_2)_5-\underset{\underset{O}{\|}}{C} \right]_n + (2n-1)\,H_2O$$

Nylon -2-nylon - 6

**31. How do you classify the following into various class of drugs? (JULY-2020)**

**(A) Milk of Magnesia** **(B) Aspirin**
**(C) Penicillin** **(D) Procaine**

| | |
|---|---|
| (A) Milk of Magnesia | Antacids |
| (B)Aspirin | Analgesics |
| (C)Penicillin | Antimicrobials |
| (D)Procaine | Anesthetics |