UNIT I- METALLURGY

1.Choose the correct 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) $2Zn + O_2 \rightarrow 2ZnO$ 2 b) $2ZnS + 3O_2 \rightarrow ZnO + 2SO_2$

c) $MgCO_3 \rightarrow MgO + CO_2$ d)Both (a) and

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^0 of sulphide is greater than those for CS_2 and H_2S.

b) ΔG_r^0 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 proces	(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	B
(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) $Cu(s) + 2Ag^{+}(aq) \longrightarrow Ag(s) + Cu^{2+}(aq)$

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

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) Hematite **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 **c) Displacement with zinc** d) liquation

17. Considering Ellingham diagram, which of the following metals can be used to reduce alumina?

a) Fe b) Cu **c) Mg** d) Zn

18. The following set of reactions are used in refining Zirconium

Zr (impure) + 2I ZrI ZrI Zr (pure) + 2I 2 523 K 4 4 1800K ___ _____ ___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) ΔG^0 Vs T**

c) ΔG^0 Vs 1/T d) ΔG^0 Vs T^2

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

a) $\left(\frac{\Delta S^0}{\Delta T}\right)$ is negative b) $\left(\frac{\Delta S^0}{\Delta T}\right)$ is positive

c. **$\left(\frac{\Delta G^0}{\Delta T}\right)$ is negative** d) initiall $\left(\frac{\Delta T}{\Delta G^0}\right)$ is positive after 700^0 c $\left(\frac{\Delta G^0}{\Delta T}\right)$ is negative

24. 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) $3TiO_2 + 4Al \rightarrow 2Al_2O_3 + 3Ti$ 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 CO2 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 is the difference between minerals and ores?**

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**. ch minerals thatcontains a high percentage of metal, from which it can be extracted conveniently andeconomically are called **ores**.Hence all ores are minerals but all minerals are not.Bauxite and china clay ($Al_2O_3.SIO_2.2H_2O$). Both are mineralsof aluminium. However, aluminium can be commercially extracted from bauxite whileextraction from china clay is not a profitable one.Hence the mineral, bauxite is an ore of aluminium while china clay is not.

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?

In the extraction of Iron, limestone (CaO) is used as a basic flux Since the silica gangue present inthe ore is acidic in nature, the limestone combines with it to form calcium silicate (slag).

$$\underset{\text{Flux}}{CaO\,(s)} + \underset{\text{Gangue}}{SiO_2\,(s)} \longrightarrow \underset{\text{Slag}}{CaSiO_3\,(s)}$$

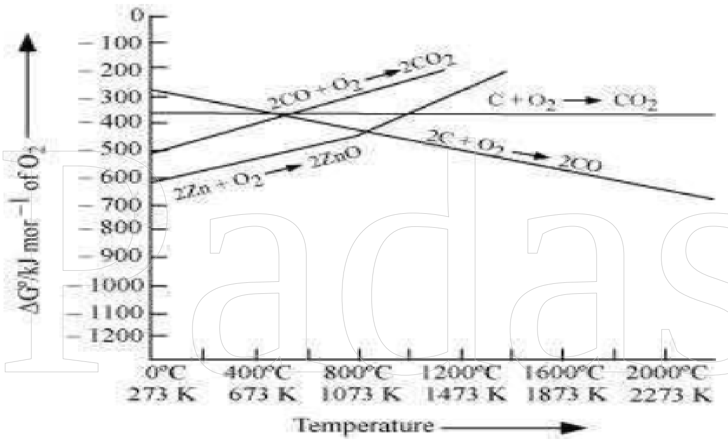
4. Which type of ores can be concentrated by froth floatation method? Give two examples for such ores.

Froth floatation method is commonly used to concentrate sulphide ores.

*E*xamples are 1. Galena (PbS), 2. Zinc blende (ZnS)

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

Why?



Reduction of ZnO to Zn is usually carried out at 1673 K. From the above figure, it can be observed that above 1073 K, the Gibbs free energy of formation of CO from C and above 1273 K, the Gibbs free energy of formation of CO_2 from C is lesser than the Gibbs free energy of formation of ZnO. Therefore, C can easily reduce ZnO to Zn.

On the other hand, the Gibbs free energy of formation of CO_2 from CO is always higher than the Gibbs free energy of formation of ZnO. Therefore, CO cannot reduce ZnO. Hence, C is a better reducing agent than CO for reducing ZnO.

6. Describe a method for refining nickel.

Nickel is refined by Mond's process. In this process, nickel is heated in the presence of carbon monoxide to form nickel tetracarbonyl, which is a volatile complex.

$$Ni + 4CO \xrightarrow{330-350K} \underset{\text{Nickel tetracarbonyl}}{Ni(CO)_4}$$

Then, the obtained nickel tetracarbonyl is decomposed by subjecting it to a higher temperature (450 – 470 K) to obtain pure nickel metal.

$$\underset{\text{Nickel tetracarbonyl}}{Ni(CO)_4} \xrightarrow{450-470K} \underset{\text{Nickel}}{Ni} + 4CO$$

7. Explain zone refining process with an example using the Ellingham diagram given below

8 ***(A) Predict the conditions under which***

(i) Aluminium might be expected to reduce magnesia.

Above 1350^0 C the standard Gibbs free energy formation of Al_2O_3 ,from Al is less than that of MgO from Mg. Therefore above 1350^0 C Al can reduce MgO.

(ii) Magnesium could reduce alumina:

Temperature below the point the intersection of Al_20_3 and MgO curves,magnesium could reduce alumina .but the process will be uneconomical.MgO can reduce Al203 at any temperature below 1400 degree celcius

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

Both thermodynamic and kinetic factors make carbon monoxide (CO) a better reducing agent than Carbon.When coke or coal is used to reduce a metal oxide, it gets oxidized to CO. And, when CO itself is the reducing agent, it is oxidized to CO2 .

MO + C = M + CO ; MO + CO = M + CO2

Thermodynamically, CO2 is much more stable than CO, as evident from the vast difference in their standard heats of formation. So, the second reaction with CO as the reducing agent is more favourable than the first one.

Metal oxides are solids at normal conditions, and so their reduction with carbon (having a high melting point) is a solid-solid interaction. But, when CO is the reducing agent, the process becomes a solid-gas interaction that is more vibrant and effective at a high temperature. Thus, kinetic factors also favour CO as a better reducing agent in metallurgy.

(iv) it is possible to reduce Fe_2O_3 by coke at a temperature around 1200K

The coke is added to the haematite to provide a reducing agent for the iron(III) oxide. Some iron(III) oxide is reduced by carbon in contact with the haematite ore

iron(III) oxide + carbon → iron + carbon dioxide

$2 Fe_2O_3(s) + 3 C(s) \rightarrow 4 Fe(l) + 3 CO_2(g)$

However, most of the iron(III) oxide is reduced by carbon monoxide gas. As a gas, this can circulate freely in the blast furnace. It is made when carbon dioxide (made from the coke burning in the blasts of hot air) reacts with more hot coke.

First:

carbon + oxygen → carbon dioxide

$C(s) + O_2(g) \rightarrow CO_2(g)$

Then:

carbon dioxide + carbon → carbon monoxide

$CO_2(g) + C(s) \rightarrow 2 CO(g)$

The carbon monoxide then reduces iron(III) oxide:

iron(III) oxide + carbon monoxide → iron + carbon dioxide

$Fe_2O_3(s) + 3 CO(g) \rightarrow 2 Fe(l) + 3 CO_2(g)$

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.Zinc is also used 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

In this method, electrolysis is carried out in an iron tank lined with carbon which actsas a cathode. The carbon blocks immersed in the electrolyte acts as a anode. A 20% solution of alumina, obtained from the bauxite ore is mixed with molten cyrolite and is taken in the electrolysis chamber.About 10% calcium chloride is also added to the solution.

Here calciumchloride helps to lower the melting point of the mixture. The fused mixture is Maintained at a temperature of above 1270 K.

The chemical reactions involved in this process are as follows.

Ionisation of alumina $Al_2O_3 \longrightarrow 2Al^{3+} + 3O^{2-}$

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

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

Since carbon acts as anode the following reaction takes place

$$C(s) + O^{2-}(melt) \longrightarrow CO + 2e^-$$

$$C(s) + 2O^{2-}(melt) \longrightarrow CO_2 + 4e^-$$

Due to the above two reactions, anodes are slowly consumed during the electrolysis. Thepure 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: The ores are associated with nonmetallic impurities, rocky materials and siliceous matter which are collectively known as gangue. The most common componentof gangue is silica SiO_2

(ii) slag: The flux combines with impurities (gangue) to form a fusible substance called slag.

12.Give the basic requirement for vapour phase refining.

In this method, the metal is treated with a suitable reagent which can form a volatilecompound with the metal. Then the volatile compound is decomposed to give the pure metal.We can understand this method by considering the following process.

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

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

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

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

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

(i) Silica in the extraction of copper.

In the extraction of copper from copper pyrites, the concentrated ore is heated in a reverberatory furnace after mixing with silica, an acidic flux. The ferrous oxide formed dueto melting is basic in nature and it combines with silica to form ferrous silicate (slag). The remaining metal sulphides Cu_2S and FeS are mutually soluble and form a copper matte.

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

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

$$\underset{\text{Flux}}{FeO\ (s)} + \underset{\text{Gangue}}{SiO_2\ (s)} \longrightarrow \underset{\text{Slag}}{FeSiO_3\ (s)}$$

(ii) Cryolite in the extraction of aluminium.

In this method, electrolysis is carried out in an iron tank lined with carbon which actsas a cathode. The carbon blocks immersed in the electrolyte acts as a anode. A 20% solution of alumina, obtained from the bauxite ore is mixed with molten cyrolite and is taken in the electrolysis chamber.About 10% calcium chloride is also added to the solution.

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(iii)Iodine in the refining of Zirconium.:

Van-Arkel method for refining zirconium/titanium:

This method is based on the thermal decomposition of metal compounds which lead tothe formation of pure metals. Titanium and zirconium can bepurified using this method.For example, the impure titanium metal is heated in an evacuated vessel with iodine at a temperature of 550 K to form the volatile Zirconium tetra-iodide.(ZrI_4). The impurities are left behind, as they do not react with iodine.

$$Zr\ (s) + 2I_2\ (s) \longrightarrow ZrI_4\ (vapour)$$

The volatile Zirconium tetraiodide vapour is passed over a tungsten filament at a temperature around 1800 K. The Zirconium tetraiodide is decomposedand pure titanium is deposited on the filament. The iodine is reused. $ZrI_4\ (vapour) \longrightarrow Zr\ (s) + 2I_2\ (s)$

(iv) Sodium cyanide in froth floatation.:

In the froth floatation process, the role of the depressants is to separate two sulphide ores by selectively preventing one ore from forming froth. Fr example, to separate two sulphide ores (ZnS and Pbs), NaCN is used as a depressant which selectively allows PbS to come with froth, but prevents ZnS from coming to froth. This happens because NaCN reacts with ZnS to form Na2[Zn(CN)4].

$$4\ NaCN + ZnS \longrightarrow Na_2[Zn(CN)_4] + Na_2S$$

14Explain the principle of electrolytic refining with an example.

(ii) Electrolytic refining;

Electrolytic refining is the process of refining impure metals by using electricity. In this process, impure metal is made the anode and a strip of pure metal is made the cathode. A solution of a soluble salt of the same metal is taken as the electrolyte. When an electric current is passed, metal ions from the electrolyte are deposited at the cathode as pure metal and the impure metal from the anode dissolves into the electrolyte in the form of ions. The impurities present in the impure metal gets collected below the anode.

This is known as anode mud.

Let us understand this process by considering electrolytic refining of silver as an example.

Cathode	:	Pure silver
Anode	:	Impure silver rods
Electrolyte	:	Acidified aqueous solution of silver nitrate

When a current is passed through the electrodes the following reactions will take place

Reaction at cathode $Ag\ (s) \longrightarrow Ag^+(aq) + 1e^-$

Reaction at anode $Ag^+(aq) + 1e^- \longrightarrow Ag(s)$

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.

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

Thermodynamic factor has a major role in selecting the reducing agent for a particular reaction. Only that reagent will be preferred which will lead to decrease in the free energy (ΔG^0) at a certain specific temperature e.g., can reduce ZnO to Zn but not CO. $ZnO(s)+C(s) \longrightarrow Zn(s)+CO(g)$ (i) $ZnO(s)+CO(g) \longrightarrow Zn(s)+CO_2(g)$?(ii) In the first case, there is increase in the magnitude of ΔS^0 while n the second case, it almost remains the same. In other words, ΔG^0 will have more negative value in the first case when C(s) is the reducing agent than in the second case when CO(g) acts as the reducing agent. Therefore, C(s) is a better reducing agent.

16. Give the limitations of Ellingham diagram.

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. More over, it does not give any idea about the possibility of other reactions that might be taking place.
2. The interpretation of ΔG is based on the assumption that the reactants are in equilibrium with the product 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 oresby using electrochemical methods.
In this technique, the metal salts are taken in a fused formor 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

$$\Delta G° = -nFE°$$

Where n is number of electrons involved in the reduction process, F is the Faraday and E^0 is the electrode potential of the redox couple.

If E^0 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,

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

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