Principles and processes of isolation of elements.

(1x20)

1. Name chief ore of Iron and Aluminium.
2. At what temperature CO is better reducing agent than carbon?
3. What is meant by gangue?
4. Name the impurities associated with bauxite.
5. What is the basis of zone refining?
6. What is the basis of vapour phase refining?
7. Name the refining method used for high degree of purity of metal.
8. How is copper extracted from low grade copper ore?
9. What is the role of collectors in froth floatation process?
10. Name two metals that occur in nature as oxides.
11. Out of C and CO which is better reducing agent for ZnO?
12. What is the role of cryolite in electrometallurgy of aluminum?
13. Why is Bauxite not heated to remove the impurities of water associated with it?
14. Copper can be extracted by hydrometallurgy but not Zn. Why?
15. What is the role of CaF_2 in electrometallurgy of aluminum?
16. Why is $CaCO_3$ added to blast furnace during reduction of Haematite?
17. Though thermodynamically feasible below given reaction, does not happen at room temperature?

    $3TiO_2 + 4\ Al \text{ ----------} \rightarrow 3Ti + 2Al_2O_3$, ΔG^0 = - ve
18. What is the role of graphite rods in electrometallurgy of aluminum?
19. Why is it not advisable to reduce MgO with carbon?
20. What is the % of carbon in cast and pig iron?

Answer:

1. Haematite (Fe_2O_3) and Bauxite($Al_2O_3.2H_2O$)
2. 673K and Above temperature.
3. Unwanted impurities associated with the ores.
4. SiO2 ,TiO2 and Fe2O3
5. Impurities are more soluble in melt than the metal.
6. Metal should form volatile compound and it should be easily decomposable.
7. Zone refining.
8. Hydrometallurgy
   $Cu^{2+} + H_2$ ----------→ $2H^+ + Cu$
9. Collects lighter sulphide ore in it.
10. Iron and Aluminium.
11. C
12. Reduces the melting point of Alumina.
13. Because aluminium has low melting point and water is chemically associated, so heating causes loss of metal.
14. The E0 of Zn is lower than that of Cu thus Zn can displace Cu^{2+} ion from its solution. On other hand side to displace Zn from Zn^{2+} ion, we need a more reactive metal than it.
15. Increases conductivity.
16. Provides flux on decomposition (CaO)
17. Requires activation energy.
18. Acts as anode.
19. Requires very high temperature thus it is not economical.
20. Cast Iron: about 3% pig iron: About 4%

(2x10)

Q.1 Describe the method of refining of Titanium.
Q.2- What is Zone Refining? Explain with example.
Q.3 Write the principal of electro-refining.
Q.4- Write difference between calcinations and roasting .
Q.5- Describe the method of refining of Zirconium.
Q.6- Out of C & CO, which is better reducing agent for ZnO?
Q.7- The value of Δf G0 for Cr_2O_3 is -540kJ/mole & that of Al_2O_3 is -827kJ/mole. Is the reduction of Cr_2O_3 possible with aluminium?
Q.8:- Why copper matte is put in silica lined converter?
Q.9- What is meant by term chromatography?
Q.10-Why is reduction of metal oxide easier if metal formed is in liquid state at temperature of reduction.

Answer:

A.1- In the Van- Arkel Process, Ti is heated in a stream of I2 forming a volatile complex, which then decomposes at higher temperature to giveTi.
$Ti + 2I_2 \rightarrow TiI_4$
$TiI_4 \rightarrow Ti + 2I_2$

A.2- Zone refining is a method of obtaining a metal in very pure state. It is based on the principal that impurities are more soluble in molten state of metal than solidified state.
In this method, a rod of impure metal is moved slowly over circular heater. The portion of the metal being heated melts & forms the molten zone. As this portion of the rod moves out of heater, it solidified while the impurities pass into molten zone. The process is repeated to obtain ultrapure metal and end of rod containing impure metal cutoff.

A.3- In this method of purification impure metal is made Anode and pure metal is made the cathode. On passing electricity, pure metal is deposited at the cathode while the impurities dissolve dissolve in solution as anode mud. E.g. electro- refining of copper:-
At Cathode: - $Cu^{2+} + 2e \rightarrow Cu$
At Anode: - $Cu \rightarrow Cu^{2+} + 2e$

A.4 (1) Calcination: it carried out in limited/no supply of air but roasting is carried in the presence of air.
(2) In roasting sulphide ore is converted to its oxide while in calcination hydroxide, hydrates, carbonates are converted to oxides.

A.5- Van Arkel process is used for obtaining ultrapure metal. The impure metal is converted into volatile compound, which then decomposes electrically to get pure metal.
At 850K: - Zr impure) + $2\ I_2 \rightarrow ZnI_4$
At 2075K:- $ZnI_4 \rightarrow$ Zr (pure) + $2\ I_2$

A.6- Since free energy of formation of CO from C is lower at temperature above 1120K while that of CO_2 from carbon is lower above 1323K than free energy of formation 0f ZnO. However, the free energy of formation of CO_2 from CO is always higher than that of ZnO. Hence, C is better reducing agent of ZnO.

A.7- The desired conversion is
$4\ Al + 2Cr_2O_3 \rightarrow 2Al_2O_3 + 4Cr$
It is obtained by addition of following two reactions:-
$4Al + 3O_2 \rightarrow 2\ Al_2O_3\ \Delta f\ G^0$=-827kJ/mole
$2Cr_2O_3 \rightarrow 4Cr + 3O_2\ \Delta f\ G^0$==+ 540 kJ/mole
Therefore, Δ G0 for desired reaction is -827+540=-287, as a result reduction is possible.

A.8:- Copper matte consists of Cu_2S and FeS. When blast of air is passed through molten matte in silica-lined converter, FeS present in matte is oxidized to FeO, which combines with silica to form slag.
(i) $2FeS + 3O_2 \rightarrow 2FeO + 2\ SO_2$, (ii) $FeO + SiO_2 \rightarrow FeSiO_3$ (slag),
(III) $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$, (IV) $2Cu_2O + 2Cu_2S \rightarrow 6Cu + SO_2$

A.9-Chromato means Colour and graphy means writing because the method was first used for separation of coloured substance. It is based on selective distribution of various constituents of a mixture between two phases, a stationary phase and a moving phase. The stationary phase can be either solid or liquid on solid support.

A.10- The entropy of a substance is higher in liquid state than solid state. In the reduction of metal oxide, the entropy change will be positive if metal formed is in liquid state. Thus, the value of Δ G0 becomes negative and reduction occurs easily.

(3x10)

Q.1- Explain the following:-
(i) Zinc but not copper is used for recovery of Ag from the complex $[Ag(CN)_2]^-$.
(ii) Partial roasting of sulphide ore is done in the metallurgy of copper.
(iii) Extraction of Cu from pyrites is difficult than that from its oxide ore through reduction.
The reduction of metal sulphide does not have large negative value.
Q.2- Explain the role of each of the following in the extraction of metals from their ores.
(1) CO in the extraction of Nickel
(2) Zn in the extraction of Ag
(3)Silica in the extraction of Copper.

A.3- Describe the principle behind each of the following processes-
(A)Vapour phase refining of a metal
(B) Electrolytic refining
(C) Froth floatation process

Q.4- Describe the principles of extraction of Zinc from zinc blende .
Q.5- Predict the modes of occurrence of the following three types of metals:
(1) Highly reactive metals
(2) Moderately metals
(3) Noble metals
Q6. What happens when:
(a) Cinnabar is roasted
(b) Silver sulphide is shaken with a dilute solution of NaCN
(c) HgO is heated
Q7. What is Ellingham's diagram? What is its use?
Q8. What is the role of depressant in froth floatation process?
Q9. Define following terms:
(a)Roasting (B) Calcination (C) Smelting
Q10. How are metals used as semiconductors refined? What is the principle of method used?

Answer:

A.1- (i) Zn is more powerful reducing agent in comparison to copper.Zn is also cheaper than Cu.

(ii) Partial roasting of sulphide ore forms some oxide. This oxide then reacts with remaining sulphide ore to give copper i.e. self-reduction occurs.

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$,

$2Cu_2O + 2Cu_2S \rightarrow 6Cu + SO_2$.

(iii) Though carbon is good reducing agent for oxide but it is poor reducing agent for sulphides.

A2. (1) Forms volatile compound with Ni i.e. $Ni(CO)_4$

(2) Leaching of the Ag.

(3) Acts as flux and reacts with FeO to form $FeSiO_3$(Slag)

A3. (A) Metal should form volatile compound and it should be easily decomposable.

(B) Less reactive metals undergo reduction at cathode when electricity is passed in the aqueous solution of their salts making impure metal as anode and pure metal as cathode.

A4. Chief ore of Zinc: ZnS

1. Enrichment: froth floatation process
2. Roasting:

$2ZnS + 3O_2 \text{ ----} \rightarrow 2ZnO + 2SO_2$

3. Reduction:

$ZnO + C \text{ -----} \rightarrow Zn + CO$

4. Refining: Distillation

A.5 (1) Highly reactive metals- oxides and halides

(2) Moderately metals- Sulphide and oxides and carbonates

(3) Noble metals- pure form/Native state

A6.

(a) $2HgS + 3O_2 \text{ ----} \rightarrow 2HgO + 2SO_2$

(b) $Ag_2S + NaCN \text{ ------} \rightarrow Na[Ag(CN)_2]$

(c) $2HgO \text{ ----------} \rightarrow 2Hg + O_2$

A.7

The plots between ΔG^0 of formation of oxides of elements against temperature are called Ellingham's diagram.

They are useful in deciding the suitable reducing agent in the metallurgical processes.

A.8

They are used to separate two sulphide ores. For example PbS and ZnS are separated by NaCN as depressant.NaCN selectively prevents ZnS from coming to the froth.

A9. (a)Roasting : Heating of Sulphide ores in the presence of air to obtain its oxide

(B) Calcination : Heating of metal carbonates/hydroxides/hydrates to obtain oxides in absence/limited supply of air

(C) Smelting : Reduction of metal oxide to its metal using carbon as reducing agent.

A10.

Zone refining.

Impurities are more soluble in melt than the metal.

5- marks

Q.1- Explain the method for obtaining pig iron from magnetite.

A.1- Extraction of iron from Magnetite takes place in following steps:-

(i) Concentration of ore: - It is done by Gravity separation followed by magnetic separation process.

(ii) Calcination: - It involve heating when the volatile matter escapes leaving behind metal oxide.

$Fe_2O_3.xH_2O \rightarrow Fe_2O_3 + xH_2O$.

(iii) Roasting: - It involves heating of ore in presence of air, thus moisture,CO_2,SO_2, As_2O_3 removed And FeO oxidized to Fe_2O_3.

(iv) Smelting of roasted ore: - A mixture of ore, coke & $CaCO_3$ is smelted in long BLAST FURNACE. Following reaction takes place at different temperature zones:-

(i) Zone of reduction: - Temperature range 250°C-700°C

$Fe_2O_3+3CO \rightarrow 2FeO+3CO_2$

$Fe_3O_4+4CO \rightarrow 3FeO+ 4CO_2$

$FeO +CO \rightarrow Fe+ CO_2$

(ii) Zone of slag formation:- Temperature range 800°C-1000°C

$CaCO_3 \rightarrow CaO+CO_2$

$CaO+SiO_2 \rightarrow CaSiO_3$, $P_4O_{10}+10C \rightarrow 4P+10CO$,

$SiO_2+2C \rightarrow Si+2CO$, $MnO_2+2C \rightarrow Mn+2CO$

(iii) Zone of fusion:- Temperature range 1150°C-1350°C

$CO_2 + C \rightarrow 2CO$

(iv) Zone of fusion:- Temperature range 1450°C-1950°C

$C +O_2 \rightarrow CO_2$

Thus, Pig iron is obtained from Blast Furnace.

Q.2- Name the principle ore of aluminium and describe how Al is extracted from its ore.

Ans2Step:-1 Bauxite is treated with NaOH .Following reaction takes place:-

$Al_2O_3 +2NaOH + 3 H_2O \rightarrow 2 Na [Al(OH)_4]$

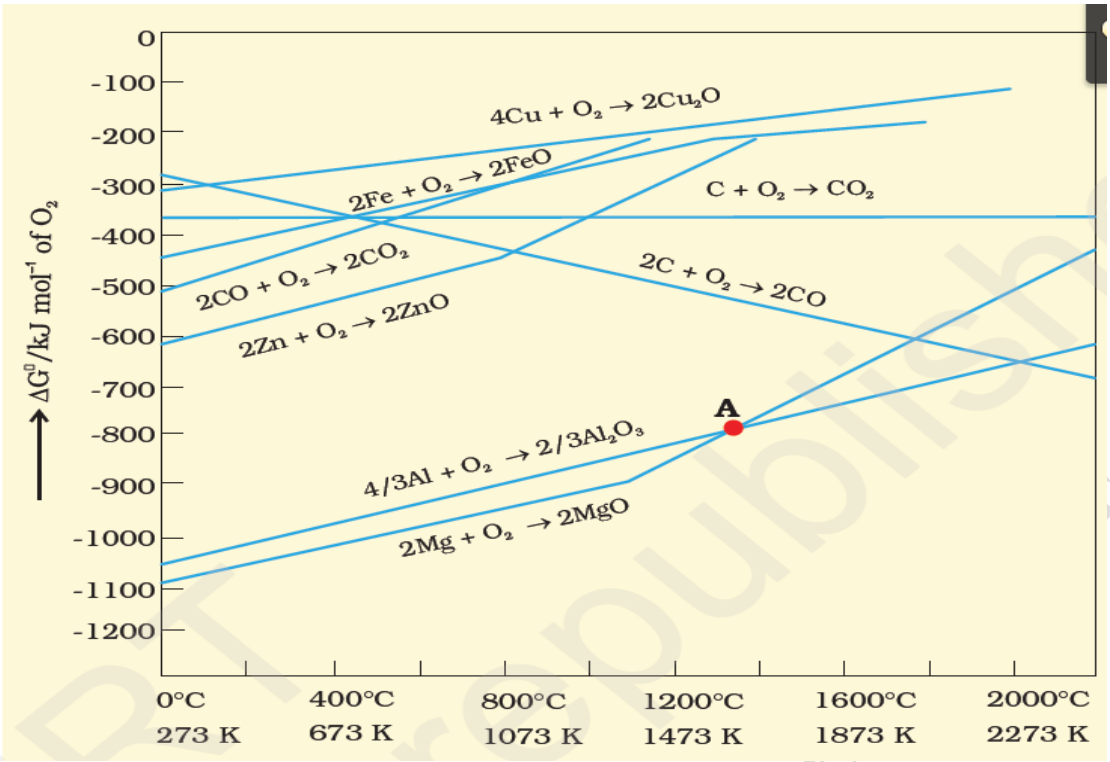
and impurities of Fe_2O_3,TiO_2&SiO_2 are removed . $Na [Al(OH)_4]$,then reacts with CO_2 then pure Alumina is obtained.

$Na [Al(OH)_4] + 2CO_2 \rightarrow Al_2O_3.xH_2O + 2NaHCO_3$

Step:-2 Electrolytic reduction of pure alumina takes place in iron box (cathode) with cryolite (Na_3AlF_6) & fluorspar CaF_2.Graphide rods act as anode. Following reactions take place:-

At cathode:- $Al^{3+} + 3e \rightarrow Al$, At Anode:- $2O^{2-} \rightarrow O_2$ + By this process 98.8% pure Aluminum is obtained.

Q.3-Given is the Ellingham diagram. With the help of this diagram answer the following questions.



Q1. Which of Al and Mg is better reducing agent below and above 1673K?

A: Below 1673 K – Mg and above 1673 K – Al

Q2. Which of C and CO can reduce MgOat 2000K temperature?

A: CO

Q3.Suggest a condition under which magnesium could reduce alumina.

A: Below the temperature 1600K