

#457697

**Topic:** Extraction of crude metals from concentrated ores

Copper can be extracted by hydrometallurgy but not zinc. Explain.

**Solution**

More electropositive zinc ( $E^\circ = -0.76\text{ V}$ ) is highly reactive and cannot be easily displaced from zinc sulphate solution. Less electropositive copper ( $E^\circ = +0.34\text{ V}$ ) is less reactive and can be displaced from copper sulphate solution by using more active metal such as zinc.  $\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$

#457698

**Topic:** Concentration or benefaction of ore (Ore-dressing)

What is the role of depressant in froth floatation process?

**Solution**

Depressants prevent certain types of particles from forming froth with bubbles. Due to this, we can separate two sulphide ores. For example, sodium cyanide is a depressant used for an ore containing  $\text{ZnS}$  and  $\text{PbS}$ .  $\text{NaCN}$  forms a layer of the complex  $\text{Na}_2[\text{Zn}(\text{CN})_4]$  on the surface of  $\text{ZnS}$  and prevents it from forming a froth. Thus, it acts as a depressant. However,  $\text{NaCN}$  does not prevent  $\text{PbS}$  from forming froth and allows it to come with froth.

#457700

**Topic:** Refining

Explain: (i) Zone refining (ii) Column chromatography.

**Solution**

(i) Zone refining

It is used for refining  $\text{Si}$ ,  $\text{B}$ ,  $\text{Ga}$ ,  $\text{In}$  etc. Impurities are more soluble in the molten state of metal than in solid state. There is a circular mobile heater at one end of a rod of impure metal. Heater and the molten zone moves from one end to another end. Pure metal crystallizes out of the melt and the impurities pass onto the adjacent molten zone. Repetition of this process several times segregates impurities at one end of a rod. The end with impurities can then be cut off.

(ii) Column chromatography.

It is used for the separation and purification. It is based on the difference in the tendency for adsorption of a metal and its impurities on a suitable adsorbent. Different components of a mixture are differently adsorbed on an adsorbent.

#457701

**Topic:** Thermodynamic principles of metallurgy

Out of  $\text{C}$  and  $\text{CO}$ , which is a better reducing agent at  $673\text{ K}$ ?

**Solution**

At  $673\text{ K}$ , the  $\Delta G^\circ$  vs  $T$  line for  $\text{CO}$ ,  $\text{CO}_2$  is lower than that of  $\text{C}$ ,  $\text{CO}$  line. Hence,  $\text{CO}$  can be used as better reducing agent than  $\text{C}$  at  $673\text{ K}$ .

#457702

**Topic:** Extraction of copper

Name the common elements present in the anode mud in electrolytic refining of copper. Why are they present?

**Solution**

In the electrolytic refining of copper, the anode mud contains antimony, selenium, tellurium, silver gold and platinum. These are impurities in blister copper. They are less reactive and unaffected by  $\text{CuSO}_4 - \text{H}_2\text{SO}_4$  solution and hence, settle down under anode as anode mud.

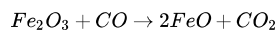
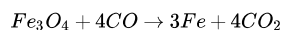
#457703

**Topic:** Extraction of crude metals from concentrated ores

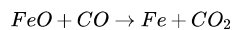
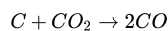
Write down the reactions taking place in different zones in the blast furnace during the extraction of iron.

**Solution**

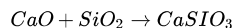
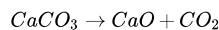
In blast furnace, iron oxides are reduced at different temperature ranges. In the lower part of the blast furnace, the temperature is as high as  $2200\text{ K}$ . It is called combustion zone. At the top, the temperature is as low as  $500 - 800\text{ K}$ . It is called reduction zone. In the lower temperature range, carbon is the reducing agent and in the higher temperature range,  $CO$  is the reducing agent. In the reduction zone ( $500 - 800\text{ K}$ ), following reactions occur.



In the temperature range  $900-1500\text{ K}$ , following reactions occur.



Around  $1270\text{ K}$  (middle portion), decomposition of limestone gives lime ( $CaO$ ) and  $CO_2$ . Lime is a flux and combines with silicate impurity to form slag of calcium silicate.



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#### #457704

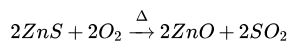
**Topic:** Extraction of crude metals from concentrated ores

Write chemical reactions taking place in the extraction of zinc from zinc blende.

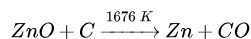
#### Solution

During extraction of Zn from zinc blende ( $ZnS$ ), following reactions occur:

(i)  $ZnS$  is roasted in excess air at  $1200\text{ K}$  to form  $ZnO$ .



(ii)  $ZnO$  is heated with crushed coke at  $1673\text{ K}$ , where it is reduced to Zn.



(iii) Electrorefining is carried out for refining of impure zinc. Anode is impure zinc and cathode is pure zinc. Electrolyte is a mixture of zinc sulphate and dilute sulphuric acid (small amount). When current is passed, zinc is deposited on cathode and is collected.

At anode:  $Zn \rightarrow Zn^{2+} + 2e^-$

At cathode:  $Zn^{2+} + 2e^- \rightarrow Zn$

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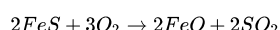
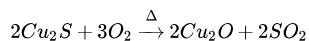
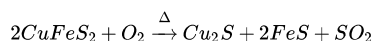
#### #457706

**Topic:** Extraction of crude metals from concentrated ores

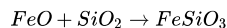
State the role of silica in the metallurgy of copper.

#### Solution

During roasting, copper pyrites give  $FeO$  and  $Cu_2O$ .



Roasted ore is then mixed with silica (acidic flux) and heated to remove  $FeO$  (basic) as a slag of iron silicate.



Lighter slag forms upper layer and is removed through slag hole.

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#### #457707

**Topic:** Refining

What is meant by the term chromatography?

#### Solution

Chromatography is used for the separation and purification. It is based on the difference in the tendency for adsorption of a metal and its impurities on a suitable adsorbent.

Different components of a mixture are differently adsorbed on an adsorbent.

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#### #457708

**Topic:** Refining

What criterion is followed for the selection of the stationary phase in chromatography?

#### Solution

The stationary phase is an adsorbent and has following characteristics:

- (1) Its adsorption power should be high and selective.
- (2) To offer greater surface area for adsorption, it should be finely divided.
- (3) It should have high mechanical stability. This will prevent dust formation.
- (4) It should be chemically inert to sample and eluting solvents.
- (5) It should have high purity.

#457709

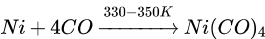
Topic: Refining

Describe a method for refining nickel.

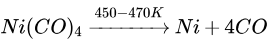
Solution

The method for refining nickel involves the following:

Ni is heated with  $CO$  to form volatile nickel tetracarbonyl.



At high temperature, nickel tetracarbonyl decomposes to pure Ni.



This is Mond's process for refining Ni.

#457710

Topic: Extraction of Aluminium

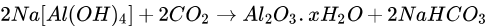
How can you separate alumina from silica in a bauxite ore associated with silica? Give equations, if any.

Solution

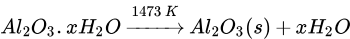
Bauxite ore containing silica is heated with conc.  $NaOH$  solution at  $473 - 523\text{ K}$  and  $35 - 36$  bar pressure. Alumina forms sodium aluminate and silica forms sodium silicate. Impurities are left behind.



Carbon dioxide neutralizes the aluminate to precipitate hydrated alumina.



Sodium silicate remains in the solution and hydrated alumina is filtered and dried. On heating, hydrated alumina gives pure alumina.



#457711

Topic: Extraction of crude metals from concentrated ores

Giving examples, differentiate between roasting and calcination.

Solution

Calcination	Roasting
Ore is heated in absence of air. $Fe_2O_3 \cdot xH_2O \xrightarrow{\Delta} Fe_2O_3 + xH_2O$ $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$ $CaCO_3 \cdot MgCO_3 \xrightarrow{\Delta} CaO + MgO + 2CO_2$	Ore is heated in regular air supply below the melting temperature for metal. $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$ $2Cu - 2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$ $2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$
It is used for carbonates and oxide ores.	It is used for sulphide ores.
Moisture and organic impurities are removed.	Volatile impurites are removed as oxides such as $SO_2, P_2O_5, As_2O_4$ .

#457712

Topic: Extraction of iron

How is cast iron different from pig iron?

Solution

Pig iron is obtained from blast surface. It contains 4% C and trace of impurities such as  $S, P, Si, Mn$  etc.

Pig iron is melted (using hot air blast) with scrap iron and coke to form cast iron. Carbon content is around 3% and cast iron is extremely hard and brittle.

#457713

Topic: General Introduction

Differentiate between minerals and ores.

#### Solution

Minerals are naturally occurring chemical substances. They are present in earth's crust and obtained by mining. Ores are the minerals from which a metal can be economically and conveniently extracted.

Thus, bauxite ( $Al_2O_3 \cdot 2H_2O$ ) and clay ( $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ ) are minerals of  $Al$ . However, bauxite is an ore of  $Al$  as  $Al$  can be economically and conveniently extracted from bauxite.

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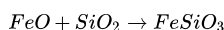
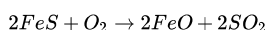
#### #457714

**Topic:** Extraction of copper

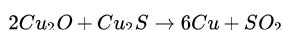
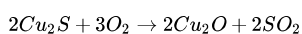
Why copper matte is put in silica lined converter?

#### Solution

Copper matte contains  $Cu_2S$  and  $FeS$ . Hot air blast converts  $FeS$  to  $FeO$ .  $FeO$  is removed as slag when it reacts with silica. Hence, copper matte is placed in silica lined converter.



$Cu_2S$  or  $CuO$  is converted to copper.



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#### #457715

**Topic:** Extraction of Aluminium

What is the role of cryolite in the metallurgy of aluminium?

#### Solution

Before electrolysis, cryolite is added to bauxite ore because of the following reasons.

(1) It acts as a solvent.

(2) It decreases the melting temperature of alumina to 1173 K.

(3) It increases the electrical conductivity.

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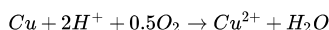
#### #457716

**Topic:** Extraction of copper

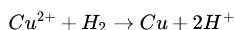
How is leaching carried out in case of low grade copper ores?

#### Solution

Acid in presence of air is used to leach out copper from low grade copper.



Solution is then treated with scrap iron or hydrogen.



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#### #457717

**Topic:** Thermodynamic principles of metallurgy

Why is zinc not extracted from zinc oxide through reduction using CO?

#### Solution

Zinc is not extracted from zinc oxide through reduction using CO.

Reducing agent should have more negative  $\Delta G$  value. However in present case, Zn has more negative  $\Delta G$  value than CO, so it can not be reduced by CO.

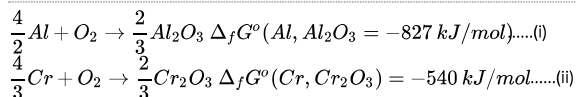
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#### #457718

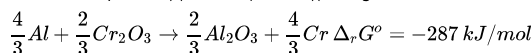
**Topic:** Extraction of Aluminium

The value of  $\Delta_f G^0$  for formation of  $Cr_2O_3$  is  $-540 \text{ kJmol}^{-1}$  and that of  $Al_2O_3$  is  $-827 \text{ kJmol}^{-1}$ . Is the reduction of  $Cr_2O_3$  possible with  $Al$ ?

#### Solution



Subtract equation (ii) from equation (i), we get



Because, for the combined reaction,  $\Delta_r G^\circ < 0$  (negative), the reaction is spontaneous and the reduction of  $Cr_2O_3$  by  $Al$  is possible.

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**#457719**

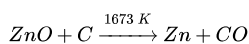
**Topic:** Thermodynamic principles of metallurgy

Out of  $C$  and  $CO$ , which is a better reducing agent for  $ZnO$ ?

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**Solution**

Out of  $C$  and  $CO$ , the better reducing agent for  $ZnO$  is  $C$ .



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**#457720**

**Topic:** Thermodynamic principles of metallurgy

The choice of a reducing agent in a particular case depends on thermodynamic factor. How far do you agree with this statement? Support your opinion with two examples.

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**Solution**

For the reduction of given metal oxide to metal, consideration of thermodynamic factors helps in selecting a suitable reducing agent. Ellingham diagrams (plots of  $\Delta_f G^\circ$  vs  $T$ ) can predict the feasibility of thermal reduction. Metals with a more negative standard free energy of formation of oxides can reduce the metal oxides with a less negative standard free energy of formation of respective oxides. Metal will reduce the oxides of other metals which lie above it in Ellingham diagram as the standard free energy change for combined redox reaction will be negative by an amount equal to the difference in  $\Delta_f G^\circ$  of two metal oxides. Thus, both  $Al$  and  $Zn$  can reduce  $FeO$  to  $Fe$  but  $Fe$  cannot reduce  $Al_2O_3$  to  $Al$  or  $ZnO$  to  $Zn$ . Also,  $C$  can reduce  $ZnO$  to  $Zn$  but not  $CO$ .

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**#457721**

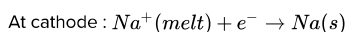
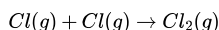
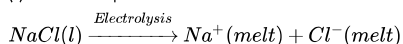
**Topic:** Thermodynamic principles of metallurgy

Name the processes from which chlorine is obtained as a by-product. What will happen if an aqueous solution of  $NaCl$  is subjected to electrolysis?

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**Solution**

(1) In Down's process for the manufacture of sodium, the electrolysis of  $NaCl$  gives chlorine as a byproduct.



(2) In Castner Kellner cell, electrolysis of brine solution is carried out to manufacture  $NaOH$  (caustic soda). Chlorine is obtained as a byproduct.

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**#457722**

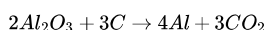
**Topic:** Thermodynamic principles of metallurgy

What is the role of graphite rod in the electrometallurgy of aluminium?

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**Solution**

During electrometallurgy of aluminium, graphite rod reduces alumina to aluminium.



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**#457723**

**Topic:** Refining

Outline the principles of refining of metals by the following methods:

(i) Zone refining

(ii) Electrolytic refining

(iii) Vapour phase refining

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**Solution**

## (i) Zone refining

It is used for refining  $Si$ ,  $B$ ,  $Ga$ ,  $In$  etc. Impurities are more soluble in the molten state of metal than in solid state. There is a circular mobile heater at one end of a rod of impure metal. Heater and the molten zone moves from one end to another end. Pure metal crystallizes out of the melt and the impurities pass onto the adjacent molten zone. Repetition of this process several times segregates impurities at one end of a rod. The end with impurities can then be cut off.

## (ii) Electrolytic refining

It is carried out for refining of impure zinc. The anode is impure zinc and cathode is pure zinc. The electrolyte is a mixture of zinc sulphate and dilute sulphuric acid (small amount). When current is passed, zinc is deposited on the cathode and is collected.

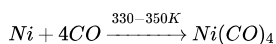
At anode:  $Zn \rightarrow Zn^{2+} + 2e^{-}$

At cathode:  $Zn^{2+} + 2e^{-} \rightarrow Zn$

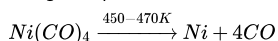
## (iii) Vapour phase refining

Metal is converted into volatile compound and then decomposed to obtain pure metal. This method is used for refining  $Ni$ ,  $Zr$  and  $Ti$ .

$Ni$  is heated with  $CO$  to form volatile nickel tetracarbonyl.



At high temperature, nickel tetracarbonyl decomposes to pure Ni.



This is Mond's process for refining Ni.

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**#457725**

**Topic:** Thermodynamic principles of metallurgy

Predict conditions under which  $Al$  might be expected to reduce  $MgO$ .

**Solution**

Below  $1350^{\circ}C$ ,  $Mg$  can reduce  $Al_2O_3$  and above  $1350^{\circ}C$ ,  $Al$  can reduce  $MgO$ . This can be inferred from  $\Delta G^{\ominus} Vs T$  plots.

$\Delta G^{\ominus} Vs T$  plot for  $Mg$ ,  $MgO$  is below  $\Delta G^{\ominus} Vs T$  plot for  $Al$ . At the point of intersection ( corresponding to  $1350^{\circ}C$ ),  $\Delta G^{\ominus}$  for combined reaction is zero. After  $1350^{\circ}C$ ,  $MgO$  curve is higher than  $Al$   $Al_2O_3$  curve. There are practical difficulties to attain higher temperature.