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12

CHEMISTRY

Study material

Unit - 1

Metallurgy

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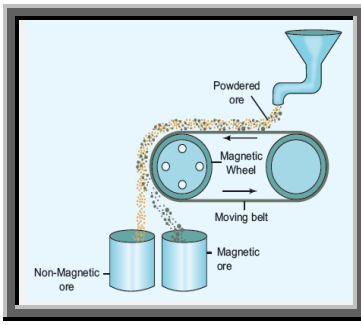


UNIT – 1

METALLURGY

TEXTBOOK QUESTIONS

I) Choose the best answer :

1. Bauxite has the composition
   a) Al_2O_3 **b) $Al_2O_3.nH_2O$** c) $Fe_2O_3.2H_2O$ d) None of these
2. Roasting of sulphide ore gives the gas (A). (A) is a colourless gas. Aqueous solution of (A) is acidic. The gas (A) is
   a) CO_2 b) SO_3 **c) SO_2** d) H_2S
3. Which one of the following reaction represents calcinations?
   a) $2Zn + O_2 \longrightarrow 2ZnO$ b) $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$
   c) $MgCO_3 \longrightarrow MgO + CO_2$ d) Both (a) and (c)
4. The metal oxide which cannot be reduced to metal by carbon is
   a) PbO **b) Al_2O_3** c) ZnO d) FeO
5. Which of the metal is extracted by Hall-Heroult process?
   a) Al b) Ni c) Cu d) Zn
6. Which of the following statements, about the advantage of roasting of sulphide ore before reduction is not true?
   a) ΔG_f^o of sulphide is greater than those for CS_2 and H_2S
   b) ΔG_f^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.
7. Match items in column - I with the items of column – II and assign the correct code.

Column-I		Column-II	
A	Cyanide process	(i)	Ultrapure Ge
B	Froth floatation process	(ii)	Dressing of ZnS
C	Electrolytic reduction	(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)

8. Wolframite ore is separated from tinstone by the process of
   a) Smelting b) Calcination
   c) Roasting **d) Electromagnetic separation**
9. Which one of the following is not feasible
   a) $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$
   b) $Cu_{(s)} + Zn^{2+}_{(aq)} \longrightarrow Zn_{(s)} + Cu^{2+}_{(aq)}$
   c) $Cu_{(s)} + 2Ag^{+}_{(aq)} \longrightarrow 2Ag_{(s)} + Cu^{2+}_{(aq)}$)
   d) $Fe_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Cu_{(s)} + Fe^{2+}_{(aq)}$
10. Electrochemical process is used to extract
    a) Iron b) Lead **c) Sodium** d) silver
11. Flux is a substance which is used to convert
    a) Mineral into silicate
    b) Infusible impurities to soluble impurities
    c) Soluble impurities to infusible impurities
    d) All of these
12. Which one of the following ores is best concentrated by froth – floatation method?
    a) Magnetite b) Haematite **c) Galena** d) Cassiterite
13. In the extraction of aluminium from alumina by electrolysis, cryolite is added to
    a) Lower the melting point of alumina b) Remove impurities from alumina
    c) Decrease the electrical conductivity d) Increase the rate of reduction
14. Zinc is obtained from ZnO by
    a) Carbon reduction b) Reduction using silver
    c) Electrochemical process d) Acid leaching
15. Cupellation is a process used for the refining of
    a) Silver b) Lead c) Copper d) iron
16. Extraction of gold and silver involves leaching with cyanide ion. silver is later recovered by
    a) Distillation b) Zone refining **(NEET – 2017)**
    c) Displacement with zinc d) liquation
17. Considering Ellingham diagram, which of the following metals can be used to reduce alumina? **(NEET – 2018)**
    a) Fe b) Cu **c) Mg** d) Zn
18. The following set of reactions are used in refining Zirconium
    $Zr_{(impure)} + 2I_2 \xrightarrow{523K} ZrI_4$
    $ZrI_4 \xrightarrow{1800K} Zr_{(pure)} + 2I_2$
    This method is known as
    a) Liquation **b) Van Arkel process** c) Zone refining d) Mond's process
19. Which of the following is used for concentrating ore in metallurgy?
    a) Leaching b) Roasting c) Froth floatation **d) Both (a) and (c)**
20. The incorrect statement among the following is
    a) Nickel is refined by Mond's process
    b) Titanium is refined by Van Arkel's process
    c) Zinc blende is concentrated by froth floatation
    d) In the metallurgy of gold, the metal is leached with dilute sodium chloride solution
21. In the electrolytic refining of copper, which one of the following is used as anode?
    a) Pure copper **b) Impure copper** c) Carbon rod d) Platinum electrode

22. Which of the following plot gives Ellingham diagram

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

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

a) $\left(\frac{\Delta S^o}{\Delta T}\right)$ is negative b) $\left(\frac{\Delta G^o}{\Delta T}\right)$ is positive $\left(\frac{\Delta G^\circ}{\Delta T}\right)$ *is negative*

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

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

a) $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$ **b) $Al_2O_3 + 2Cr \longrightarrow Cr_2O_3 + 2Al$**

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

25. 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.

Answer the following questions :

1. What are the differences between minerals and ores?

S.No	Minerals	Ores
1.	A naturally occurring substance obtained by mining which contains the metal in free state or in the form of compounds like oxides, sulphides etc. is called a mineral.	Minerals that contain a high percentage of metal, from which it can be extracted conveniently and economically are called ores.
2.	All minerals are not ores.	All ores are minerals.
3.	Eg: China clay is the mineral of Al	Bauxite is the ore of Al

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

(i) Concentration of the ore
(ii) Extraction of crude metal
(iii) Refining of crude metal

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

- The extraction of iron from its oxide Fe_2O_3, a basic flux, limestone (CaO) is used.
- The silica gangue present in the ore is acidic in nature, the limestone combines with it to form calcium silicate (slag).

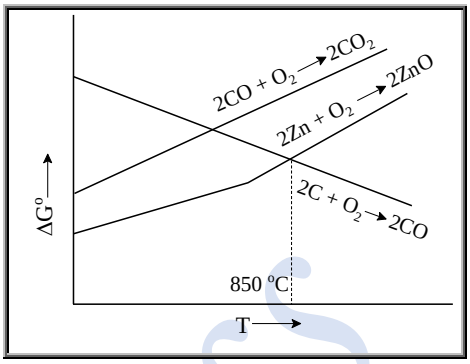
$$\underset{\text{Flux}}{CaO_{(s)}} + \underset{\text{Gangue}}{SiO_{2\,(s)}} \longrightarrow \underset{\text{Slag}}{CaSiO_{3\,(s)}}$$

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

- Sulphide ores are concentrated by froth floatation method.
- Eg: galena (PbS), zinc blende (ZnS)

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

- Coke (C) is better reducing agent for the reduction of ZnO.
- Ellingham diagram shows that at temperatures above 850°C, the **C ⟶ CO** line lies below the **Zn ⟶ ZnO line.**



- The value of ΔG^o for the change of C to CO is less than the value of ΔG^o for the change of Zn to ZnO.This indicates that CO is more stable than ZnO and therefore oxygen from ZnO combines with C. So in this range coke will reduce ZnO.
- **CO ⟶ CO_2** line lies above **Zn ⟶ ZnO** line at all temperatures.
- The value of ΔG^o for the change of CO to CO_2 is greater than the value of ΔG^o for the change of Zn to ZnO. This indicates that ZnO is more stable than CO_2 and therefore oxygen remains with Zn.
- So, the reduction of ZnO by CO is not thermodynamically feasible.

6. Describe a method for refining nickel.

Mond process for refining nickel:

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

$$Ni_{(s)} + 4CO_{(g)} \longrightarrow Ni(CO)_{4(g)}$$

(Impure)

- On heating the nickel tetracarbonyl around 460 K, the complex decomposes to give pure metal.

$$Ni(CO)_{4(g)} \longrightarrow Ni_{(s)} + 4CO_{(g)}$$

(Pure)

7. Explain zone refining process with an example.

- Zone refining process 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. i.e. impurities are more soluble in the melt than in the solid state metal. In this process the impure metal is taken in the form of a rod.
- One end of the rod is heated using a mobile induction heater which results in melting of the metal on that portion of the rod.
- When the heater is slowly moved to the other end the pure metal crystallises while the impurities will move on to the adjacent molten zone formed due to the movement of the heater. As the heater moves further away, the molten zone containing impurities also moves along with it.
- The process is repeated several times by moving the heater in the same direction again and again to achieve the desired purity level.
- This process is carried out in an inert gas atmosphere to prevent the oxidation of metals.
- Elements such as germanium (Ge), silicon (Si) and galium (Ga) that are used as semiconductor are refined using this process.

8. Using the Ellingham diagram.

A) Predict the conditions under which

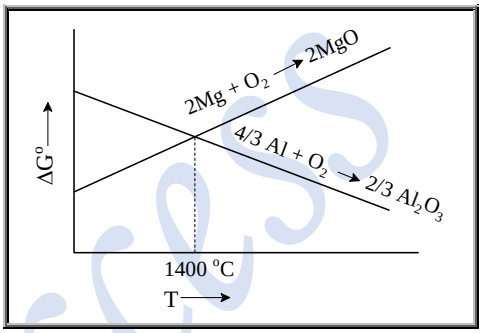
(i) Aluminium might be expected to reduce magnesia.

(ii) Magnesium could reduce alumina.

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

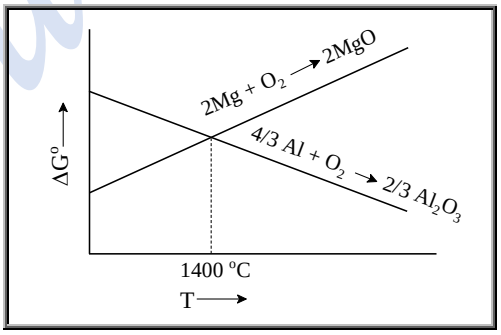
(C) Is it possible to reduce Fe_2O_3 by coke at a temperature around 1200K

A) (i) Aluminium might be expected to reduce magnesia.



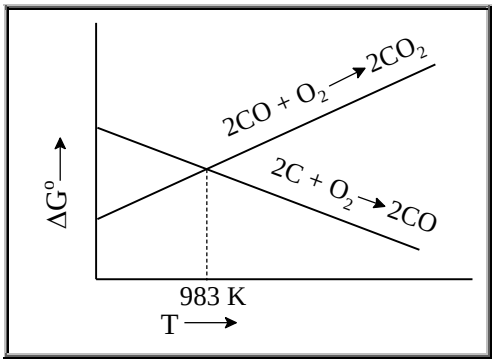
- Ellingham diagram shows that at temperatures above 1400°C, the $Al \longrightarrow Al_2O_3$ line lies below the **$Mg \longrightarrow MgO$ line.**
- The value of ΔG^o for the change of Al to Al_2O_3 is less than the value of ΔG^o for the change of Mg to MgO.
- This indicates that Al_2O_3 is more stable than MgO and therefore oxygen from MgO combines with Al. So at
- Temperatures above 1400°C, Al will reduce MgO.

(A) (ii) Magnesium could reduce alumina.



- Ellingham diagram shows that at temperatures below1400°C, the $Mg \longrightarrow MgO$ line lies below the **$Al \longrightarrow Al_2O_3$ line.**
- The value of ΔG^o for the change of Mg to MgO is less than the value of ΔG^o for the change of Al to Al_2O_3.
- This indicates that MgO is more stable than Al_2O_3 and therefore oxygen from Al_2O_3 combines with Mg. So at temperatures below 1400°C, Mg will reduce Al_2O_3.

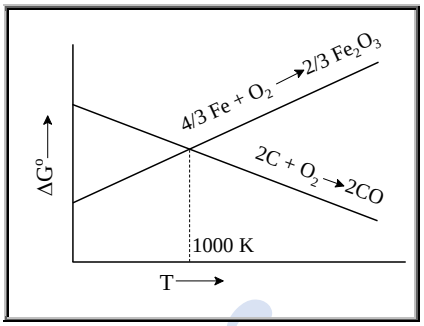
(B) Carbon monoxide is more effective reducing agent than carbon below 983K but, above this temperature, the reverse is true –Explain.



- Ellingham diagram shows that at 983 K, the curves intersect.
- The temperatures below 983K, the $CO \longrightarrow CO_2$ line lies below the $C \longrightarrow CO$ line.
- The value of ΔG^o for the change of CO to CO_2 is less than the value of ΔG^o for the change of C to CO.
- Therefore, CO is more effective reducing agent than carbon below 983K.
- But above 983 K, the **$C \longrightarrow CO$** line lies below the **$CO \longrightarrow CO_2$** line.
- The value of ΔG^o for the change of C to CO is less than the value of ΔG^o for the change of CO to CO_2. Therefore, C is more effective reducing agent than CO above 983K.

(c) Is it possible to reduce Fe_2O_3 by coke at a temperature around 1200K

- Ellingham diagram shows that at 1000 K, the curves intersect.
- The temperatures above 1000K, the **C ⟶ CO** line lies below the **Fe ⟶ Fe_2O_3** line.
- The value of ΔG^o for the change of C to CO is less than the value of ΔG^o for the change of Fe to Fe_2O_3.Therefore, coke (C) can reduce Fe_2O_3 into Fe at a temperature around 1200K.



9. Give the uses of zinc.

1. Metallic zinc is used in galvanising metals such as iron and steel structures to protect them from rusting and corrosion.
2. To produce die-castings in the automobile, electrical and hardware industries
3. Zinc oxide is used in the manufacture of many products such as paints, rubber, cosmetics, pharmaceuticals, plastics, inks, batteries, textiles and electrical equipment.
4. Zinc sulphide is used in making luminous paints, fluorescent lights and x-ray screens.
5. Brass an alloy of zinc is used in water valves and communication equipment as it is highly resistant to corrosion.

10. Explain the Electrometallurgy of aluminium.

Anode	The carbon blocks
Cathode	Iron tank lined with carbon
Electrolyte	❖ 20% solution of alumina (Al_2O_3), obtained from the bauxite ore is mixed with molten cyrolite (Na_3AlF_6). ❖ About 10% calcium chloride is also added to the solution.
The chemical reactions involved in this process are as follows :	
Ionisaiton of alumina	❖ $Al_2O_3 \longrightarrow 2Al^{3+} + 3O^{2-}$
Reaction at anode	❖ $6O^{2-}{}_{(melt)} \longrightarrow 3O_2 + 12e^-$
Reaction at cathode	❖ $2Al^{3+}{}_{(melt)} + 6\,e^- \longrightarrow 2\,Al_{(l)}$
Carbon acts as anode the following reaction also takes place on it.	
$C_{(s)} + O^{2-}{}_{(melt)} \longrightarrow CO + 2e^-$	$C_{(s)} + 2O^{2-}{}_{(melt)} \longrightarrow CO_2 + 4e^-$
The above two reactions, anodes are slowly consumed during the electrolysis. The pure aluminium is formed at the cathode and settles at the bottom. The net electrolysis reaction can be written as follows. $4Al^{3+}{}_{(melt)} + 6O^{2-}{}_{(melt)} + 3C_{(s)} \longrightarrow 4Al_{(l)} + 3CO_{2(g)}$	

11. Explain the following terms with suitable examples. (i) Gangue (ii) slag.

(i) Gangue :

- The nonmetallic impurities, rocky materials and siliceous matter which are associated with the ores are collectively known as gangue.
- Eg: Aluminosilicate is the gangue present in gold ore.

(ii) slag :

- Slag is easily fusible material, which is formed when gangue present in roasted ore combines with the flux.
- Eg: CaO (flux) + SiO_2 (gangue) → $CaSiO_3$ (slag)

12. Give the basic requirement for vapour phase refining.

Vapour phase refining method is defined as that, the metal is converted into its volatile compound and then decomposed to give pure metal.

The two requirements are:

(i) The metal should form a volatile compound with an available reagent.

(ii) The volatile compound should be easily decomposable, so that the recovery is easy.

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

(i) Role of Silica in the extraction of copper.

- Silica (SiO_2) acts as a flux in the extraction of copper. It removes the gangue FeO by forming ferrous silicate slag.

$$SiO_2 \text{ (flux)} + FeO \text{ (gangue)} \longrightarrow FeSiO_3 \text{ (slag)}$$

(ii) Role of Cryolite in the extraction of aluminium.

1. Cryolite (Na_3AlF_6) decreases the melting point of alumina (Al_2O_3)
2. It increases the electrical conductivity of alumina.

(iii) Role of Iodine in the refining of Zirconium

- Iodine is used in the purify zirconium by Van-Arkel method. Impure zirconium metal is heated in an evacuated vessel with iodine at 550 K to form the volatile zirconium tetraiodide.(ZrI_4). The impurities are left behind, as they do not react with iodine.

$$\mathbf{Zr_{(s)} + 2I_{2\,(s)} \longrightarrow ZrI_{4\,(vapour)}}$$

- The volatile zirconium tetraiodide vapour is passed over a tungsten filament at a temperature around 1800 K. The titanium tetraiodide is decomposed and pure titanium is deposited on the filament. The iodine is reused.

$$\mathbf{ZrI_{4\,(vapour)} \longrightarrow Zr_{(s)} + 2I_{2\,(s)}}$$

(iv) Role of Sodium cyanide in froth floatation :

- In froth floatation process, sodium cyanide is used as a depressing agent. It selectively prevents other metal sulphides from coming to the froth.
- **Eg: ZnS** is present as impurity in galena (PbS).
- NaCN is added as a depressing agent. It depresses the flotation property of ZnS by forming a layer of zinc complex $Na_2[Zn(CN)_4]$ on the surface of zinc sulphide. In this way NaCN prevents ZnS from coming to froth.

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

Electrolytic refining of silver.	
Anode	Impure silver rods
Cathode	Pure silver
Electrolyte	Acidified aqueous solution of silver nitrate.
When a current is passed through the electrodes the following reactions will take place	
Reaction at anode	$\mathbf{Ag_{(s)} \longrightarrow Ag^+_{(aq)} + 1e^-}$
Reaction at cathode	$\mathbf{Ag^+_{(aq)} + 1e^- \longrightarrow Ag_{(s)}}$
Explanation	❖ 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. ❖ During electrolysis, the less electropositive impurities in the anode, settle down at the bottom and are removed as anode mud.

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

- A suitable reducing agent is selected based on the thermodynamic considerations.
- For a spontaneous reaction, the change in free energy (ΔG) should be negative.
- Therefore, thermodynamically, the reduction of metal oxide with a given reducing agent can occur if the free energy change 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.
- **Eg : Reduction of ZnO by carbonmonoxide**:

$$ZnO + CO \longrightarrow Zn + CO_2 \quad \Delta G^o = + \text{ve (non spontaneous)}$$

- **Reduction of ZnO by coke:**

$$ZnO + C \longrightarrow Zn + CO \quad \Delta G^o = - \text{ve (spontaneous)}$$

- So, coke is better reducing agent for the reduction of ZnO into Zn.

16. Give the limitations of Ellingham diagram.

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

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

- The reduction of oxides of active metals such as sodium, potassium etc., by carbon is thermodynamically not feasible. Such metals are extracted from their ores by using electrochemical methods.
- In this technique, the metal salts are taken in a fused form or in solution form. The metal ion present can be reduced by treating it with some suitable reducing agent or by electrolysis.
- Gibbs free energy change for the electrolysis process is given by the following expression $\mathbf{\Delta G^\circ = -nFE^\circ}$.
- Where n is number of electrons involved in the reduction process, F is the Faraday and E° is the electrode potential of the redox couple.
- If E° is positive then the ΔG is negative and the reduction is spontaneous and hence a redox reaction is planned in such a way that the e.m.f of the net redox reaction is positive.
- When a more reactive metal is added to the solution containing the relatively less reactive metal ions, the more reactive metal will go into the solution.
- For example, $\mathbf{Cu_{(s)} + 2Ag^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}}$

$$\mathbf{Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}}$$