SAIVEERA ACADEMY
CENTUM GUIDE

UNIT - 1

METALLURGY

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- Easy To Read
- Important Questions For Every Chapters
- Public Examination Key Based Answers
- Public Examination Based Additional Questions
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SAIVEERA ACADEMY

REVOLUTION FOR LEARNING

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UNIT –1 METALLURGY

Important Question

Short Answers	
Book Back	**Book Inside**
1.What is the difference between minerals and ores? **May 22** 2.What are the various steps involved in extraction of pure metals from their ores? 3.What is the role of Limestone in the extraction of Iron from its oxide Fe_2O_3? **Sep 20** 4.Which type of ores can be concentrated by froth floatation method? Give two examples for such ores. **Sep 20,Mar 23** 5. Explain the following terms with suitable examples. i) Gangue ii) Slag 6. Give the basic requirement for vapour phase refining. 7.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. 8. Give the limitations of Ellingham diagram.	1.Explain auto reduction of metallic ores or give some example for the ore which does not need any reducing agent 2.What do you meant by cementation? 3.Acid leaching with example **Jul 22** 4.Write the differences between roasting and calcination 5. What is blister copper? How it is obtained?
Long Answers	
1.Describe a method for refining nickel / mond process **May 22** 2. Explain zone refining process **Mar 20,Mar 23** 3.Explain the electrometallurgy of aluminium(Hall Herald Process) 4. Explain the principle of electrolytic refining with an example **Jul 22**	1.Explain froth floatation method 2. Gravity separation **May 22** 3. Explain about Van-Arkel method for refining zirconium/titanium 4. Explain aluminothermite process 5.Application of zinc , copper, gold , aluminium , silver

Points To Remember

- **Ore:** Minerals that contains a high percentage of metal, from which it can be extracted conveniently and economically are called ores.
- **Gangue:** Ores are associated with non-metallic impurities, rocky materials and siliceous matter which are collectively known as gangue.
- **Metallurgical processes consists of**
    1. Concentration of the ore
    2. Extraction of crude metal

- **Ellingham diagram:** The graphical representation of variation of the standard Gibbs free energy of reaction for the formation of various metal oxides with temperature is called Ellingham diagram.

3.Refining of crude metal

1. Distillation
2. Liquation
3. Electrolytic refining
4. Zone Refining
5. Vapour phase method

- **Distillation:** In this method, the impure metal is heated to evaporate and the vapour are condensed to get pure metal
- **Liquation:** This method is employed to remove the impurities with high melting points from metals having relatively low melting points such as tin.
- **Electrolytic refining:** The crude metal is refined by electrolysis. It is carried out in an electrolytic cell containing aqueous solution of the salts of the metal of interest. The rods of impure metal are used as anode and thin strips of pure metal are used as cathode.
- **Zone Refining :**This method is based on the principles of fractional crystallisation. When an impure metal is melted and allowed to solidify, the impurities will prefer to be in the molten region
- **Vapour phase method** : In this method, the metal is treated with a suitable reagent which can form a volatile compound with the metal. Then the volatile compound is decomposed to give the pure metal.

Uses

Aluminium(Al)	Zinc(Zn)	Iron(Fe)	Copper(Cu)	Gold (Au)
1.wraps 2.packing materials for food items chemical reactors, 3.Medical equipments, 4.refrigeration units gas pipelines.	1.produce die-castings in the automobile, electrical and hardware industries. 2.**Zinc oxide** - paints, rubber, cosmetics Zinc sulphide luminous paints	1.**Cast iron** pipes, valves and pumps stoves 2.**alloy of iron** stainless steel cutlery, surgical instruments	1.making coins and ornaments 2.making wires, water pipes and other electrical parts	1.Gold nanoparticles increasing the efficiency of solar cells and also used as catalysts. used extensively 2.in jewellery

Notable Reactions

1.**Cyanide leaching:**

$$4Au(s) + 8CN^-(aq) + O_2(g) + 2H_2O(l) \rightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$$

2.**Alkali leaching:** $Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$

3.**Acid leaching:** $2ZnS(s) + 2H_2SO_4(aq) + O_2(g) \rightarrow 2ZnSO_4(aq) + 2S(s) + H_2O(aq)$

4. $2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2 \uparrow$

5. $4As + 3O_2 \rightarrow 2As_2O_3 \uparrow$

6. $S_8 + 8O_2 \rightarrow 8SO_2 \uparrow$

7. $P_4 + 5O_2 \rightarrow P_4O_{10} \uparrow$

a) ΔG_f^o of sulphide is greater than those for CS_2 and H_2S .

b) ΔG_r^o is negative for roasting of sulphide ore to oxide

c) Roasting of the sulphide to its oxide is thermodynamically feasible.

d) Carbon and hydrogen are suitable reducing agents for metal sulphides

Ans. d) Carbon and hydrogen are suitable reducing agents for metal sulphides

7.Match items in column - I with the items of column – II and assign the correct code

Column – I		**Column - 2**	
A	Cyanide process	(i)	Ultrapure Ge
B	Froth flotation process	(ii)	Dressing of ZnS
C	Electrolytic refining	(iii)	Extraction of Al
D	Zone refining	(iv)	Extraction of Au
		(v)	Purification of Ni

	A	B	C	D
a)	(i)	(ii)	(iii)	(iv)
b)	(iii)	(iv)	(v)	(i)
c)	(iv)	(ii)	(iii)	(i)
d)	(ii)	(iii)	(i)	(v)

Ans. c) A – (iv) , B – (ii) , C – (iii) , D – (i)

8. Wolframite ore is separated from tinstone by the process of

a) Smelting b) Calcination

c) Roasting d) Electromagnetic separation

Ans. d) Electromagnetic separation

9. Which one of the following is not feasible

a) $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$

b) $Cu(s) + Zn^{2+}(aq) \rightarrow Zn(s) + Cu^{2+}(aq)$

c) $Cu(s) + 2Ag^{+}(aq) \rightarrow Ag(s) + Cu^{2+}(aq)$

d) $Fe(s) + Cu^{2+}aq) \rightarrow Cu(s) + Fe^{2+}(aq)$

Ans. b) $Cu(s) + Zn^{2+}(aq) \rightarrow Zn(s) + Cu^{2+}(aq)$

10. Electrochemical process is used to extract

a) Iron b) Lead c) Sodium d) silver

Ans. c) Sodium

11. Flux is a substance which is used to convert

a) Pure copper b) Impure copper c) Carbon rod d) Platinum electrode

Ans. b) Impure copper

21.Which of the following plot gives Ellingham diagram

a) ΔS Vs T b) ΔG° Vs T c) ΔG° Vs $\frac{1}{T}$ d) ΔG° Vs T^2

Ans. b) ΔG° Vs T

22. In the Ellingham diagram, for the formation of carbon monoxide

a) $\left(\frac{\Delta S^\circ}{\Delta T}\right)$ is negative

b $\left(\frac{\Delta G^\circ}{\Delta T}\right)$ is positive

c) $\left(\frac{\Delta G^\circ}{\Delta T}\right)$ is negative

d) initially $\left(\frac{\Delta T}{\Delta G^\circ}\right)$ is positive, after 700°C , $\left(\frac{\Delta G^\circ}{\Delta T}\right)$ is negative

Ans. c) c) $\left(\frac{\Delta G^\circ}{\Delta T}\right)$ is negative

23.Which of the following reduction is not thermodynamically feasible?

a) $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$ b) $Al_2O_3 + 2Cr \rightarrow Cr_2O_3 + 2Al$

c) $3TiO_2 + 4Al \rightarrow 2\,Al_2O_3 + 3Ti$ d) none of these

Ans. b) $Al_2O_3 + 2Cr \rightarrow Cr_2O_3 + 2Al$

24.Which of the following is not true with respect to Ellingham diagram?

a) Free energy changes follow a straight line. Deviation occurs when there is a phase change.

b) The graph for the formation of CO_2 is a straight line almost parallel to free energy axis.

c) Negative slope of CO shows that it becomes more stable with increase in temperature.

d) Positive slope of metal oxides shows that their stabilities decrease with increase in temperature.

Ans. b) The graph for the formation of CO_2 is a straight line almost parallel to free energy axis.

Additional Questions

1.Which metal is used for extraction of Au and Ag and also for galvanization of iron object?

a)Mg b) Zn c) Cr d)Co

Ans. b) Zn

2.Which of the following is not a mineral of aluminium?

a) Bauxite b) Cryolite

c) China clay d) Malachite

Ans. d) Malachite

3.Name the process by which elements such as germanium ,silicon and galium are refined.

a) Vapour phase method b) Electrolytic refining

c) Zone refining d) Van–Arkel method.

Ans. c) Zone refining

Ans. b) $CuCO_3Cu(OH)_2$

14.Zinc blende is

a)ZnS b) PbS c) Ag_2S d) Cu_2S

Ans. a)ZnS

15.In acid leaching process, the insoluble sulphide is converted into soluble sulphate and elemental

a) Carbon b) Lead c) Sulphur d) Zinc

Ans. c) Sulphur

16.Sulphide ore is converted to oxide form by using the process

a) Calcination b) Roasting c) Smelting d) Leaching

Ans. b) Roasting

17.Magnetic separation it is based on the difference in the _____of the ore and the impurities.

a) Magnetic properties b) Chemical properties

c) Physical properties d) Melting point .

Ans. a) Magnetic properties

18.Zinc is extracted from zinc blende by

a) Carbon reduction process b) Nitrogen reduction process

c) Oxygen reduction process d) All of these.

Ans. a) Carbon reduction process

19.Gibb's free energy is given by

a) $\Delta G^\circ = -nFE^\circ$ b) $\Delta G^\circ = nF$ c) $\Delta G^\circ = nFE^\circ$ d) $\Delta E^\circ = -nFG^\circ$

Ans. a) $\Delta G^o = -nFE^o$

20.$Na[Ag(CN)_2]$ is

a) Sodium aurocyanide b) Sodium meta aluminate

c) Aluminosilicate d) Sodium dicyano argentate

Ans. d) Sodium dicyano argentate

21.Semi conductors are purified by method

a) Zone refining b) Electrolytic refining

c) Mond's process d) Bessemerisation

Ans. a) Zone refining

22.Magnesite is

a) magnesium oxide b) magnesium carbonate

c) magnesium sulphate d) magnesium chloride

Ans. b) magnesium carbonate

23.In the metallurgy of iron, limestone is added to coke which acts as a

a) reducing agent b) oxidizing agent c) slag d) Flux

Ans. d) Flux

a) suitable reducing agent
b) appropriate temperature
c) both (a) and (b)
d) oxidizing agent

Ans. c) both (a) and (b)

47.In Hall – Herold process calcium chloride helps to

a) increase the melting point
b) decrease the melting point
c) maintain the temperature
d) increase the boiling point

Ans. b) decrease the melting point

48. Cr_2O_3 can be reduced by

a) Aluminothermic process
b) Mond's process
c) Cyande process
d) hydrogen reduction

Ans. a) Aluminothermic process

49. Leaching process is a

a) reduction
b) dehydration
c) redox reaction
d) dehydrogenation

Ans. c) redox reaction

50. The complex formed when NaCN is added to galena in which ZnS is the impurity

a) $2Na[Zn(CN)_4]$
b) $Na_2[Zn(CN)_4]$
c) $2Zn[Zn(CN)_4]$
d) $Na_4[Zn(CN)_4]$

Ans. b) $Na_2[Zn(CN)_4]$

51. In the froth floatation process for the purification of ores the particles that because

a) they are light
b) their surface is not easily wetted by water
c) they bear electrostatic charge
d) they are insoluble

Ans. b) their surface is not easily wetted by water

52. In a metallurgical process,an acid flux is used for removing

a) slag
b) basic flux
c) acidic gangue
d) basic gangue

Ans. d) basic gangue

53. Aluminium is extracted from alumina (Al_2O_3) by electrolysis of a molten mixture of

a) $Al_2O_3 + KF + Na_3AlF_6$
b) $Al_2O_3 + HF + NaAlF_4$
c) $Al_2O_3 + CaF_2 + NaAlF_4$
d) $Al_2O_3 + Na_3AlF_6 + CaF_2$

Ans. d) $Al_2O_3 + Na_3AlF_6 + CaF_2$

54. Oxide ores are concentrated by

a) roasting
b) hydraulic washing
c) froth floatation
d) magnetic separation process

Ans. b) hydraulic washing

55. Froth flotation process is to concentrate

a) oxide ores
b) carbonate ores
c) chloride ores
d) sulphide ores

Ans. d) sulphide ores

Textual Questions

1.What is the difference between minerals and ores?

Minerals	Ores
Metal of interest present in small amount	Metal of interest present in high amount
All minerals are not ores	All ores are minerals
Ex : Clay – Mineral of aluminium	**Ex :** Bauxite – Ore of aluminium

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

1) Concentration of the ore.
2) Extraction of the crude metal.
3) Refining of the crude metal.

3. What is the role of Limestone in the extraction of Iron from its oxide Fe_2O_3?

In the extraction of iron , a basic flux limestone is used which decomposes to form CaO which reacts with silica gangue present in the iron ore is acidic in nature to form calcium silicate (slag)

$CaCO_3 \longrightarrow CaO + CO_2$

$CaO\ (s) + SiO_2\ (s) \longrightarrow CaSiO_3\ (s)$

Flux Gangue slag

4.Which type of ores can be concentrated by froth floatation method? Give two examples for such ores.

Sulphide ores can be concentrated by froth floatation method.

Example: Galena (PbS), Zinc blende (ZnS)

5. Describe a method for refining nickel.

- ✓ **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.

  $Ni(s) + 4CO(g) \longrightarrow NiCO_4(g)$

- ✓ On heating **nickel tetra carbonyl** around **460K**, the complex decomposes to give **pure nickel**.

  $Ni(CO)_4(g) \longrightarrow Ni(s) + 4CO(g)$

6. Explain zone refining process with an example

1) The principle used in this process is **fractional crystallisation**.
2) 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.
3) 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.
4) As the heater moves further away, the molten zone containing impurities also moves along with it.
5) This process is repeated several times by moving the heater in the same direction again and again to achieve the desired purity level.
6) This process is carried out in an inert gas atmosphere to prevent the oxidation of metals.
7) **Germanium, Silicon and gallium** which are used as semiconductor are refined by this process.

ii) Slag

Slag is a fusible chemical substance formed by the reaction of gangue with a flux.

In the extraction of iron , a basic flux limestone is used which decomposes to form CaO which reacts with silica gangue present in the iron ore is acidic in nature to form calcium silicate (slag)

11.Give the basic requirement for vapour phase refining.

- ✓ The metal should form a volatile compound ,when treated with a suitable reagent
- ✓ Then the volatile compound should decomposed to give the pure metal.

12. 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 $FeSiO_3$.

$FeO + SiO_2(s) \longrightarrow FeSiO_3$

Flux **Slag**

ii) Cryolite serves as an added impurity and lowers the melting point of the Al_2O_3 .

iii) First Iodine forms a Volatile tetraiodide with impure metal, which decomposes to give pure metal. 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.

iv) Sodium cyanide acts as a depressing agent in froth floatation process. When a sulphide ore of a metal of interest contains other metal sulphides the depressing agent sodium cyanide selectively prevent other metal sulphides from coming to the froth.

13. Explain the principle of electrolytic refining with an example.

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

Electro refining of silver

1) **Cathode :** Pure silver
2) **Anode :** Impure silver rods.
3) **Electrolyte :** Acidified aqueous solution of silver nitrate.
4) On passing current the following reactions will take place.
5) **Reaction at anode :** $Ag\,(s) \longrightarrow Ag^+\,(aq) + 1e^-$
6) **Reaction at cathode :** $Ag^+\,(aq) + 1e^- \longrightarrow Ag$
7) During electrolysis, at the anode the silver atoms lose electrons and enter the solution. The positively charged silver cations migrate towards the cathode and get discharged by gaining electrons and deposited on the cathode.
8) Less electro positive impurities in the anode settle down as anode mud.

14. 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 reactionΔG 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.

For example

1) Above 1623 K, Al has more negative ΔG^{o} value than Mg
2) Hence Al is used to reduce magnesia
3) Below 1623 K , Mg more negative ΔG^{o} value than Al
4) Hence Mg is used to reduce Al

15. Give the limitations of Ellingham diagram.

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

16. Write a short note on electrochemical principles of metallurgy.

1) Reduction of oxides of active metals such as sodium, potassium etc. by carbon is thermodynamically not feasible.
2) Such metals are extracted from their ores by using electrochemical methods.
3) In this method the metal salts are taken in fused form or in solution form.
4) The metal ion present can be reduced by treating the solution with suitable reducing agent or by electrolysis.
5) Gibbs free energy change for the electrolysis is $\Delta G^{\circ} = -nFE^{\circ}$
   n = number of electrons involved in the reduction
   F = Faraday = 96500 coulombs
   E°= electrode potential of the redox couple.
6) If E° is positive, ΔG° is negative and the reduction is spontaneous.
7) Hence a redox reaction is planned in such a way that the e.m.f of the net redox reaction is positive.
8) A more reactive metal displaces a less reactive metal from its salt solution.Zinc is more reactive than copper and displaces copper from its salt solution.

$$Cu(s) + 2Ag^{+}(s) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$
$$Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

Additional Questions – Short 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?

10.Which method is used to refine volatile metals? Explain it

- ✓ Distillation method is employed for low boiling volatile metals like zinc (boiling point 1180 K) and mercury (630 K).
- ✓ In this method, the impure metal is heated to evaporate and the vapours are condensed to get pure metal.

11. Explain liquation with suitable example (or) How will refine the metals having low boiling liquid ?

1. This method, is employed to remove the impurities with high melting points from metals having relatively low melting points such as tin (Sb, lead , mercury , and bismuth .
2. In this process, the crude metal is heated to form fusible liquid and allowed to flow on a sloping surface.
3. 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 pure metal flows down and the impurities are left behind.
4. The molten metal is collected and solidified.

12.What do you meant by cementation?

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

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

13.Explain Cyanide leaching

In the concentration of gold ore, the crushed ore of gold is leached with aerated dilute solution of sodium cyanide. Gold is converted into a soluble cyanide complex. The gangue, aluminosilicate remains insoluble.

$$4Au\,(s) + 8CN^-\,(aq) + O_2\,(g) + 2H_2O\,(l) \longrightarrow 4[Au(CN)_2]^-\,(aq) + 4OH^-(aq)$$

14. What is Acid leaching

Leaching of sulphide ores such as ZnS, PbS etc., can be done by treating them with hot aqueous sulphuric acid.

$$2ZnS\,(s) + 2H_2SO_4\,(aq) + O_2(g) \longrightarrow 2ZnSO_4\,(aq) + 2S\,(s) + H_2O$$

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

15. ZnO can be reduced to the metal by heating with carbon but not Cr_2O_3.Jusitify your answer

Carbon has more affinity for oxygen than zinc , whereas chromium has higher affinity for oxygen than zinc.Hence ZnO can be reduced to the metal by heating with carbon but not Cr_2O_3

16.Write the differences between roasting and calcination

Roasting	Calcination
In this concentrated ore is oxidised by heating it with excess of oxygen in a suitable furnace below the melting point of the metal.	It is the process in which the concentrated ore is strongly heated in the absence of air or limited supply of air below the melting point of the metal
It is used for concentrating sulphide ores	It is used for concentrating carbonate ores
During this process SO_2 is released	During this process CO_2 is released

17.What is smelting?

It is a process of reducing the roasted metallic oxide to metal in molten condition .In this process , impurities are removed by addition of flux as slag and reducing agent is added.

18.List out the common refining methods

1. Distillation
2. Liquation
3. Electrolytic refining
4. Zone refining
5. Vapour phase method

19.What is blister copper? How it is obtained?

- ✓ It is an impure copper.
- ✓ In Bessemerization process, the metallic copper is solidified and it has blistered appearance due to evolution of SO_2 gas formed in this process. This copper is called blistered copper.

20. Sulphide and carbonate ores are converted to oxide before reduction. Why?

Since the reduction of oxide ores involves a decrease in Gibb's free energy making ΔG value more negative, it is easier to reduce oxides therefore suphide and carbonate ores are converted to oxides before reduction.

21. What are Ellingham diagrams?

Ellingham diagrams are graphical representation of variation of ΔG vs T for the formation of oxides of elements

22. Give two examples of metal refined by a) Distillation b) Liquation c) Electrolytic refining

a) Distillation – Zinc and Mercury
b) Liquation – Tin and Antimony
c) Electrolytic refining – Copper and Zinc

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

1. Conversion of metal into metal oxide
2. Reduction of metal oxide into metal

24.Name the collector and depressing agent used in Froth Flotation Process

Sodium Ethyl Xanthate and Sodium Cyanide

25.How to choose the best reducing agent?

It is selected in such a way that it provides a large negative ΔG values

Additional Questions - Long answers

1. Explain froth floatation method.

1. This is used to **concentrate sulphide ores** such as galena (PbS) Zinc blende (ZnS) etc.
2. Metallic ore particles preferentially wetted by oil can be separated from gangue.
3. Crushed ore is mixed with water and a frothing agent like pine oil or eucalyptus oil.

5. The volatile titanium tetraiodide vapour is passed over a tungsten filament at a temperature aroud 1800 K.
6. The titanium tetraiodide is decomposed and pure titanium is deposited on the filament. The iodine is reused. $TiI_4 \xrightarrow[\Delta]{1800K} Ti\,(s) + 2I_2$

5.Give the Application of Al

- ✓ Many heat exchangers/sinks and cooking vessels are made of aluminium.
- ✓ It is used as wraps (aluminium foils) and is used in packing materials for food items,
- ✓ Its alloys with copper, manganese, magnesium and silicon are used in design of aeroplanes and other forms of transport.
- ✓ It is used in the design of chemical reactors, medical equipments ,refrigeration units and gas pipelines.
- ✓ It is used in electrical overhead electric cables with steel core for strength.

6.Explain about alkali leaching [OR]

How will you get pure alumina from impure alumina using leaching ? [OR]

What is the significance of leaching in the extraction of aluminium?

- ✓ In this method, the ore is treated with aqueous alkali to form a soluble complex.
- ✓ Bauxite, an important ore of aluminium is heated with a solution of sodium hydroxide or sodium carbonate in the temperature range 470 - 520 K at 35 atm to form soluble sodium meta-aluminate leaving behind the impurities, iron oxide and titanium oxide.

$$Al_2O_3\,(s) + 2NaOH\,(aq) + 3H_2O\,(l) \longrightarrow 2Na[Al(OH)_4]\,(aq)$$

- ✓ The hot solution is decanted, cooled, and diluted. This solution is neutralised by passing CO_2 gas, to the form hydrated Al_2O_3 precipitate.

$$2Na[Al(OH)_4]\,(aq) + 2CO_2\,(g) \longrightarrow Al_2O_3.xH_2O\,(s) + 2NaHCO_3\,(aq)$$

- ✓ The precipitate is filtered off and heated around 1670 K to get pure alumina Al_2O_3.

7.Explain about extraction of copper from copper pyrite

1. Ore is concentrated by froth flotation process
2. The concentrated ore is heated in a reverberatory furnace after mixing with silica, an acidic flux. The ferrous oxide formed due to melting is basic in nature and it combines with silica to form ferrous silicate (slag).
3. The remaining metal sulphides Cu_2S and FeS are mutually soluble and form a copper matte.

$2CuFeS_2\,(s) + O_2\,(g) \longrightarrow 2FeS\,(l) + 2Cu_2S\,(l) + 2SO_2\,(g)$

$FeS\,(l) + O\,(g) \longrightarrow FeO\,(l) + SO_2\,(g)$

$FeO\,(s) + SiO_2\,(s) \longrightarrow FeSiO_3\,(s)$

Flux Gangue Slag
4. The matte is separated from the slag and fed to the converting furnace. During conversion, the FeS present in the matte is first oxidised to FeO. This is removed by slag formation with silica. The remaining copper sulphide is further oxidised to its oxide which is subsequently converted to metallic copper as shown below.
5. The metallic copper is solidified and it has blistered appearance due to evolution of SO_2 gas formed in this process. This copper is called blistered copper.

$Cu_2S\,(l,s) + 3O_2\,(g) \longrightarrow 2Cu_2S\,(l,s) + 2SO_2\,(g)$

$2Cu_2O\,(l) + Cu_2S\,(l) \longrightarrow 6Cu\,(l) + SO_2\,(g)$

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1.Give any three characteristics of ionic crystals 2.Classify the following solids (*a*) P_4 (*b*) Brass (*c*) Diamond (*d*) NaCl (*e*) Iodine **Apr 21** 3. What is meant by the term "coordination number"? What is the coordination number of atoms in a bcc structure? **Apr 21,Mar 22**	1.Define isotropy and anisotropy **Sep20** 2.What are covalent solids? **Mar 22** 3.Define Unit cell,crystal lattice **Jul 22** (180) 4.Sketch FCC and find number of unit cell **PTA** 5.What is Braggs's equation**? PTA** 6.What is packing efficiency? **Jul 22 , PTA** **7.**If the radius of the compound is between $0.155 - 0.225$, find out the coordination number and structure **Jul 20** 8.Define F center with a neat diagram **PTA** 9. What is Piezoelectric crystals ? 10. Sketch bcc fcc sc **11.**Calculate the number of atoms in fcc **Mar 23**
Long Answers	
1**.** Differentiate crystalline solids and amorphous solids **Mar 22, PTA** 2**.** Calculate the percentage efficiency of packing in case of body centered cubic crystal **PTA** 3. Explain Schottky defect **Sep 20,Mar 23** 4. Write a note on Frenkel defect **Mar 20 , Jul 22** 5.Distinguish between hexagonal close packing and cubic close packing 6. Distinguish tetrahedral and octahedral voids 7. Write short note on metal excess and metal deficiency defect with an example	1.Calculate packing efficiency of fcc unit cell 2.Classification of point defects PTA 3.Explain about impurity defect

Points To Remember

- **Types of solids :** (i) Crystalline solids (ii)Amorphous solids.
- **Crystalline solid :** Solid in which its constituents (atoms, ions or molecules), have an orderly arrangement extending over a long range.
- **Amorphous solids :** In Greek, amorphous means no form , the constituents are randomly arranged.
- **Isotropy :** Having identical values of physical properties such as refractive index, electrical conductance etc., in all directions
- **Anisotropy :** Different values of physical properties when measured along different directions

- **ABCABAC arrangement:** Cubic Closely packed
- Radius ratio: Ratio of radius of cation to anion $\left(\frac{r_{C^+}}{r_{A^-}}\right)$

$\left(\frac{r_{C^+}}{r_{A^-}}\right)$	**Coordination number**	**Structure**	**Example**
0.155 – 0.225	3	Trigonal planar	B2O3
0.225 – 0.414	4	Tetrahedral	ZnS
0.414 – 0.732	6	Octahedral	NaCl
0.732 – 1.0	8	Cubic	CsCl

- **Crystal defects classification**
  1) Point defect
  2) Line defect
  3) Interstitial defect
  4) Volume defect

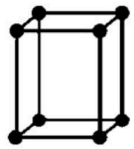
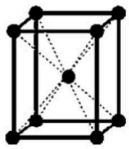
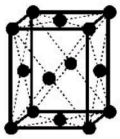
- **Schottky defect :** Missing of equal number of cations and anions from the crystal lattice. **Example:** NaCl
- **Frenkel defect** : Dislocation of ions from its crystal lattice. The ion which is missing from the lattice point occupies an interstitial position. **Example:** AgBr
- **Metal excess defect :** Presence of more number of metal ions as compared to anions. **Example:** ZnO
- **Metal deficiency defect** : Presence of less number of cations than the anions. **Example:** FeO
- **Impurity defect** : Adding impurity ions which are in different valance state from that of host, vacancies are created in the crystal lattice of the host. **Example:** $CdCl_2$

Unit Cell	**Packing Fraction**	**Vacancy percentage**
Simple cubic	52.38 %	47.62
Body centered cubic	68 %	32
Face centered cubic	74 %	26

Seven Primitive crystal systems

Unit cell	Edge length	Interfacial angles
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°, \beta \neq 90$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$

Cubic Unit cell

Simple cubic unit cell (SC)	**Body centered cubic unit cell(BCC)**	**Face centered cubic unit cell (FCC)**
		
Number of atoms in SC $= \frac{N_c}{8} = \frac{8}{8} = 1$	Number of unit cell in bcc $= \frac{N_c}{8} + \frac{N_b}{1} = \frac{8}{8} + \frac{1}{1} = 2$	Number of unit cell in fcc $= \frac{N_c}{8} + \frac{N_f}{2} = \frac{8}{8} + \frac{6}{2} = 4$
Radius $r = \frac{a}{2}$	Radius $r = \sqrt{2}a$	Radius $r = \frac{\sqrt{3}}{4}a$

Textual Questions

1. Graphite and diamond are

a) Covalent and molecular crystals b) ionic and covalent crystals

c) both covalent crystals d) both molecular crystals

Ans : c) both covalent crystals

2. An ionic compound A_xB_y crystallizes in fcc type crystal structure with B ions at the centre of each face and A ion occupying entre of the cube. the correct formula of A_xB_y is

a) AB b) AB_3 c) A_3B d) A_8B_6

Ans : b) AB_3

3. The ratio of close packed atoms to tetrahedral hole in cubic packing is

a) 1:1 b) 1:2 c) 2:1 d) 1:4

Ans : b) 1:2

4. Solid CO_2 is an example of

a) Covalent solid b) metallic solid c) molecular solid d) ionic solid

Ans : c) molecular solid

5. Assertion : monoclinic sulphur is an example of monoclinic crystal system

Reason: for a monoclinic system, a $\neq$ b $\neq$ c and $\alpha = \gamma = 90°, \beta \neq 0$

a) Both assertion and reason are true and reason is the correct explanation of assertion.

b) Both assertion and reason are true but reason is not the correct explanation of assertion.

c) Assertion is true but reason is false.

d) Both assertion and reason are false.

Ans : a) Both assertion and reason are true and reason is the correct explanation of assertion.

6. In calcium fluoride, having the flourite structure the coordination number of Ca^{2+} ion and F^- ion are

a) 4 and 2 b) 6 and 6 c) 8 and 4 d) 4 and 8

Ans : c) 8 and 4

7. The number of unit cells in 8 gm of an element X (atomic mass 40) which crystallizes in bcc pattern is (N_A is the Avogadro number)

a) 6.023×10^{23} b) 6.023×10^{22} c) 60.23×10^{23} d) $\left(\frac{6.023 \times 10^{23}}{8 \times 40}\right)$

Ans : b) 6.023×10^{23}

8. In a solid atom M occupies ccp lattice and $\left(\frac{1}{3}\right)$ of tetrahedral voids are occupied by atom N. find the formula of solid formed by M and N.

a) MN b) M_3N c) MN_3 d) M_3N_2

Ans : d) M_3N_2

9.The ionic radii of A^+ and B^- are 0.98×10^{-10} m and 1.81×10^{-10}m. the coordination number of each ion in AB is

a) 8 b) 2 c) 6 d) 4

Ans : c) 6

10.CsCl has bcc arrangement, its unit cell edge length is 400pm, its inter atomic distance is

a) 400pm b) 800pm c) $\sqrt{3} \times 100$pm d) $\left(\frac{\sqrt{3}}{2}\right) \times 400$pm

Ans : d) $\left(\frac{\sqrt{3}}{2}\right) \times 400$pm

11. A solid compound XY has NaCl structure. if the radius of the cation is 100pm , the radius of the anion will be

a) $\left(\frac{100}{0.414}\right)$ b) $\left(\frac{0.732}{100}\right)$ c) 100×0.414 d) $\left(\frac{0.414}{100}\right)$

Ans : a) $\left(\frac{100}{0.414}\right)$

12. The vacant space in bcc lattice unit cell is

a) 48% b) 23% c) 32% d) 26%

a) Schottky defect b) F center

c) Frenkel defect d) non-stoichiometric defect

Ans : c) Frenkel defect

21. Assertion: due to Frenkel defect, density of the crystalline solid decreases.

Reason : in Frenkel defect cation and anion leaves the crystal.

a) Both assertion and reason are true and reason is the correct explanation of assertion.

b) Both assertion and reason are true but reason is not the correct explanation of assertion.

c) Assertion is true but reason is false.

d) Both assertion and reason are false

d) Both assertion and reason are false

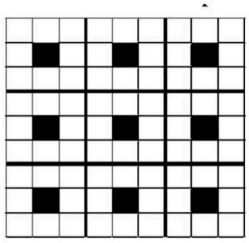
Ans : d) Both assertion and reason are false

22. The crystal with a metal deficiency defect is

a) NaCl b) FeO c) ZnO d) KCl

Ans : b) FeO

23. A two dimensional solid pattern formed by two different atoms X and Y is shown below. The black and white squares represent atoms X and Y respectively. the simplest formula for the compound based on the unit cell from the pattern is



a) XY_8 b) X_4Y_9

c) XY_2 d) XY_4

Ans : a) XY_8

Additional Questions

1.An example for metal deficiency defect is

a) NaCl b) AgCl c) FeO d) CsCl

Ans : c) FeO

2. An ion leaves its regular site and occupies a position in the space between the lattice sites. This defect is called as

a) Schottky defect b) Frenkel defect c) impurity defect d) vacancy defect

Ans : b) Frenkel defect

3. In a simple cubic cell, each point on a corner is shared by

a) one unit cell b) two unit cells c) eight unit cells d) four unit cells

Ans : c) eight unit cells

4.In Bragg's equation 'n' represent

a) number of moles b) Avogadro number

c) quantum number d) order of diffraction

Ans : d) order of diffraction

a)14 % b) 15% c)16% d)18%

Ans : a)14 %

17. Which one is Non Stoichiometric defect ;

a) Metal excess effect b) Frenkel defect

c) Metal deficiency defect d) Both a and c

Ans : d)Both a and c

18. Percentage of free space (vacant) in Simple cubic , Body centered , Face centered cubic unit cell (Cubic close packing) are

a) 47.69 % , 32 % , 26 % b) 47.69 % , 30 % , 26 %

c) 48.69 % , 32 % , 26 % d) 47.69 % , 32 % , 28 %

Ans : a) 47.69 % , 32 % , 26 %

19. In AAA type each sphere is arranged in contact with ---------- of its neighbours

a) six b) four c) two d) none of these

Ans : b)four

20.In ABAB… type each sphere is arranged in contact with ---------- of its neighbours

a)six b)four c) two d)none of these

Ans : a)six

21.Three atoms P , Q , R crystallize in a cubic solid lattice having P atoms at corners , Q atom at body centre , R atom at face centre .Identify the formula of the compound

a) PQR b) PQR_2 c) PQ_2R d) PQR_3

Ans : d) PQR_3

22.The general formula of an ionic compound which crystallines in body-centred cubic structure is

a) AB b) AB_2 c) A_2B d) AB_3

Ans: a) AB

23.What is the arrangements of layers in a cubic close packing of spheres?

a) AB AB AB… b) ABC ABC ABC…

c) AAAAA… d) None of these

Ans : a) AB AB AB…

24. What is the arrangements of layers in a hexagonal close packing of atom?

a) AB AB AB… b) ABC ABC ABC… c) AAAAA… d) None of these

Ans : b) ABC ABC ABC…

24. If $\left(\frac{r_C^+}{r_A^-}\right)$ is 0.225 – 0.414, the coordination number is

a) 3 b) 4 c) 6 d) 8

Ans : b) 4

25. In which crystal system $a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$

a) tetragonal b) orthorhombic c) rhombohedral d) hexagonal

36. Which one of the following is a covalent crystal?

a) Glass b) Diamond c) Anthracene d) Glucose

Ans : b) Diamond

37. Molecular solids contains neutral molecules held together by

a) strong cohesive forces b) weak vanderwals forces

c) weak ionic forces d) strong electrostatic forces

Ans : b) weak vanderwals forces

35. Silicon carbide is an example of

a) ionic solid b) covalent solid

c) polar molecular solid d) non – polar molecular solid

Ans : b) covalent solid

36. Solid NH_3 solid CO_2 are examples of

a) covalent solids b) polar molecular solids

c) molecular solids d) ionic solids

Ans : c) molecular solids

37. Each atom in the corner of the cubic unit cell is shared by how many unit cell?

a) 8 b) 6 c) 1 d) 12

Ans : a) 8

38.Which one of the following metal shows non – stoichiometric defect?

a) FeO b) AgBr c) ZnO d) Both a and c

Ans : d) Both a and c

39. Which is the coordination number of each atom in a simple cubic unit cell?

a) 8 b) 6 c) 12 d) 4

Ans : b) 6

40. The number of atoms belongs to bcc unit cell is

a) 2 b) 4 c) 6 d) 12

Ans : a) 2

41. The number of atoms belongs to fcc unit cell is

a) 2 b) 4 c) 6 d) 8

Ans : b) 4

42. The atoms the face centre is being shared by _____ unit cells.

a) 4 b) 8 c) 2 d) 6

Ans : c) 2

43. The coordination number of zinc sulphide is

a) 3 b) 4 c) 6 d) 8

Ans : b) 4

44. The coordination number of CsCl is

a) 3 b) 4 c) 6 d) 8

Ans : d) 8

45. Metal excess defect is possible in

a) AgCl b) AgBr c) KCl d) FeS

Ans : c) KCl

Textual Questions

1.Define unit cell.

- ✓ A basic repeating structural unit of a crystalline solid in a threedimensional pattern is called a unit cell.
- ✓ A unit cell is characterised by the three edge lengths or lattice constants a ,b and c and the angle between the edges α, β and γ

2. Give any three characteristics of ionic crystals

1) They have high melting points.
2) They does not conduct electricity, because the ions are fixed in their lattice positions.
3) They conduct electricity in molten state (or) when dissolved in water because, the ions are free to move in the molten state or solution.
4) They are hard as only strong external force can change the relative positions of ions.

3. Differentiate crystalline solids and amorphous solids

Crystalline Solids	Amorphous solids
Long range orderly arrangement of constituents.	Short range, random arrangement of constituents.
Definite shape	Irregular shape
Anisotropic in nature	Isotropic in nature
They are true solids	They are considered as pseudo solids (or) super cooled liquids
Definite Heat of fusion	Heat of fusion is not definite
They have sharp melting points.	Gradually soften over a range of temperature and so can be moulded
Examples: NaCl , diamond,	**Examples:** Plastics, glass

4. Classify the following solids

(*a*) P_4 (*b*) Brass (*c*) Diamond (*d*) NaCl (*e*) Iodine

(*a*) P_4 - Molecular solid

(*b*) Brass – Metallic solid

(*c*) Diamond – Covalent solid

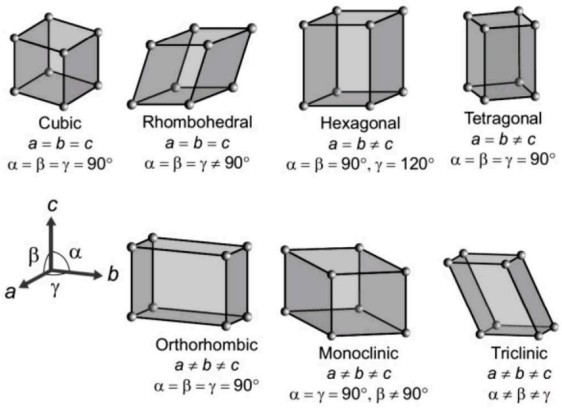
(*d*) NaCl – Ionic solid

(*e*) Iodine – Molecular solid

5. Explain briefly seven types of unit cell.

There are seven primitive crystal systems

1) Cubic
2) Tetragonal
3) Orthorhombic
4) Hexagonal
5) Monoclinic
6) Triclinic
7) Rhombohedral



6.Distinguish between hexagonal close packing and cubic close packing

Hexagonal Close packing	Cubic Close packing
'ABA' arrangement	'ABC' arrangement
The spheres of the third layer is exactly aligned as first layer	The spheres of the third layer is not aligned with those of either the first or second layer.
The unit cell of hexagonal close packing has 6 spheres.	The unit cell of cubic close packing has 4 spheres
Tetrahedral voids of the second layer are covered by the sphere of the third layer	Octahedral voids of the second layer are covered by the sphere of the third layer

7.Distinguish tetrahedral and octahedral voids.

Tetrahedral Void	Octahedral Void
When a sphere of second layer (b) is above the void (x) of the first layer (a), tetrahedral void is formed.	When the voids (y) in the first layer (a) are partially covered by the spheres of layer (b), octahedral void (a)
number of tetrahedral voids generated is equal to 2n.	number of octahedral voids generated is equal to n
This constitutes four spheres, three on the lower (a) and one in the upper layer (b).	This constitutes six spheres the lower layer (a) and three in the upper layer (b)
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.
The coordination number is 4.	The coordination number is **6.**

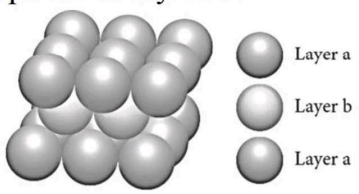
8. What are point defects?

- ✓ If the deviation in the perfect crystal occurs due to missing atoms , displaced atoms or extra atoms the imperfection is called as point defect.
- ✓ It occurs due to imperfect packing during the original crystallisation or they may arise from thermal vibrations of atoms at elevated temperature.

Types: Stoichiometric, Non stoichiometric , Impurity defect

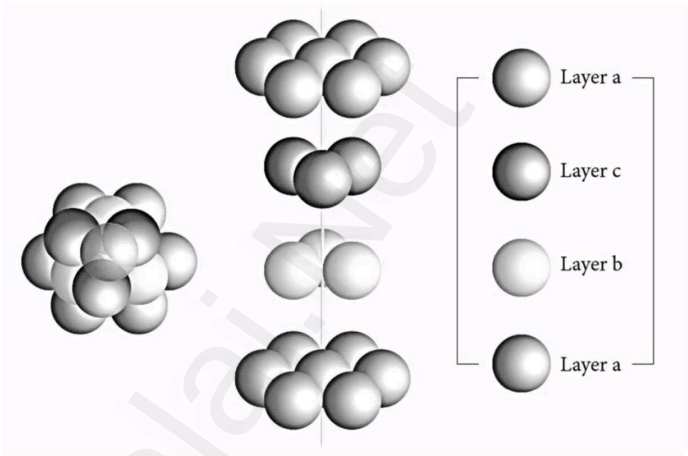
(ii) ABAB.. Type

- ✓ In this arrangement, the spheres in the first layer (A type) are slightly separated and the second layer is formed by arranging the spheres in the depressions between the spheres in layer A .
- ✓ The third layer is a repeat of the first.
- ✓ This pattern ABABAB is repeated throughout the crystal.
- ✓ In this arrangement, each sphere has a coordination number of 8, four neighbors in the layer above and four in the layer below.



Body Certered Cubic (BCC)

(iii) ABCABC type arrangement



- ✓ In this arrangement, the first layer is formed by arranging the spheres as in the case of two dimensional ABAB arrangements.
- ✓ The spheres of second row fit into the depression of first row. This is layer 'a'.
- ✓ The second layer is formed by placing the spheres in the depressions of the first layer. This is layer 'b'.
- ✓ There are two types of voids x and y.
- ✓ Wherever a sphere of second layer (b) is above the void (x) of the first layer (a), a tetrahedral void is formed. This constitutes four spheres – three in the lower (a) and one in the upper layer (b). When the centers of these four spheres are joined, a tetrahedron is formed.
- ✓ At the same time, the voids (y) in the first layer (a) are partially covered by the spheres of layer (b), now such a void in (a) is called a octahedral void.
- ✓ The third layer may be 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), and hence, the third layer is designated (c). If the stacking of layers is continued in abcabcabc… pattern, then the arrangement is called cubic close packed (ccp) structure.
- ✓ In ccp arrangements, the coordination number of each sphere is 12 – six neighbouring spheres in its own layer, three spheres in the layer above and three sphere in the layer below.

13.Why ionic crystals are hard and brittle?

- ✓ Only strong forces can change the relative position of its constituent ions, so they are hard
- ✓ In ionic compounds the ions are rigidly held in a lattice because the positive and negative ions are strongly attracted to each other and difficult to separate.
- ✓ But the brittleness of a compound is how easy it is to shift the position of atoms or ions in a lattice

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

The spheres are touching along the leading diagonal of the cube

In ΔABC

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

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

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

% of Ni in Ni^{2+} = 91.66%

Fraction of Ni^{3+} = (atom of Ni^{3+} / total number of atoms of Ni)

$= \left(\left(\frac{0.08}{0.96}\right)\right)$

= 0.083

% of Ni in Ni^{3+} = 8.33%

17. What is meant by the term "coordination number"? What is the coordination number of atoms in a bcc structure?

- ✓ The number of nearest neighbour that surrounding a particle in a crystal is called coordination number.
- ✓ The coordination number of atoms in a bcc structure is 8.

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

let 'a' is the edge of the cube and 'r' is the radius of atom.

Given : r = 125 pm

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

Sub the **value of 'r'** we get,

$a = 2 \times 1.414 \times 125$ pm

= 354 pm (approximately)

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

Given : Concentration of $SrCl_2 = 10^{-2}$mole %

Concentration is in percentage so that take total 100 mole of solution

Number of moles of NaCl =100 – moles of $SrCl_2$

Moles of $SrCl_2$ is very negligible as compare to total moles.

Number of moles of NaCl = 100

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

$= 10^{-4}$mole of $SrCl_2$

cation vacancies per mole of NaCl = 10^{-4}mole

1 mole = 6.023×10^{23} particles

So, cation vacancies per mole of NaCl $= 10^{-4} \times 6.023 \times 10^{23}$

$= 6.023 \times 10^{19}$vacancies

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})

Given : $\rho = 2.48$ g cm^{-3}

Since it is face centered , number of unit cell = 4 , Molar mass of KF = 58.8

$a^3 = \frac{nM}{\rho N_A}$

$= \frac{4 \times 58.8}{2.48 \times 6.023 \times 10^{23}}$

$a^3 = 1.57 \times 10^{-22}$ cm^3

Edge length $= (a)$ = 538 pm

$d = \frac{a}{\sqrt{2}}$

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 : a = 352.4 pm , n = 4 (face centered cubic) , $\rho = 8.9 gcm^{-3}$, $N_A = 6.023 \times 10^{23}$

$$M = \frac{\rho a^3 N_A}{n}$$

$$= \frac{8.9 \times (352.4 \times 10^{-12})^3 \times 6.023 \times 10^{23}}{4}$$

$$= 586.47 \times 10^{-1} = 58.65 g$$

58.65 g of the element contains 6.023×10^{23} atom

100g of the element will contain $= \frac{6.023 \times 10^{23} \times 100}{58.65}$ atoms

$= 1.026 \times 10^{22}$ atoms

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

Given : M = 168.5 , n = 2 , a = 412.1×10^{-12} , $N_A = 6.023 \times 10^{23}$

$$\rho = \frac{nM}{a^3 N_A}$$

$$\rho = \frac{2 \times 168.5}{(412.1 \times 10^{-12})^3 \times 6.023 \times 10^{23}}$$

$$= 0.779 \times 10$$

$$= 7.99 = 8 gcm^{-3}$$

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

Given : $a = 4Å = 4 \times 10^{-10}$, M = 60 , n = 4 (face centered cubic)

$$\rho = \frac{nM}{a^3 N_A}$$

$$= \frac{4 \times 60}{(4 \times 10^{-10})^3 \times 6.023 \times 10^{23}} = 0.6626 \times 10 = 6.626\ gcm^{-3}$$

Additional Questions - Short Answers

1.What are General characteristics of solids

- ✓ Solids have definite volume and shape.
- ✓ Solids are rigid and incompressible
- ✓ Solids have strong cohesive forces.
- ✓ Solids have short inter atomic, ionic or molecular distances.
- ✓ Their constituents have fixed positions and can only oscillate about their mean positions

2.What are two types of solids based on the arrangement of their constituents.

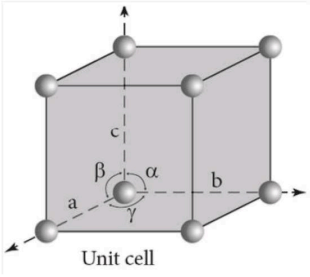
(i) Crystalline solids

(ii) Amorphous solids.

3.Define isotropy and anisotropy

- Isotropy means uniformity in all directions. In solid state isotropy means having identical values of physical properties such as refractive index, electrical conductance etc., in all directions,

λ – the wavelength of X-ray used for diffraction.
θ – The angle of diffraction
n – Order of diffraction



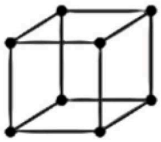
Unit cell

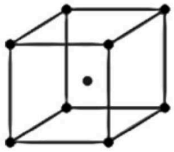
10.What are characteristic parameters of a unit cell?
Three edge lengths or lattice constants - a ,b and c
angle between the edges - α, β and γ

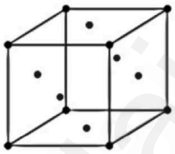
11.What is meant by packing efficiency ? How it is measured?

- ✓ The percentage of total volume occupied by these constituent spheres gives the packing efficiency of an arrangement
- ✓ Packing fraction $= \frac{\text{Total volume occupied by sphere in a unit cell}}{\text{volume of unit cell}} \times 100$

12.Sketch the a) Simple cubic b) Body-centered cubic c) Face centered cubic lattices


Simple cubic


Body centered cubic


Face centered cubic

13.How will you classify point defects

Point defects

Stoichiometric defect	Non stoichiometric defect	Impurity defect
(i) Shocttky defect	(i) Metall Excess defect	
(ii) Frenkel defect	(ii) Metal deficiency defect	

14.How will you classify crystal defects?
1) Point defects
2) Line defects
3) Interfacial defects
4) Volume defects

15. What is Piezoelectric crystals?

- ✓ Piezoelectricity is the appearance of an electrical potential across the sides of a crystal when you subject it to mechanical stress.
- ✓ The word piezoelectricity means electricity resulting from pressure and latent heat.

Additional Questions - Long Answers

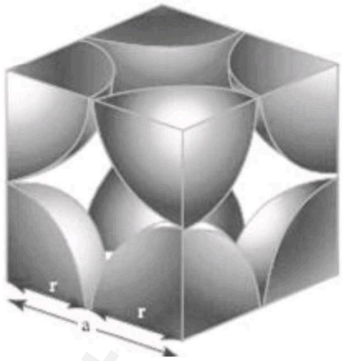
1.Calculate packing efficiency of simple cubic unit cell

Packing fraction $= \frac{\text{Total volume occupied by sphere in a unit cell}}{\text{volume of unit cell}} \times 100$**……..(1)**

Consider a cube with an edge length 'a'

Volume of the cube with edge length a $= a^3$**……..(2)**

r – radius of the sphere



From the figure $a = 2r$ which implies $r = \frac{a}{2}$

Volume of the sphere with radius 'r'$= \frac{4}{3}\pi r^3$

$$= \frac{4}{3}\pi\left(\frac{a}{2}\right)^3$$

$$= \frac{\pi a^3}{6} \quad \text{……..(3)}$$

In a simple cubic arrangement, number of spheres belongs to a unit cell is equal to one

Total volume occupied by sphere in a sc unit cell $= 1 \times \frac{\pi a^3}{6} = \frac{\pi a^3}{6}$**……(4)**

Dividing (4) by (2)

Packing fraction $= \frac{\frac{\pi a^3}{6}}{a^3} \times 100 = 52.13\%$

only 52.31% of the available volume is occupied by the spheres in simple cubic packing, making inefficient use of available space and hence minimizing the attractive forces.

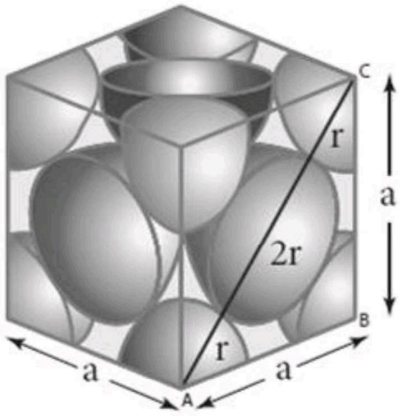
2.Calculate packing efficiency of fcc unit cell

From the figure

AC = 4r

$4r = a\sqrt{2}$

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



In ΔABC

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

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

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

Volume of the sphere with radius 'r'$= \frac{4}{3}\pi r^3$

$$= \frac{4}{3}\pi\left(\frac{a\sqrt{2}}{4}\right)^3$$

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

Number of spheres belong to a unit cell in fcc arrangement is equal to 4 and hence the total volume of all spheres

$$= 4 \times \frac{\sqrt{2}}{24}\pi a^3 = \frac{\sqrt{2}\pi a^3}{6}$$

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

$$= \frac{\left(\frac{\sqrt{2}\pi a^3}{6}\right)}{(a)^3} \times 100$$

$$= \frac{1.414 \times 3.14 \times 100}{6} = 74\%$$

74 % of the available volume is occupied. The available space is used more efficiently than in simple cubic packing.

3.How is radius ration is useful in determination of structure of an ionic compound?

- ✓ The ratio of radius of cation and anion $\frac{r_C^+}{r_A^-}$ plays an important role in determining the structure.

$\left(\frac{r_C^+}{r_A^-}\right)$	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

4.How will you derive the formula of density of a unit cell

By Using the edge length of a unit cell, we can calculate the density of the crystal by considering a cubic unit cell as follows.

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

Mass of the unit cell = $\left\{\begin{matrix}\text{total number of atoms belongs} \\ \text{to that unit cell}\end{matrix}\right\} \times$ mass of one atom**.....(1)**

Mass of one atom $= \frac{\text{molar mass } (\text{gmol}^{-1})}{\text{Avagardo number } (\text{mol}^{-1})}$

$$m = \frac{M}{N_A}\text{.....(2)}$$

Sub (2) in (1)

Mass of the unit cell= $n \times \frac{M}{N_A}$

For a cubic unit cell, all the edge lengths are equal i.e , a=b=c

Volume of the unit cell $= a^3$

$$\boldsymbol{\rho = \frac{n \times M}{a^3 N_A}}$$

5.Explain about classification of solids

Ionic Solids

- ✓ The structural units of an ionic crystal are cations and anions.
- ✓ They are bound together by strong electrostatic attractive forces.
- ✓ Ionic crystals possess definite crystal structure

Example: NaCl

Covalent solids

- ✓ In covalent solids, the constituents (atoms) are bound together in a three dimensional network entirely by covalent bonds.
- ✓ Such covalent network crystals are very hard, and have high melting point. They are usually poor thermal and electrical conductors.

Examples: Diamond, silicon carbide

Molecular solids

- ✓ In molecular solids, the constituents are neutral molecules.
- ✓ They are held together by weak van der Waals forces. Generally molecular solids are soft and they do not conduct electricity.
- ✓ These molecular solids are further classified into three types.

(i) Non-polar molecular solids

In non polar molecular solids constituent molecules are held together by weak dispersion forces or London forces

Examples: Naphthalene, anthracene etc.,

(ii) Polar molecular solids

Thee constituents are molecules formed by polar covalent bonds. They are held together by relatively strong dipole-dipole interactions. They have higher melting points than the non-polar molecular solids**.**

Examples : Solid CO_2 , solid NH_3 etc.

(iii) Hydrogen bonded molecular solids

The constituents are held together by hydrogen bonds. They are generally soft solids under room temperature.

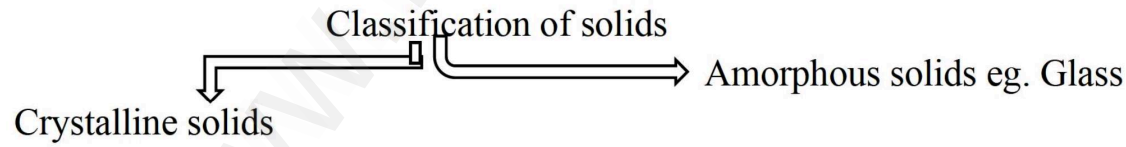
Examples: Solid ice (H_2O), glucose, urea etc**.,**

iv)Metallic solids

In metallic solids, the lattice points are occupied by positive metal ions and a cloud of electrons pervades the space. They are hard, and have high melting point. Metallic solids possess excellent electrical and thermal conductivity. They possess bright lustre. Examples: Metals and metal alloys belong to this type of solids,

Example : Cu,Fe,Zn, Ag ,Au, Cu-Zn etc.

6.Classification of solids



(i) Ionic crystals Ex.NaCl

(ii) Covalent crystals Ex: Diamond

(iii) Molecular crystals Ex: naphthalene, anthracene, glucose

(iv)Metallic crystals Ex: All metallic elements (Na, Mg,Cu,Au,Ag etc..)

(v) Atomic solids - ex: frozen elements of Group 18

SAIVEERA ACADEMY
CENTUM GUIDE

UNIT - 11

HYDROXY COMPOUNDS AND ETHERS

Why Our Guide?

- Easy To Read
- Important Questions For Every Chapters
- Public Examination Key Based Answers
- Public Examination Based Additional Questions
- Notes For Organic Problems
- Model Question Papers For Quarterly and Half Yearly

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UNIT-11 HYDROXY COMPOUNDS AND ETHERS

Important Questions

Short Answers	
Book Back	**Book Inside**
1.Identify the product (s) is / are formed when 1 – methoxy propane is heated with excess HI. Name the mechanism involved in the reaction 2.Is it possible to oxidise t – butyl alcohol using acidified dichromate to form a carbonyl compound 3.Explain Kolbe's reaction 4. What is meta merism? Give the structure and IUPAC name of metamers of 2-methyoxy Propane 5.Phenol is distilled with Zn dust followed by friedel – crafts alkylation with propyl chloride to give a compound B, B on oxidation gives (c) Identify A,B and C.	1.What is Saytzeff's rule 2.Explain Swern oxidation 3.How will you get ethene from ethylene glycol? 4.Write about Test to differentiate alcohol and phenols 5. How will you prepare 1,2 – epoxyethane (oxirane) and dioxane from ethylene glycol? **Apr 21** 6. How will you prepare ethanal? **Apr 21** (acetaldehyde)from ethylene glycol? 7.How will you prepare acrolein from glycerol ? 8. How will you prepare acrolein from glycerol 9.What is Baeyer's reagent? How it converts ethane to ethylene glycol? **Sep 20** 10.Uses of diethyl ether and glycerol
Long Answers	
1. How is phenol prepared from i) chloro benzene (Dows process) ii) isopropyl benzene 17. Complete the following reactions i) $CH_3CH_2OH \xrightarrow{PBr_2} A \xrightarrow{aq.NaOH} B \xrightarrow{Na} C$ ii) $C_6H_5OH \xrightarrow{Zn\ dust} A \xrightarrow{CHCl_3} B \xrightarrow{KMnO_4\backslash H^+} C$	1.Write a note on coupling reaction of phenol or dye test of phenol **Mar 20** 2.Write a short note on Riemer Tiemann Reaction 3.How will you differentiate primary,secondary and tertiary alcohols by Lucas test? **Jul 20 , Sep 20** 4.Starting from phenol how will you prepare the following (i)Aniline (ii)Benzoquinone (iii)Cyclohexanol (iv) Picric acid

Points To Remember

1) 1° alcohol - Functional Group attached carbon directly boned to one carbon atom
   For example : CH_3CH_2OH
2) 2° alcohol - Functional Group attached carbon directly boned to two carbon atoms
   For example : $(CH_3)_2CHOH$
3) 1° alcohol - Functional Group attached carbon directly boned to three carbon atoms
   For example : $(CH_3)_3COH$

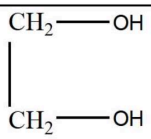
Basic rules to name the alcohols.

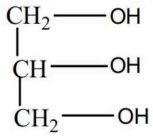
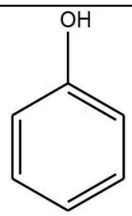
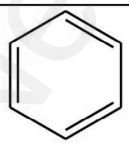
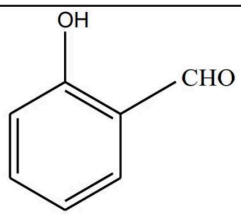
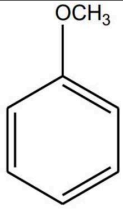
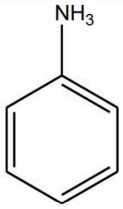
1. Select the longest continuous chain of carbon atoms (root word) containing the functional group (-OH).
2. Number the carbon atoms in the chain so that the carbon bearing the -OH group has the lowest possible number.
3. Name the substituent (if any)
4. Write the name of the alcohol as below.

Prefix + Root word + Primary suffix + Secondary suffix
(substituents) (longest chain) (Saturation /unsaturation) (ol)

- Lithium aluminium hydride does not reduce the carbon–carbon double bond present in unsaturated carbonyl compound and hence it is a best reagent to prepare unsaturated alcohols.
- Among isomeric alcohols primary alcohols have higher boiling point and the tertiary alcohols have lower boiling points.
- The relative reactivities of alcohols in the dehydration reaction follows the order
  - **primary < secondary < tertiary**
- **Pyridinium chlorochromate (PCC)** – To stop the oxidation of aldehyde , ketone to acid
- **Acidity of 1°, 2°and 3° alcohols**: 1° alcohol > 2° alcohol > 3° alcohol

Notes For Organic Problems

Molecular Formula	Compound Name	Structure
C_2H_6O (alcohol)	Ethanol	CH_3CH_2OH
$C_2H_6O_2$(alcohol)	Ethylene Glycol	

$C_3H_8O_3$(alcohol)	Glycerol	
C_6H_6O	Phenol	 OR C_6H_5OH
C_2H_4(alkene)	ethene	$CH_2 = CH_2$
C_6H_6	Benzene	
CH_2O(aldehyde)	Formaldehyde	HCHO
C_2H_4O(aldehyde)	Acetaldehyde	CH_3CHO
$C_7H_7O_2$(aldehyde)	Salicyclicaldehyde	
$C_4H_{10}O$ (ether)	Ethoxyethane(diethylether)	$C_2H_5OC_2H_5$
C_7H_8O (ether)	anisole	
C_6H_7N	Aniline	 Or $C_6H_5NH_2$

Preparation of alcohol

1. $R - X + NaOH \xrightarrow{\Delta} R - OH + NaX$

2.Alkene + water $\xrightarrow{\text{conc.}H_2SO_4}$ 2° Alcohol

3.From Grignard reagent

(i) HCHO + RMgX ⟶ 1° Alcohol

(ii) Aldehyde except HCHO + RMgX ⟶ 2° Alcohol

(iii) Ketone + RMgX ⟶ 3° Alcohol

4. Hydroboration: Diborane + alkene $\xrightarrow{H_2O_2}$ 1°Alcohol

5.Reduction of carbonyl compounds

Aldehyde $\xrightarrow{[H]}$ 1°Alcohol

Ketone $\xrightarrow{[H]}$ 2°Alcohol

Preparation of glycol [ethane 1,2-diol]

Ethene $\xrightarrow[[O]]{\text{Cold alk.}KmNO_4}$ ethylene glycol

Chemical Properties of alcohol

1.Alcohol + HBr $\xrightarrow[-H_2O]{}$ Bromoalkane

2. Alcohol + PCl_5 $\xrightarrow[-HCl]{}$ Chloroalkane

3. Alcohol + $SOCl_2$ $\xrightarrow[-HCl,-SO_2]{}$ Chloroalkane

4. Alcohol $\xrightarrow[-H_2O]{\text{Dehydrating agent } (\text{Conc.}H_2SO_4)}$ Alkene

5.Catalytic dehydrogenation

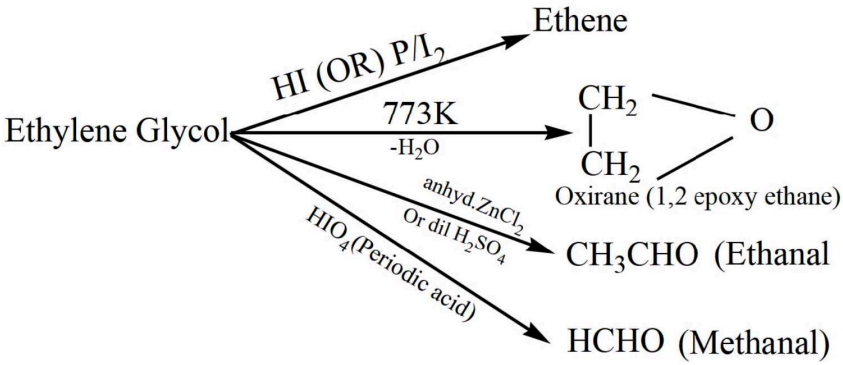
(i) 1°Alcohol $\xrightarrow[573K]{Cu}$ Aldehyde

(ii) 2°Alcohol $\xrightarrow[573K]{Cu}$ Ketone

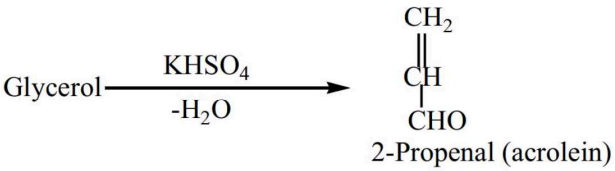
6.Dehydration reaction

3°Alcohol $\xrightarrow[573K]{Cu}$ Alkene

Chemical Properties of ethylene glycol (ethane 1,2-diol)



Chemical Property of Glycerol



Preparation of Phenols

1.**Dows Process**

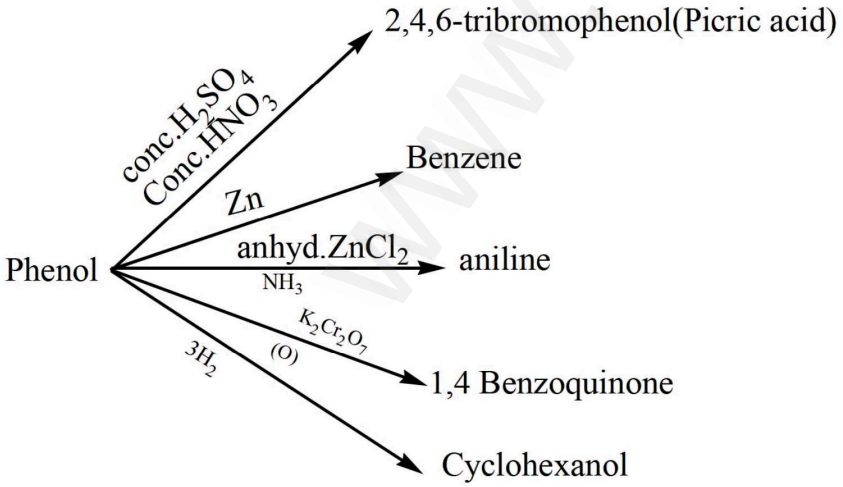
$$\text{Chlorobenzene} + \text{NaOH} \xrightarrow[300\ \text{bar}]{633\text{K}} \text{Sodium Phenoxide} \xrightarrow{\text{HCl}} \text{Phenol} + \text{NaCl}$$

2.Benzene sulphonic acid $+ \text{NaOH} \xrightarrow{623\text{K}}$ Sodium Phenoxide $\xrightarrow{\text{HCl}}$ Phenol + NaCl

3.Aniline + Nitrous acid $\longrightarrow$ Benzene diazonium chloride $\xrightarrow{H_2O}$ Phenol + N_2 + HCl

4.Cumene $\xrightarrow{(O)}$ Cumene hydroperoxide $\xrightarrow{\text{Conc.}H_2SO_4}$ Phenol + acetone

Chemical Properties of Phenol



1.Kolbe's reaction

Phenol $\xrightarrow{\text{NaOH}}$ Sodium phenoxdie $\xrightarrow{CO_2}$ Sodium salicylate $\xrightarrow{H^+/H_2O}$ Salicyclic acid

4. In the reaction sequence, Ethene $\xrightarrow{HOCl}$ A $\xrightarrow{X}$ ethane-1-2-diol.A and X respectively are

a) Chloroethane and NaOH b) ethanol and H_2SO_4

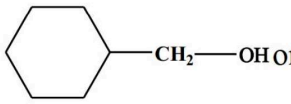
c) 2 – chloroethan -1-ol and $NaHCO_3$ d) ethanol and H_2O

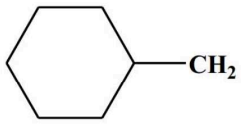
Ans : c) 2 – chloroethan -1-ol and $NaHCO_3$

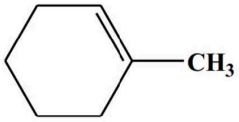
5. Which one of the following is the strongest acid

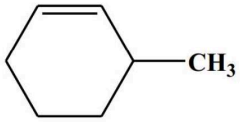
a) 2 - nitrophenol b) 4 – chlorophenol c) 4 – nitrophenol d) 3 – nitrophenol

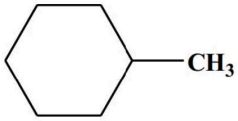
c) 4 – nitrophenol

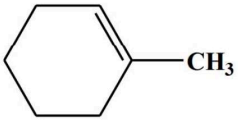
6.  on treatment with Con H_2SO_4 predominately gives

a) 

b) 

c) 

d) 

Ans : b) 

7. Carbolic acid is

a) Phenol b) Picric acid c) benzoic acid d) phenylacetic acid

Ans : a) Phenol

8. Which one of the following will react with phenol to give salicyladehyde after hydrolysis.

a) Dichloro methane b) trichloroethane c) trichloro methane d) CO_2

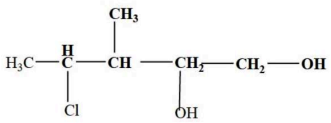
Ans : c) trichloro methane

9. $(CH_3)_3 - C - CH(OH)CH_3 \xrightarrow{H_2SO_4} X$(major product)

a) $(CH_3)_3CCH = CH_2$ b) $(CH_3)_2C = C(CH_3)_2$

c) $CH_2 = C(CH_3)CH_2 - CH_2 - CH_3$ d) $CH_2 = C(CH_3) - CH_2 - CH_2 - CH_3$

Ans : b) $(CH_3)_2C = C(CH_3)_2$

10. The correct IUPAC name of the compound 

a) 4 – chloro – 2,3 – dimethyl pentan – 1-ol

b) 2,3 – dimethyl – 4- chloropentan -1-ol

c) 2,3,4 – trimethyl – 4- chlorobutan -1-ol

d) 4 – chloro – 2,3,4 – trimethyl pentan – 1-ol

Ans : a) 4 – chloro – 2,3 – dimethyl pentan – 1-ol

11. Assertion : Phenol is more acidic than ethanol

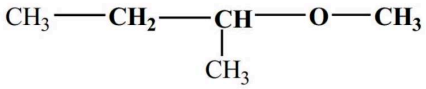
19. One mole of an organic compound (A) with the formula C_3H_8O reacts completely with two moles of HI to form X and Y. When Y is boiled with aqueous alkali it forms Z. Z answers the iodoform test. The compound (A) is

a) propan – 2-ol b) propan -1-ol c) ethoxy ethane d) methoxy ethane

Ans : d) methoxy ethane

20. Among the following ethers which one will produce methyl alcohol on treatment with hot HI?

a) $(H_3C)_3 - O - CH_3$ b) $(CH_3)_2 - CH - CH_2 - O - CH_3$

c) $CH_3 - (CH_2)_3 - O - CH_3$ d) 

Ans: $(H_3C)_3 - O - CH_3$

21. Williamson synthesis of preparing dimethyl ether is a / an /

a) SN^1 reactions b) SN^2 reaction

c) electrophilic addition d) electrophilic substitution

Ans : b) SN^2 reaction

22. On reacting with neutral ferric chloride, phenol gives

a) red colour b) violet colour c) dark green colour d) no colouration.

Ans : b) violet colour

Additional Questions

1. 1-methoxy propane and 2-methoxy propane are

a) chain isomers b) position isomers **c) metamers** d) functional isomers

2. Which one of the alcohol cannot be prepared by Grignard reagent?

a) Methanol b) ethanol c) iso propyl alcohol d) phenyl methanol

3. Which among the following statement are correct with regard to alkyl halides?

a) Alkyl halides on heating with aq NaOH gives alcohol

b) 1° alkyl halides proceed by SN_2 mechanism.

c) 2° and 3° alkyl halides undergo substitution by SN_1 mechanism.

d) all the above.

4. Which among the following reagent is not used to differentiate ethanol and phenol?

a) neutral $FeCl_3$ b) $C_6H_5N_2Cl$ c) NaOH **d) anhydrous $ZnCl_2$**

5. Which one of the following alcohols on oxidation gives carboxylic acid with lesser number of carbon atoms?

a) $(CH_3)_2 - CH - CH_2OH$ **b) $CH_3CH_2CHOHCH_3$**

c) $CH_3 - (CH_2)_3 - CH_2OH$ d) both (a) and (c)

6. An organic compound 'A' reacts with methyl magnesium chloride followed by hydrolysis to form 'B'. 'B' gives a blue colour with Victor Meyers test. Identify A and B respectively.

a) acetaldehyde, tert butyl alcohol b) acetone, isopropyl alcohol

c) $NaHCO_3$ (aqueous) d) Baeyer's reagent

19. 1-propanol and 2-propanol can be best distinguished by

a) oxidation with $KMnO_4$ followed by reaction with Fehling solution.

b) oxidation with acidic dichromate followed by reaction with Fehling solution.

c) oxidation by heating with copper followed by reaction with Fehling solution.

d) oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution.

20. Predict the structure of propane-1,2 diol

a) $CH_2(OH)-CH_2CH_2OH$ b) $HOCH_2 - CH_2OH$

c) $CH_3CH(OH)CH_2OH$ d) None of these

21. The reactivity of alcohols with respect to oxidation decreases with

a) increase in α-H **b) decrease in α-H** c) increase in β-H d) decrease in β-H

22. Intermolecular hydrogen bonding in ethylene glycol leads to its

a) high viscosity b) high boiling point c) hydroscopic nature **d) all the above**

23. The ionization constant of phenol is higher than that of ethanol because

a) phenoxide ion is bulkier than ethoxide

b) phenoxide ion is stronger base than ethoxide

c) phenoxide ion is stabilized through delocalization

d) phenoxide ion is less stable than ethoxide ion

24. Alcohols are isometric with

a) aldehyde b) ketones **c) ethers** d) esters

25. Alcohols are soluble in polar solvents like water due to

a) intermolecular hydrogen bonding b) intramolecular hydrogen

c) co-ordinate bonding d) ionic bonding.

26. Higher alcohols are not soluble in water because of

a) hydrophilic alkyl group **b) hydrophobic alkyl groups**

c) hydrophilic aryl group d) hydrophobic aryl groups.

27. With concentrated sulphuric acid, glycol undergoes intermolecular dehydration to give cyclic compound

a) diethylene glycol **b) dioxin** c) paraldehyde d) glyoxal

28. Glycerol when heated with conc. H_2SO_4 gives

a) allyl alcohol b) propyl alcohol **c) acrolein** d) propylene

29. Glycerose is a mixture of

a) glyceric acid + dihydroxy acetone **b) glyceraldehyde + dihydroxy acetone**

c) glyceraldehyde + glyceric acid d) dihydroxy acetone + mesoxalic acid

30. Which is the group that decreases the acid strength of phenol?

a) $-NO_2$ b) $-CN^-$ **c) $-NH_2$** d) both (a) and (b)

31. Which of the following has an offensive odour?

c) 2,4,6 trinitro phenol d) 2,4,6 trinitro benzoic acid.

46. The correct order of reactivity of alcohol during dehydration is

a) primary > secondary > tertiary **b) primary < secondary < tertiary**

c) tertiary < secondary < primary d) secondary < tertiary < primary.

47. Ethers in the presence of atmospheric oxygen oxidises to give hydroperoxides and dialkyl peroxides such a spontaneous reaction by atmospheric oxygen is called

a) auto oxidation b) acylation c) alkylation d) dehydration.

48. Phenol is less acidic than

a) ethanol **b) o-nitrophenol** c) o-methyl phenol d) m-chlorophenol

49. order of reactivity of alcohol towards sodium metal is

a) primary < secondary > tertiary **b) primary > secondary > tertiary**

c) primary < secondary < tertiary d) primary > secondary < tertiary

50. On oxidation of an alcohol gives an aldehyde having the same number of carbon atoms and that of alcohol is

a) 1° alcohol b) 2° alcohol c) 3° alcohol d) None

51. Oxidation of glycerol using bismuth nitrate gives

a) Tartaric acid **b) Mesoxalic acid** c) Oxalic acid d) Glyceric acid

52. The number of primary alcoholic groups in glycerol is

a) 0 b) 1 **c) 2** d) 3

53. Ethylene glycol is dehydrated to diethylene glycol by

a) conc.H_3PO_4 b) conc. H_2SO_4 c) anhy. $ZnCl_2$ d) heat at 773K

54. The test used to distinguish wish 1°,2° and 3° alcohol is

a) Lucas test b) Victor Meyer's c) dehydrogenation **d) all the above**

55. The ultimate product obtained when glycerol reacts with oxalic acid at 533K is_____.

a) formic acid b) glycerol oxalate **c) allyl alcohol** d) acrolein

56. The reaction between phenol and benzoyl chloride is the present of sodium hydroxide is named as _____ reaction.

a) Cannizaro b) Reimer-Tiemann c) Kolbe's **d) Schotten-Baumann**

57. Ethanol and methoxy methane are

a) chain isomers b) position isomers **c) functional isomers** d) metamers

58. Williamson's synthesis is an example of

a) nucleophilic addition. b) electrophilic addition.

c) electrophilic substitution. **d) nucleophilic substitution.**

59. Ether is formed when alkylhalide is treated with sodium alkoxide, this method is known as

a) Hoffmann reaction. **b) williamson's synthesis**

c) Wurtz synthesis d) Kolbe's reaction.

60. A compound that undergoes bromination easily is

a) benzoic acid **b) phenol** c) benzene d) toluene

Answer the following questions - Book Back

1. Identify the product (s) is / are formed when 1 – methoxy propane is heated with excess HI. Name the mechanism involved in the reaction

$$CH_3 - O - CH_2 - CH_2 - CH_3 + 2HI \xrightarrow[\text{EXCESS}]{\text{HI}} CH_3 - I \; + \; CH_3 - CH_2 - CH_3 - I + \; H_2O$$

1 – methoxy propane Methyl iodide 1 – iodo propane

The reaction involves nucleophile substitution reaction mechanism (S_N1)

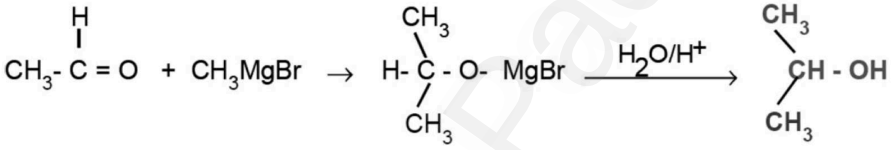
2. Draw the major product formed when 1-ethoxyprop-1-ene is heated with one equivalent of HI

$$C_2H_5 - O - CH = CH - CH_3 + HI \longrightarrow C_2H_5I \; + \; HO - CH = CH - CH_3$$

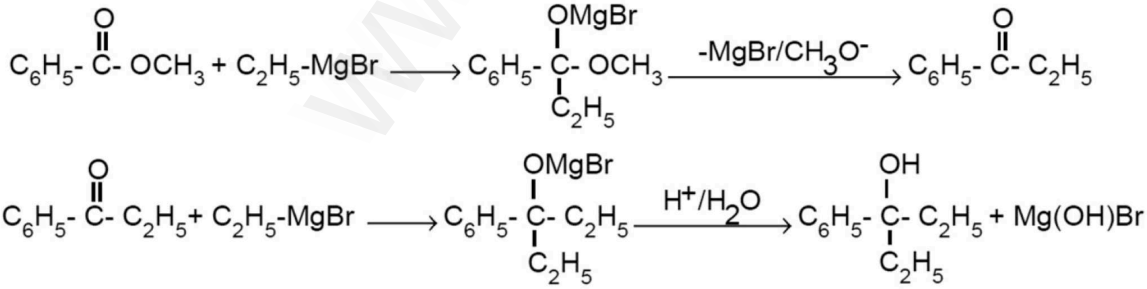
1-ethoxyprop-1-ene prop-1-ene-1-ol

3. Suggest a suitable reagent to prepare secondary alcohol with identical group using Grignard reagent.

- To prepare secondary alcohol from Grignard reagent , aldehyde other than formaldehyde must be taken.
- A suitable reagent to prepare secondary alcohol with identical group using Grignard reagent is ethanal



4. What is the major product obtained when two moles of ethyl magnesium bromide is treated with methyl benzoate followed by acid hydrolysis.



3 – phenyl 3 – pentanol

5. Predict the major product, when 2-methyl but -2-ene is converted into an alcohol in each of the following methods.

propan − 2 − ol < Propan − 1 − ol < propan − 1,3 - diol < propan − 1,2,3 − triol

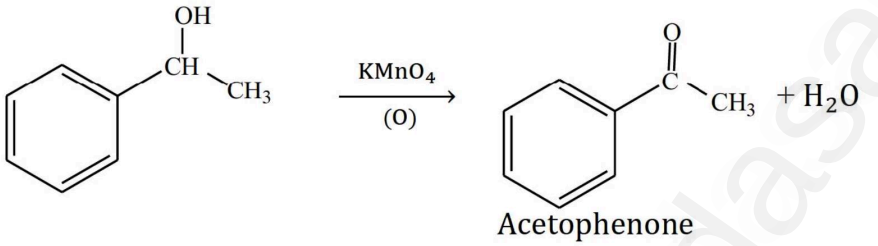
7. Can we use nucelophiles such as NH_3 , CH_3O^- for the Nucleophilic substitution of alcohols

Moderately and strong nucleophile such as NH_3 , CH_3O^- cannot be used for nucleophilic substitution, because they undergoes protonation to form NH_4^+ , CH_3OH which would be no longer nucleophile

8. Is it possible to oxidise t – butyl alcohol using acidified dichromate to form a carbonyl compound.

- Yes it is possible to oxidise t – butyl alcohol using acidified dichromate to form a carbonyl compound
- Tertiary butyl alcohol do not undergo oxidation reaction under normal conditions, but at elevated temperatures, under strong oxidising agent like acidified dichromate cleavage of C – C bond takes place to give a mixture of carboxylic acid like formic acid and acetic acid

9. What happens when 1-phenyl ethanol is treated with acidified $KMnO_4$.



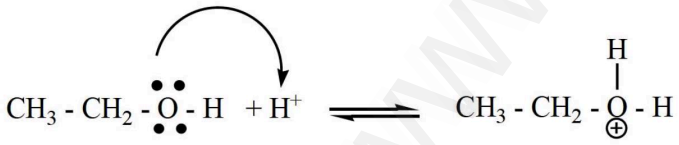
Acetophenone

10. Write the mechanism of acid catalysed dehydration of ethanol to give ethene

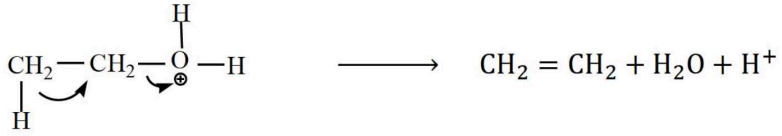
Primary alcohol undergoes dehydration by E_2mechanism

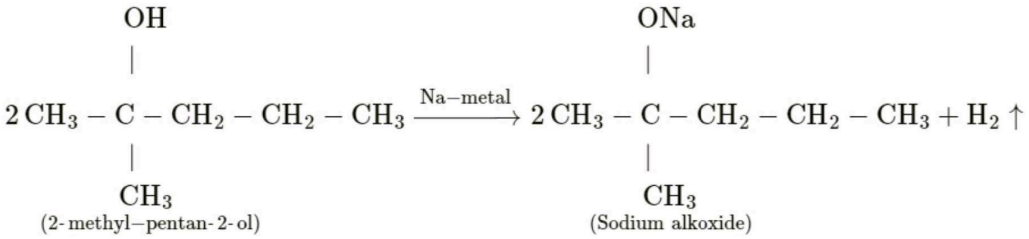
$$CH_3 - CH_2 - OH \xrightarrow[443K]{H_2SO_4} CH_2 = CH_2$$

Step 1 : Protonation of ethanol to form ethyl oxonium ion

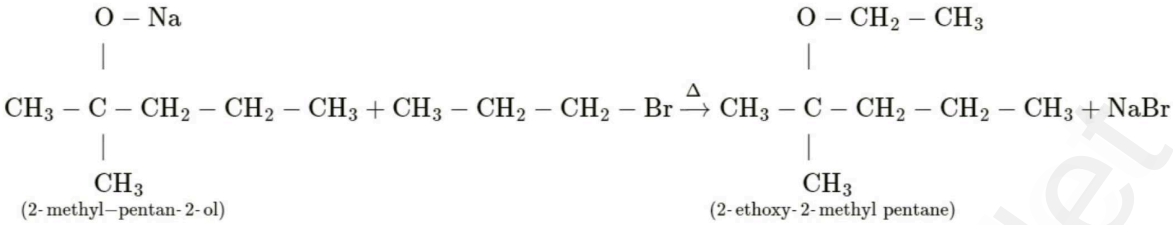


Step 2 : Elimination of water molecule to form ethene



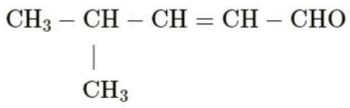


Step -3

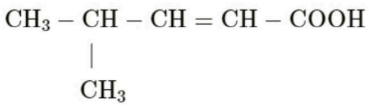


14. Write the structure of the aldehyde, carboxylic acid and ester that yield 4 − methylpent − 2 − en − 1 − ol.

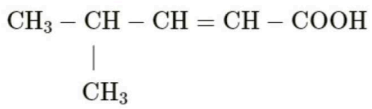
Aldehyde that yields 4 − methylpent − 2 − en − 1 − ol



Carboxylic acid that yields 4 − methylpent − 2 − en − 1 − ol



Ester that yields 4 − methylpent − 2 − en − 1 − ol



15.What is meta merism? Give the structure and IUPAC name of metamers of 2-methyoxy Propane

It is special type of isomerism in which molecules with same molecular formula and functional group differs only in the number of atoms on either side of functional group.

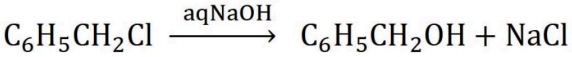
Metamers of 2-methyoxy Propane

(i) $CH_3 - O - CH_2 - CH_2 - CH_3$: 1-methoxy propane

(ii) $CH_3 - CH_2 - O - CH_2 - CH_3$: Ethoxy ethane

16. How are the following conversions effected

i) benzylchloride to benzylalcohol



Benzylchloride benzylalcohol

22400 cm^3 of methane is produced from X g of alcohol

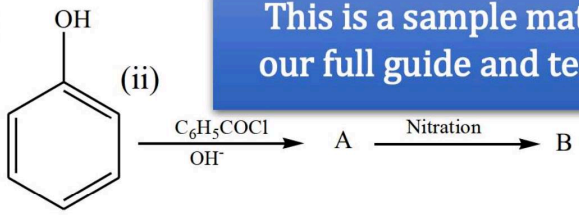
X g of alcohol $= \frac{0.44 \times 22400}{112} = 88g$

Molar mass of alcohol is 81 g

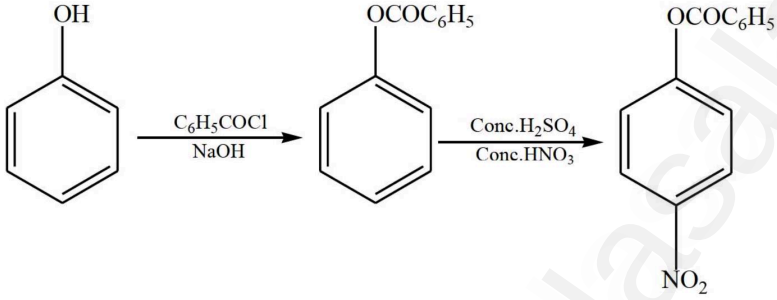
Subtract the mass of hydroxyl group from it $= 88 - (16 + 1) = 71$ g

Number of carbon can be possible with this molar mass is 5 which comprises of 60 g and the rest mass is hydrogen.So the formula of alcohol is $\mathbf{C_5H_{11}OH}$

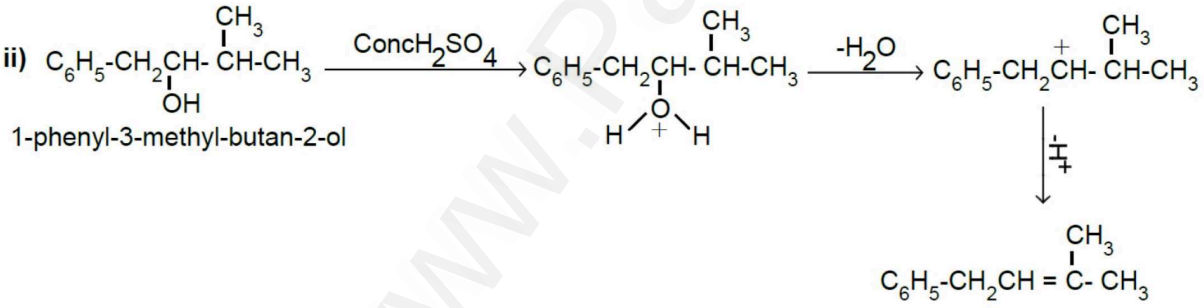
19. Complete the following reactions

(i) 

(ii) $C_6H_5 - CH_2CH(OH)CH(CH_3)_2 \xrightarrow{\text{Conc } H_2SO_4}$

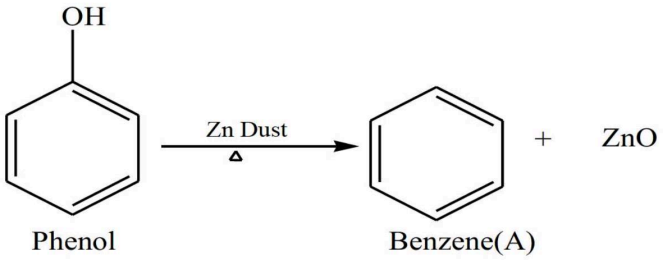
i) 

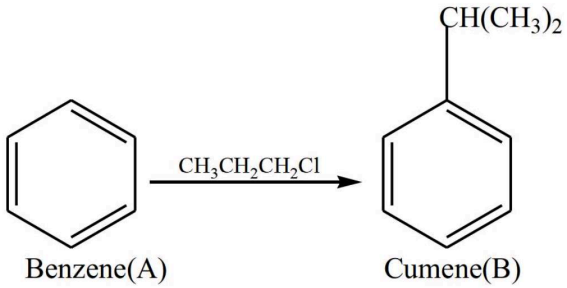
A – Phenyl benzoate, B – P – nitro phenyl benzoate

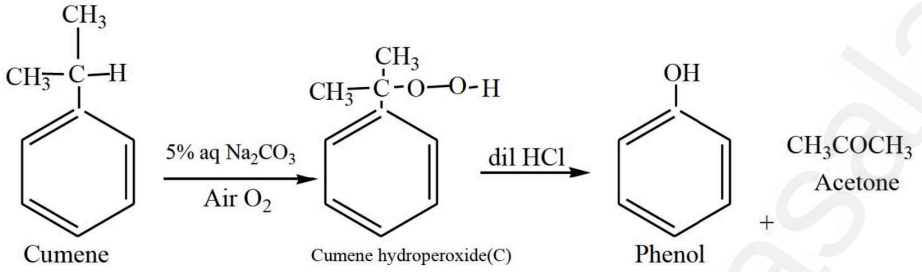
ii) 

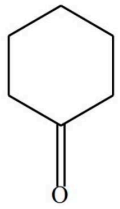
1-phenyl-3-methyl-butan-2-ol

20. Phenol is distilled with Zn dust followed by friedel – crafts alkylation with propyl chloride to give a compound B, B on oxidation gives (c) Identify A,B and C.

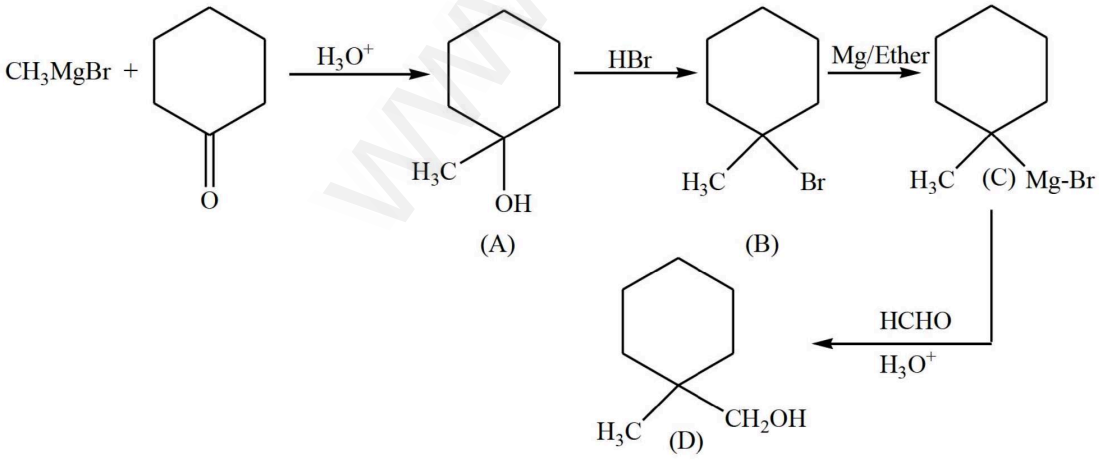






21. CH_3MgBr +  + $\xrightarrow{H_3O^+}$ **A** $\xrightarrow{HBr}$ **B** $\xrightarrow{Mg/ether}$ **C** $\xrightarrow{HCHO/H_3O^+}$ **D**

Identify A,B,C,D and write the complete equation



Compound – A : 2 – chloro – butane

Compound – B : Grignard reagent

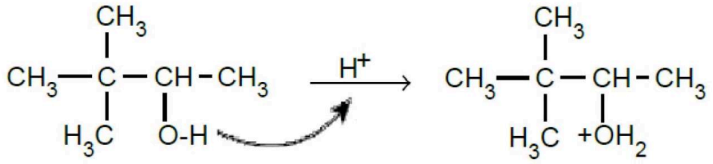
Compound – X : 2 – butanone

Compound – Y : 3, 4 – dimethyl – hexan – 3 – ol

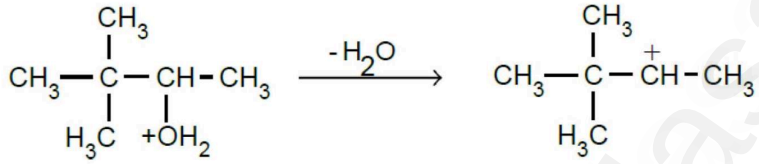
25. 3,3 – dimethylbutan -2-ol on treatment with conc.H_2SO_4 to give tetramethyl ethylene as a major product. Suggest a suitable mechanisms

When 3,3 – dimethylbutan -2-ol on treatment with conc.H_2SO_4 elimination occurs after carbocation , rearrangement lead to formation of tetramethyl ethylene

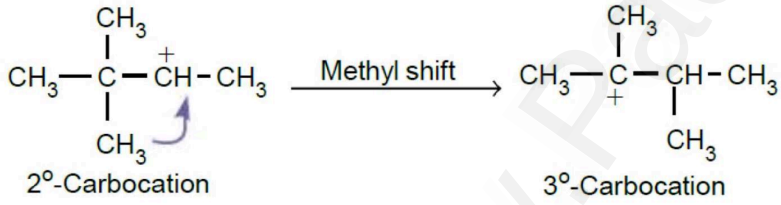
Step-1: protonation of 3,3-dimethylbutan-2-ol



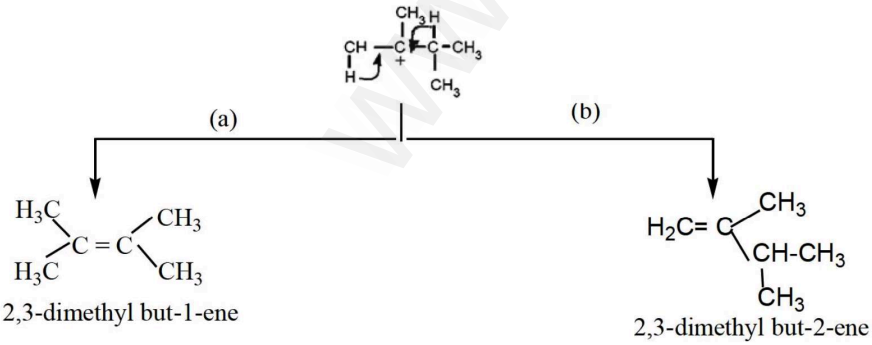
2) Removal of a water molecule from the carbonium ion formed above



3) Conversion of 2 degree carbonium to 3 degree carbonium by methyl shift:



4) Removal of H+ ion to form a double bond:



Additional Questions – Short Answers

1. Why lithium aluminium hydride a best reagent to prepare unsaturated alcohols.

Lithium aluminium hydride does not reduce the carbon–carbon double bond present in the carbonyl compound and hence it is a best reagent to prepare unsaturated alcohols.

2.How will you prepare ethylene glycol (or) what happens when ethylene reacts with Baeyer's reagent

Hydroxylation of ethylene using cold alkaline solution of potassium permanganate (Baeyer's reagent) gives **ethylene glycol.**

$$CH_2 = CH_2 + H_2O \xrightarrow[[O]]{\text{Cold alkaline } KMnO_4} \underset{\displaystyle OH}{\overset{\displaystyle CH_2}{|}} - \underset{\displaystyle OH}{\overset{\displaystyle CH_2}{|}}$$

3.How will you prepare glycerol or saponification reaction

- Glycerol occurs in many natural fats and it is also found in long chain fatty acids in the form of glyceryl esters (Triglycerides).
- The alkaline hydrolysis of these fats gives glycerol and the reaction is known as saponification.

4. Why intermolecular dehydration of alcohol is not suitable for preparing mixed ethers?

If a mixture of two different alcohols is used, mixture of different ethers will be formed and they are difficult to separate.

5.What is Saytzeff's rule

During intramolecular dehydration, if there is a possibility to form a carbon – carbon double bond at different locations, the preferred location is the one that gives the more (highly) substituted alkene i.e., the stable alkene.

6.Explain Swern oxidation

- In this method, dimethyl sulfoxide (DMSO) is used as the oxidising agent, which converts alcohols to ketones / aldehydes.
- In this method an alcohol is treated with DMSO and oxalyl chloride followed by the addition of triethylamine.

1. Ethanol is used as an important beverage.
2. It is also used in the preparation of
    a) Paints and varnishes.
    b) Organic compounds like ether, chloroform, iodoform, etc.,
    c) Dyes, transparent soaps.
3. As a substitute for petrol under the name power alcohol used as fuel for aeroplane
4. It is used as a preservative for biological specimens.

Ethylene glycol

1. Ethylene glycol is used as an antifreeze in automobile radiator
2. Its dinitrate is used as an explosive with DNG.

Glycerol

1. Glycerol is used as a sweetening agent in confectionery and beverages.
2. It is used in the manufacture of cosmetics and transparent soaps.
3. It is used in making printing inks and stamp pad ink and lubricant for watches and clocks.
4. It is used in the manufacture of explosive like dynamite and cordite by mixing it with china clay

Phenol

1) About half of world production of phenol is used for making phenol formaldehyde resin. (Bakelite).
2) Phenol is a starting material for the preparation of
    i) drugs such as phenacetin, Salol, aspirin, etc.
    ii) phenolphthalein indicator.
    iii) explosive like picric acid.
3) It is used as an antiseptic-carbolic lotion and carbolic soaps.

Diethyl ether

1. Diethyl ether is used as a surgical anesthetic agent in surgery.
2. It is a good solvent for organic reactions and extraction.
3. It is used as a volatile starting fluid for diesel and gasoline engine.
4. It is used as a refrigerant.

Anisole

1. Anisole is a precursor to the synthesis of perfumes and insecticide pheromones,
2. It is used as a pharmaceutical agent .

12. Write about Test to differentiate alcohol and phenols

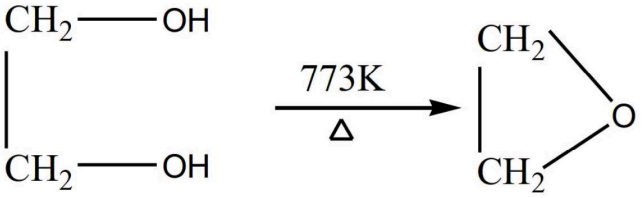
i) Phenol react with benzene diazonium chloride to form a red orange dye, but ethanol has no reaction with it.

ii) Phenol gives purple colouration with neutral ferric chloride solution, alcohols do not give such coloration with $FeCl_3$.

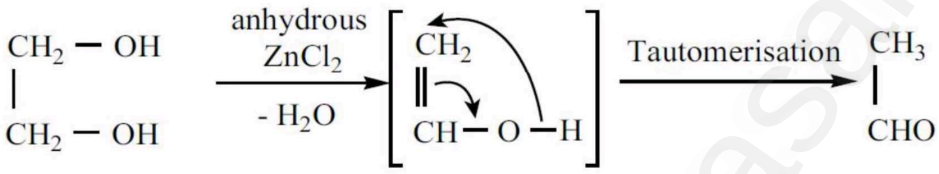
iii) Phenol reacts with NaOH to give sodium phenoxide. Ethyl alcohol does not react with NaOH.

13.How will you prepare 1,2 – epoxyethane (oxirane)from ethylene glycol?

Ethyleneglycol undergoes dehydration at 773K and forms epoxides.

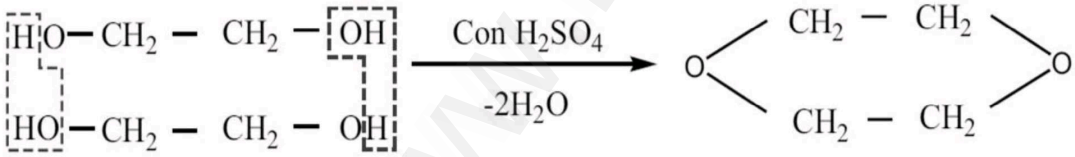


14. How will you prepare ethanal (acetaldehyde)from ethylene glycol?



When heated with dilute sulphuric acid (or) anhydrous $ZnCl_2$ under pressure in a sealed tube, ethylene glycol undergoes dehydration to gives acetaldehyde.

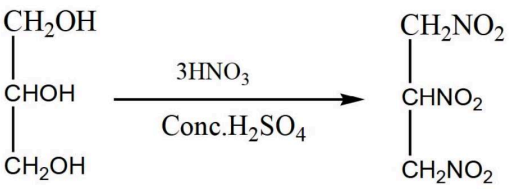
15. How will you prepare 1,4- dioxane from ethylene glycol?

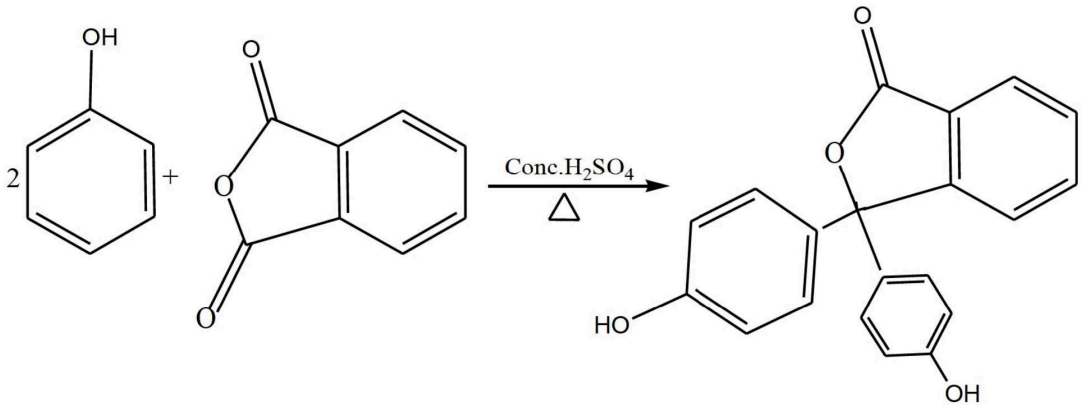


When distilled with Conc. H_2SO_4 glycol losses two molecules of water and forms dioxane

16. How will you prepare nitroglycerine from glycerol (or) nitration reaction of glycerol?

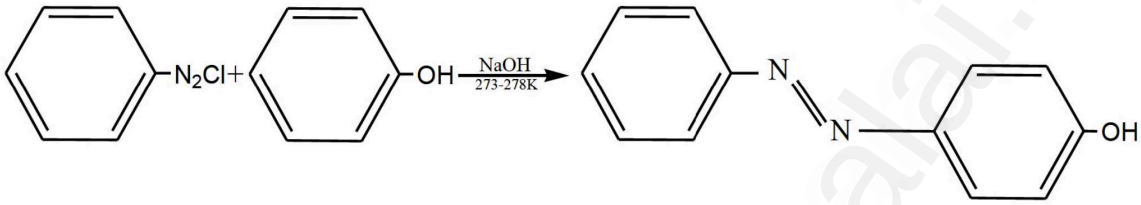
Glycerol reacts with nitric acid in the presence of sulphuric acid to form TNG (nitroglycerine).





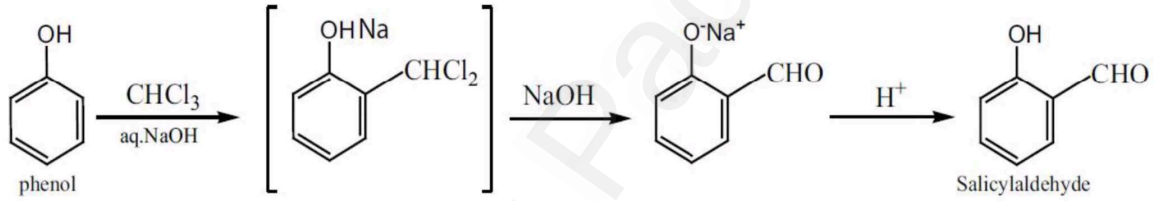
22.Write a note on coupling reaction of phenol or dye test of phenol

Phenol couples with benzene diazonium chloride in an alkaline solution to form p-hydroxy azobenzene(a red orange dye).



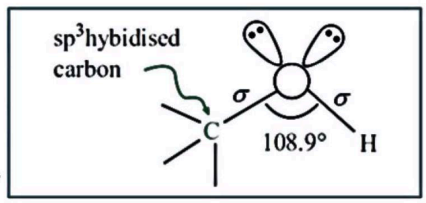
23. Write a short note on Riemer Tiemann Reaction

- On treating phenol with $CHCl_3$ /NaOH, a -CHO group is introduced at ortho position.
- This reaction proceeds through the formation of substituted benzal chloride intermediate.



Additional Questions - Long answers

1. Write about Structure of the functional group of alcohol.



- The structure of $-O-H$ group which is attached to a sp^3 hybridised carbon is similar to the structure of -O-H group attached to a hydrogen in water. i.e., 'V' shaped.
- In such alcohols, one of the sp^3 hybridised orbital of oxygen linearly overlap with the sp^3 hybridised orbital of carbon to form a $C-O$, ' σ' bond and another sp^3 hybridised orbital linearly overlap with 1s orbital of hydrogen to form a $O-H$, 'σ' bond.
- The remaining two sp^3 hybridised orbitals of oxygen are occupied by two lone pairs of electrons.

- Due to the lone pair – lone pair repulsion, the $C-O-H$ bond angle in methanol is reduced to 108.9° from the regular tetrahedral bond angle of 109.5^{o} .

2. How will you differentiate primary,secondary and tertiary alcohols by Lucas test

When alcohols are treated with Lucas agent(a mixture of concentrated HCl and anhydrous $ZnCl_2$) at room temperature

1) Tertiary alcohols react immediately to form a turbidity
2) Secondary alcohols react within 10 minutes to form a turbidity
3) Primary alcohols do don't give turbidity at room temperature but only on heating

3° Alcohol

$$(CH_3)_3COH \xrightarrow[\text{anhyd.}ZnCl_2]{\text{Conc.HCl}} (CH_3)_3C-Cl + H_2O$$

2° Alcohol

$$(CH_3)_2CHOH \xrightarrow[\text{anhyd.}ZnCl_2]{\text{Conc.HCl}} (CH_3)_2CH-Cl + H_2O$$

1° Alcohol

$$CH_3CH_2OH \xrightarrow[\text{anhyd.}ZnCl_2]{\text{Conc.HCl}} CH_3CH_2Cl + H_2O$$

3.How will you differentiate primary, secondary and tertiary alcohols by Victor's meyer test

This test is based on the behaviour of the different nitro alkanes formed by the three types of alcohols with nitrous acid and it consists of the following steps.

i) Alcohols are converted into alkyl iodide by treating it with I_2 /P .

ii) Alkyl iodide so formed is then treated with $AgNO_2$ to form nitro alkanes.

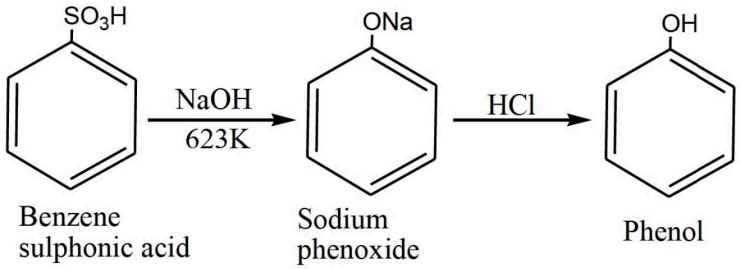
ii) Nitro alkanes are finally treated with HNO_2 (mixture of $NaNO_2$ / HCl) and the resultant solution is made alkaline with KOH.

Result

1) Primary alcohol gives red colour
2) Secondary alcohol gives blue colour.
3) No colouration will be observed in case of tertiary alcohol.

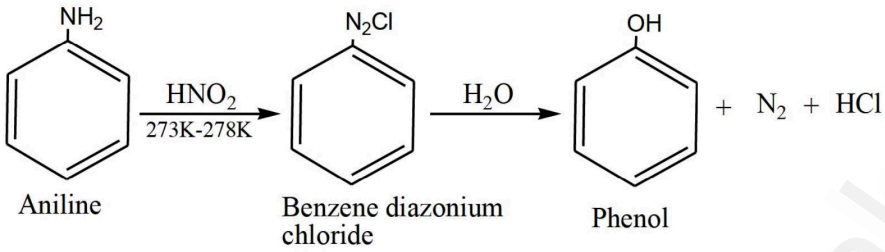
i)From benzene sulphonic acid

Benzene is sulphonated with oleum and the benzene sulphonic acid so formed is heated with molten NaOH at 623K gives sodium phenoxide which on acidification gives phenol.



ii) From aniline

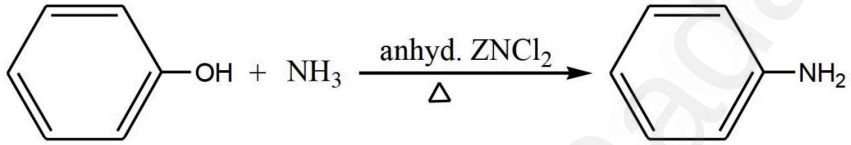
Aniline is diazotized with nitrous acid ($NaNO_2$ + HCl) at 273-278K to give benzene diazonium chloride which on further treatment with hot water in the presence of mineral acid gives phenol.



6.Starting from phenol how will you prepare the following

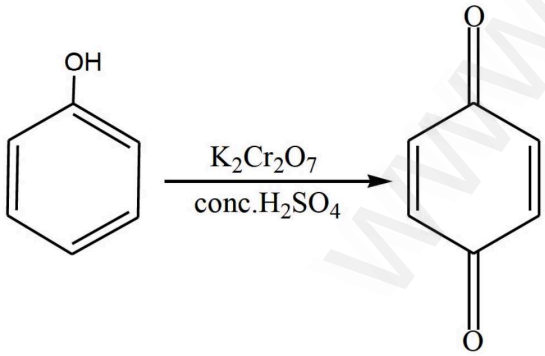
(i)Aniline

Phenol on heating with ammonia in presence of anhydrous $ZnCl_2$ gives aniline.



(ii)Benzoquinone

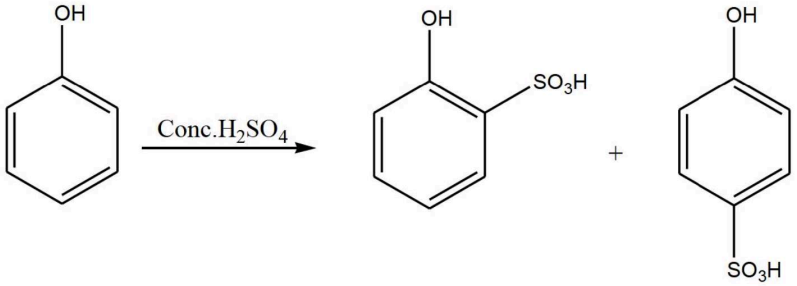
Phenol undergoes oxidation with air or acidified $K_2Cr_2O_7$ with conc. H_2SO_4 to form 1,4-benzoquinone.



(iii)Cyclohexanol

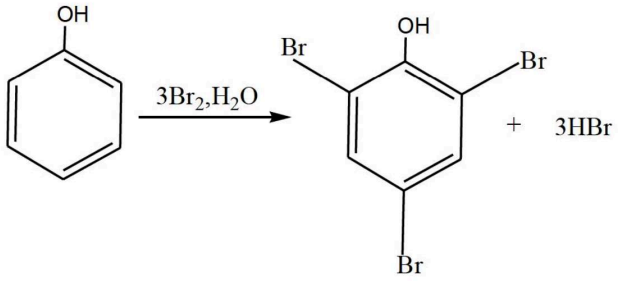
iv) Sulphonation

Phenol reacts with con. H_2SO_4 at 280K to form o-phenol sulphonic acid as the major product. When the reaction is carried out at 373K the major product is p-phenol sulphonic acid.



v) Halogenation

Phenol reacts with bromine water to give a white precipitate of 2,4,6-tri bromo phenol.



8.Write about preparation of diethyl ether

1. Inter molecular dehydration of alcohol.

When ethanol is treated with con.H_2SO_4 at 413K to form ethers.

$$2CH_3 - CH_2 - OH \xrightarrow[413K]{H_2SO_4} CH_3 - CH_2 - O - CH_2 - CH_3$$

2.Williamsons synthesis

Ethanol reacts with alkali to form sodium ethoxide which then reacts with alkyl iodide to ether.

$$C_2H_5OH + NaOH \xrightarrow[-H_2O]{} C_2H_5ONa \xrightarrow[\Delta]{C_2H_5I} C_2H_5OC_2H_5$$

3. Methylation of alcohol

Methyl ethers can be prepared by treating an alcohol with diazomethane in presence of catalyst, fluoroboric acid.

$$C_2H_5OH + C_2H_4N_2 \xrightarrow[\Delta]{HBF_4} C_2H_5OC_2H_5 + N_2$$

9.How will diethyl ether react with the following

iii) Friedel Craft's reaction

Anisole undergoes Fridel Craft's reaction in presence of anhydrous $AlCl_3$ as a catalyst.