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## Unit - 1

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## Metallurgy

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## 1. What are the differences between minerals and ores?

## Ore :

- i) Materials which contains sufficient quantity of minerals so that metals can be extracted profitably.
- ii) Ore contains a good percentage of metal.
- iii) All ores are minerals.

**Example :** ZnS (Zinc blende) ,  $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  (Bauxite),

## Minerals :

- i) Minerals are natural materials in which the metals or their compounds are found in earth.
- ii) Minerals contains small percentage of metals.
- iii) All minerals are not all minerals are not ores.

**Example:** Gypsum is a mineral from which calcium is extracted.

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

## Steps involved in extraction of metals

## A) concentration of the ore

- 1 Gravity separation or Hydraulic wash
- 2 Froth flotation
- 3 Leaching    i) Cyanide leaching    ii) Ammonia leaching    iii) Alkali leaching    iv) Acid leaching
- 4. Magnetic separation

## B) extraction of crude metal

- i) Conversion of ores into oxides                      a)Roasting    b)Calcination
- ii) Reduction of metal oxides

a) Smelting              b) Reduction by carbon              c) Reduction by hydrogen

d) Reduction by metal                      e) Auto-reduction:

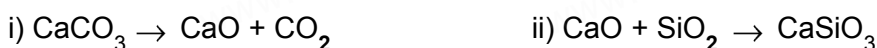
## C) refining of crude metal

- a) Distillation                      b) Liquation                      c) Electrolytic refining                      d) Zone Refining
- e) Vapour phase method

i) Mond process for refining nickel:    ii) Van-Arkel method for refining zirconium / titanium:

3. What is the role of Limestone in the extraction of Iron from its oxide  $\text{Fe}_2\text{O}_3$ ?

It acts as a basic flux to remove impurities like silica, sulphur and phosphorus in the form of slag.e.g.,



Here silica has been removed in the form of slag (calcium silicate).

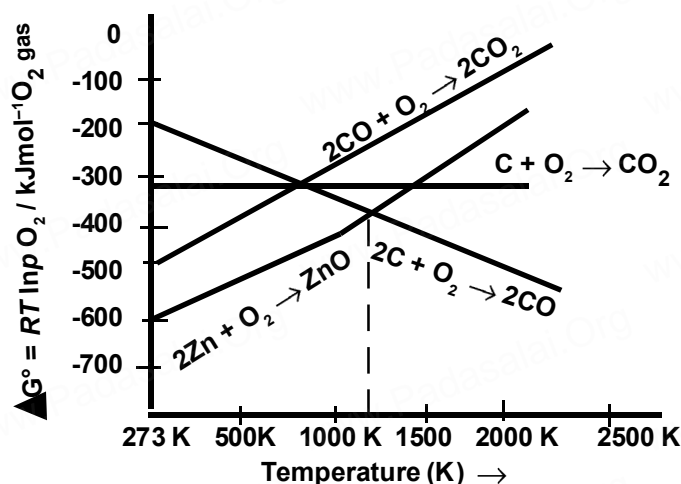
## 4. Which type of ores can be concentrated by froth floatation method?

**Give two examples for such ores.**

Sulphide ores can be concentrated by froth floatation method.

**For example-** PbS (galena),                      HgS (cinnabar) ,                      ZnS ( zinc blende )

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



From Ellingham diagram:

Coke is definitely the better reducing agent for the reduction of zinc oxide (ZnO) than (CO).

The Gibbs free energy of formation becomes lower at temperatures above 1273 K, for CO<sub>2</sub> from C.

In case of CO<sub>2</sub> from CO, the Gibbs free energy of formation is always higher than ZnO.

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.



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



7. Explain zone refining process with an example .

Principle - The impurities in the molten state are more soluble than in the solid state of the metal .

Method - In this method , a circular mobile heater is fixed at one end of a rod of the impure metal .

The molten zone moves along with the heater which is moved forward .As the heater moves forward , pure metal crystallizes out of the melt and the impurities pass on into the adjacent molten zone.

The process is repeated several times and heater is moved in the same direction. At one end ,impurities gets concentrated .This end is cut off.This method is very useful for producing semi-conductors and other metals of very high purity.

eg- B, Si ,Ge,In,Ga ,etc

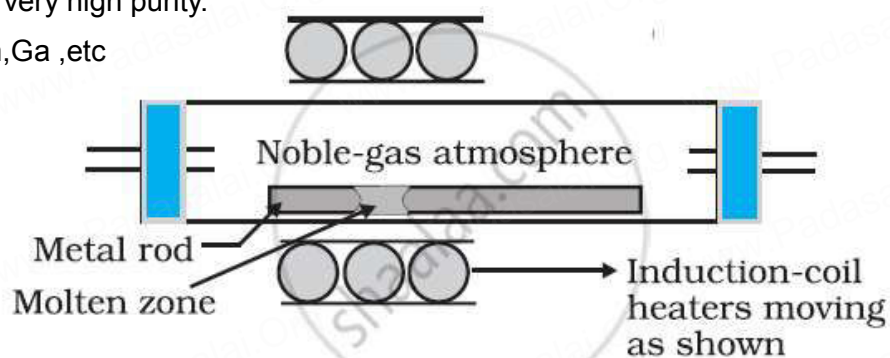
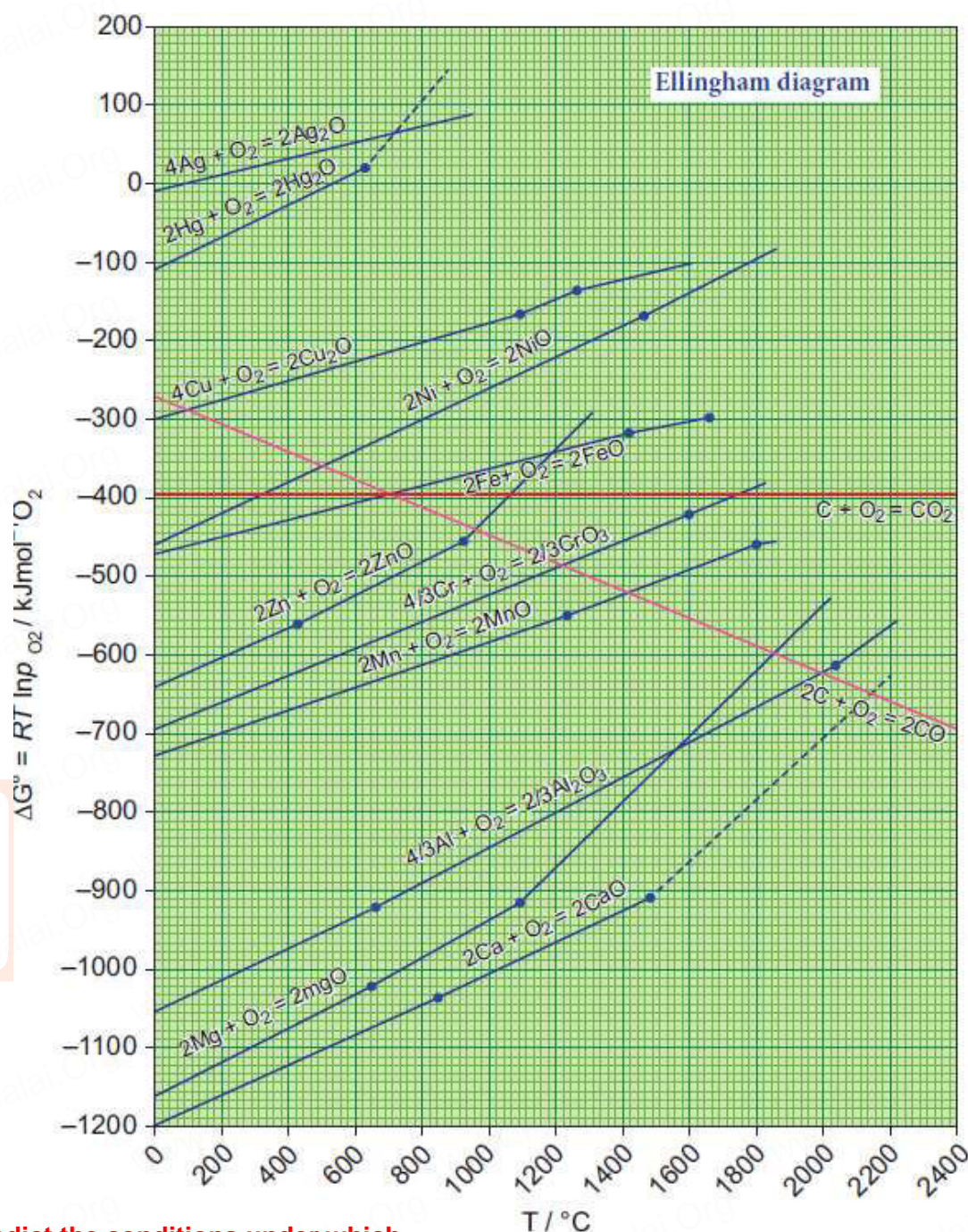


Fig. Zone refining process

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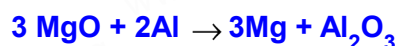
### 8. Using the Ellingham diagram given below.



#### (A) Predict the conditions under which

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

Aluminium can reduce magnesium oxide at a temperature of about 2000 K because in this temperature range the line of  $\Delta G^\circ$  (Mg, MgO) lies above the line of  $\Delta G^\circ$  (Al,  $\text{Al}_2\text{O}_3$ ) in the Ellingham diagram. Therefore, under these conditions  $\Delta_r G^\circ$  for reduction of MgO with Al will be negative and hence the reaction would be feasible.



##### (ii) Magnesium could reduce alumina.

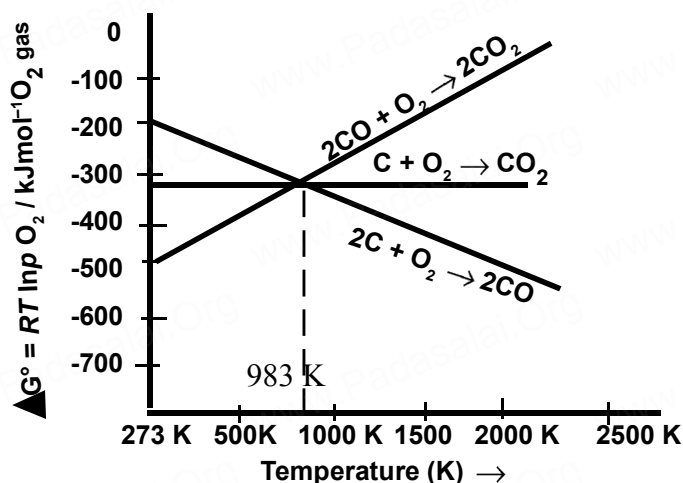
1. The reaction:  $3 \text{Mg} + \text{Al}_2\text{O}_3 \rightarrow 2 \text{Al} + 3 \text{MgO}$

2. On studying the Ellingham diagram we see that point of intersection, below which  $\Delta G$  for the above reaction is negative is above 2000 K.

3. Thus, this reaction is feasible at a very high temperature.

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



From Ellingham diagram, we find that 983 K, the curves intersect. The value of  $\Delta G^\circ$  for change of C to  $\text{CO}_2$  is less than the value of  $\Delta G^\circ$  for change of CO to  $\text{CO}_2$ . Therefore, coke (Carbon) is better reducing agent than CO at 983 K (or) above temperature, However below this temperature (eg 673 K), CO is more effective reducing agent than C

**(C) it is possible to reduce  $\text{Fe}_2\text{O}_3$  by coke at a temperature around 1200K**

Yes, it is possible for reduction

Coke is a better reducing agent for than CO above 1000K.

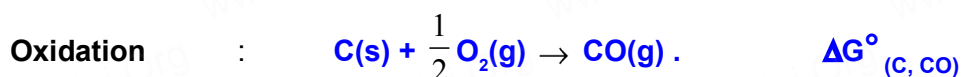
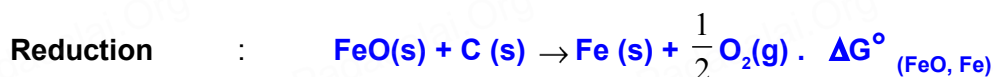
**Explanation:**

Iron(III) oxide gets converted to iron by the process of reduction. The reducing agent used for reducing iron(III) oxide to iron is carbon monoxide and coke.

The equation for the reduction of iron oxide by coke, the reaction follows:

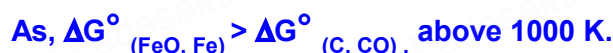


The two half reactions for the above reaction is given by the equations:



The net free energy change of the above reactions is:

Below 1000 K,  $\Delta G^\circ$  formation of  $\text{Fe}_2\text{O}_3$  is more than the formation of  $\text{CO}_2$  from CO. So, CO is the reducing agent for  $\text{Fe}_2\text{O}_3$  below 1000 K.



So,  $\Delta_r G^\circ$  becomes negative and the reaction 1 becomes favourable. Hence, C is a better reducing agent than CO above 1000 K.

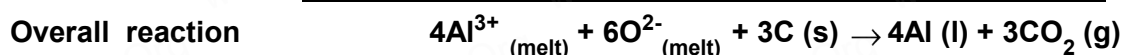
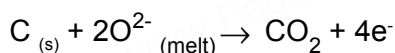
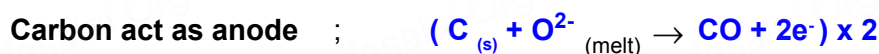
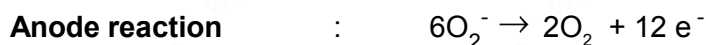
## 9. Give the uses of zinc.

- Metallic zinc is used in galvanising metals such as iron and steel structures to protect them from rusting and corrosion.
- Zinc is also used to produce die-castings in the automobile, electrical and hardware industries

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**10. Explain the electrometallurgy of aluminium.****Hall-Hérout process**

<b>Cathode</b>	:	iron tank lined with carbon
<b>Anode</b>	:	carbon blocks
<b>Electrolyte</b>	:	20% solution of $\text{Al}_2\text{O}_3$ + molten cryolite + 10% $\text{CaCl}_2$
<b>Temperature</b>	:	above 1270 K.

**Electrolysis in chamber process :****11. Explain the following terms with suitable examples.****(i) Gangue****(ii) slag**

**Gangue** :- The ores are associated with nonmetallic impurities, rocky materials and siliceous matter which are collectively known as gangue. **Ex.**  $\text{CaCO}_3$ ,  $\text{SiO}_2$

**Slag**: The light fusible substance which is made by the combination of gangue and flux, is called slag.

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

Two requirements for vapour phase refining are

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

(ii) The volatile compound should be easily recovered by decomposition.

**13. Describe the role of the following in the process mentioned.****(i) Silica in the extraction of copper.**

The role of silica in the metallurgy of copper is to remove the iron oxide obtained during the process of roasting. If the sulphide ore of copper contains iron, then silica ( $\text{SiO}_2$ ) is added as flux before roasting. Then,  $\text{FeO}$  combines with silica to form iron silicate,  $\text{FeSiO}_3$  (slag).

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

Cryolite ( $\text{Na}_3\text{AlF}_6$ ) is a flux (or solvent) that allows alumina to melt at a lower temperature and feed the igneous electrolytic cells that operate at 900 to 1000°C. Without it, alumina will melt at 2050°C which is quite challenging.

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

Zirconium Crude metal is heated with iodine in an evacuated vapour to separate from impurities and this decomposes at 1800K to give a pure Zirconium metal and iodine. Iodine is heated with Zirconium to form a volatile compound which on further heating decompose to give pure zirconium



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

In froth floatation process, depressants help to separate two sulphide ores by selective prevention of froth formation by one ore and allowing the other to come into froth **floatation**.

For example, in order to separate two sulphide ores (ZnS and PbS), NaCN is used as a depressant. It selectively allows PbS form froth, but prevents ZnS from coming to froth. This happens due to the fact that NaCN reacts with ZnS to form  $\text{Na}_2[\text{Zn}(\text{CN})_4]$ .

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

<b>Cathode</b>	:	Pure silver
<b>Anode</b>	:	Impure silver rods
<b>Electrolyte</b>	:	Acidified aqueous solution of silver nitrate.

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



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.

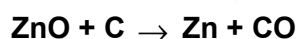
**Other metals such as copper, zinc etc., can also be refined by this process in a similar manner.**

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

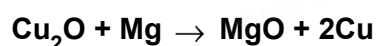
I absolutely agree with the statement that choice of reducing agent depends on thermodynamic factors most importantly free energy change.  $\Delta G^\circ$  of the reducing agent must be more than the oxide it has to reduce. i.e. oxide with more negative  $\Delta G^\circ$  reduces oxides with less negative  $\Delta G^\circ$ .

**Examples**

(1) C (more negative  $\Delta G^\circ$ ) can be used as reducing agent to reduce ZnO (less negative  $\Delta G^\circ$ ).



(2) Mg (more negative  $\Delta G^\circ$ ) can be used as reducing agent to reduce  $\text{Cu}_2\text{O}$  (less negative  $\Delta G^\circ$ ).

**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. More over, it does not give any idea about the possibility of other reactions that might be taking place.
2. The interpretation of  $\Delta G$  is based on the assumption that the reactants are in equilibrium with the products which is not always true.

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

Gibbs free energy change for the electrolysis process is given by the following expression

$$\Delta G^\circ = -nFE^\circ \text{ Where}$$

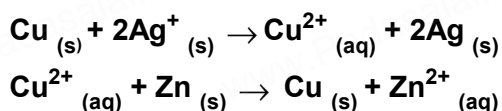
**n** - number of electrons involved in the reduction process,

**F** - Faraday

**E°** - is the electrode potential of the redox couple.

**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,



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